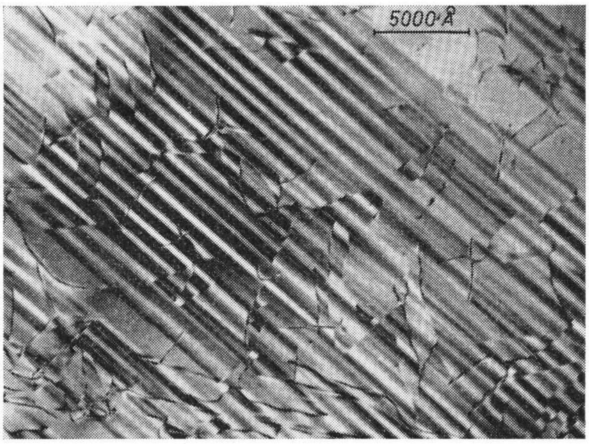
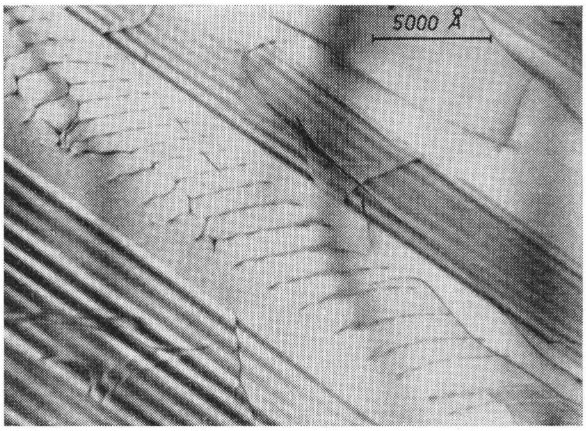


I *Massive α-phase formed in a Cu–23·7 at-% Ga alloy on quenching from 780°C to room temperature; internal stacking faults inclined to the foil normal*



J *Alloy as Figure I; showing stacking faults and a low-angle boundary*

Mr F. B. Pickering (The United Steel Cos. Ltd) asked if the substructural units of the transformation product grew across the parent crystal boundaries without let or hindrance.

Professor Wayman said that this was evidently the case, for both low- and high-angle mother boundaries.

Mr Pickering asked if it was to be inferred that there was an orientation relationship between the substructural units and any of the grains of the parent phase.

Professor Wayman said that this was a point (concerning the parent–product orientation relationship) where he and Mr Saburi differed with Dr Massalski, who did the pioneering work on the $\beta \rightarrow \zeta$ massive transformation in Cu–Ga alloys. Massalski claimed, on the basis of γ precipitates within β (prior to the massive transformation), that no orientation relationship existed. This might be true for the fully grown ζ crystal, but did not exclude an orientation relationship at the nucleation stage, bearing in mind that once nucleated the ζ crystals grew across the parent phase boundaries.

Mr R. D. Garwood (University College, Cardiff) asked if Professor Wayman could be sure in these circumstances that there was no preferred orientation in the parent phase when the stacking faults in the massive product were observed to cross β-grain boundaries?

Professor Wayman said that they had not looked for a preferred orientation.

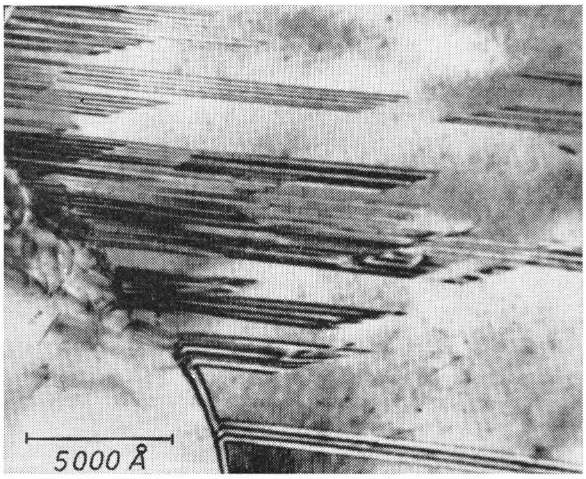
Mr Garwood said that the argument fell down if preferred orientation existed and there was an (011) plane in the two β-grains parallel.

Professor Wayman said he did not think this really bore on the linear markings observed inside the massive phase. The point was that these were evidently the result of growth.

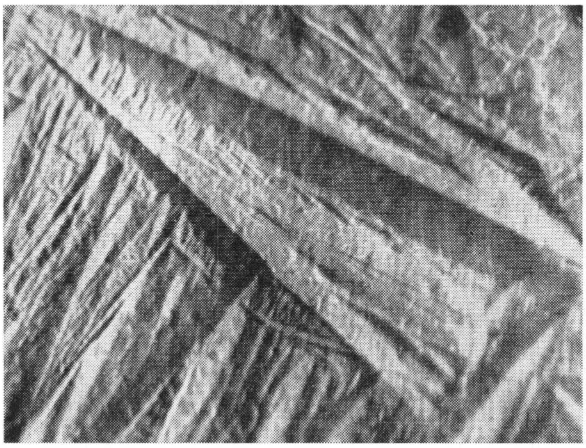
The ζ-phase was hexagonal not cubic. It seemed fairly certain that ζ crystals did grow across *high*-angle boundaries. He would rather not commit himself at all by saying that any orientation relationship between the two existed.

Dr Warlimont, replying to Professor Hull's question about the internal structure of the massive phase and what was thought about it, said his micrographs were similar to the pictures that would be shown in the paper mentioned by Professor Wayman. Figure *I*, in which the fault plane was strongly inclined to the foil normal, showed that in the massive phase there was much faulting and a number of dislocations showed up, depending on the contrast conditions. This micrograph did not exhibit the characteristic details as well as Figure *J*, which showed the stacking faults as well and that they were really very widely separated compared with stacking faults in the martensites. Secondly, one could see low-angle boundaries consisting of arrays of dislocations, which, in the present case, appeared to be a pure tilt boundary in part of the micrograph and, further up, turned into a boundary with a twist component. This might be an effect of how the specimen was sectioned.

Figure *K* showed the boundary of a massively formed grain and it could be seen that the stacking faults extended from the grain boundaries into the massive phase. The massive phase exhibited also a number of low-angle boundaries. It was thought, though they had not been working on this transformation extensively, that they could show that there was an effect of the volume change and even of some shear strain occurring during the massive transformation which produced these lattice defects: i.e. the stacking faults and the low-angle boundaries. It could be imagined that if a massive grain grew into the matrix, at some place at the interface, because of the crystallographic relation between the two grains, one might get a slight deficiency,



K *Alloy as Figure I; showing stacking faults attached to a grain boundary*



L *Ti–1·5%Cu; quenched after polishing* ×1100

and in other places along that boundary a superfluous concentration of atoms resulting in slight distortion of the grain as it was growing. If this distortion could not be accommodated by low angle boundaries, stacking faults were initiated at the interface and were expanding back into the grain as it was growing. But he would not claim that these ideas which he had put forward would be the final solution to the question of the origin of growth defects of the massive phases in these alloys.

WRITTEN CONTRIBUTIONS

Professor Parr wrote that the use of the word massive to describe a constituent rather than a process was difficult to defend, and suggested a trend back to the confusion that arose when they spoke of 'troostite' 'sorbite', and the rest.

More specific comments that arose from the paper were, firstly, the contention that the structure of Figure 5 was massive required more knowledge than that imparted by the microstructure. The microstructure did not tell them that transformation had been by short-range diffusion; and unless the word 'massive' was to be used for everything that was not 'martensitic' (whatever martensitic was) additional criteria were surely required for complete or even incomplete definition.

Second, the authors suggested that 'the more familiar acicular forms of martensite' were those 'which consist of single or connected lenticular martensite plates embedded in a matrix of retained parent phase'. This was not altogether acceptable. Structures that were not readily identified as lenticular were nonetheless martensitic by every other reasonable criterion. Figure *L* was not of lenticular plates in a retained matrix; but he would be bothered if the word martensitic were not to be applied to the process that produced the structure of Figure *L*.

Third, the prefix massive to the term martensitic should imply something that was characteristic of the massive *structure* or (if one might use words to describe processes) the massive *transformation*. Now, the massive structure was illustrated by Owen and Wilson's Figure 1. Figure 8 surely had nothing in common with Figure 1. How then could Figure 8 be called massive anything, unless one wished to impute certain characteristics that were intrinsic to the transformation *mode*, which seemed to be against the new rules suggested in the paper.

Fourth, to imply a 'dislocation mode of growth' which 'might operate during the growth of massive-α' seemed to do two things. One was that it involved an unnecessary circumlocution: for it would be much easier to say that 'the massive transformation involves a . . .' – but one must not do that any more. The second was that any transformation involving a 'dislocation mode of growth' was in some sense highly cooperative. If the term implied the *movement* of a dislocation then the process was cooperative, and (according to his dictionary) it was martensitic.

Fifthly, the driving force of 300 cal/mole was invoked again. He had never expected that their electrochemical experiments,[9] which refuted this figure, would be enthusiastically endorsed. However, their later work[10,11] showed that M_s in pure iron was about 750°C and not 540°C. Hence, ΔF in pure iron was about 100 cal/mole, not very different from the upper limit of 80 ascribed by Owen and Wilson to transformation involving short range diffusion.

Next, the authors stated that 'at lower nickel contents (i.e. lower than 4%) the product is always massive α'. This was not true.[11]

The only thing that they were sure of seemed to be this: if a transformation involved cooperative movement to the same sort of extent that was involved in plastic deformation, then the transformation was by shear, and the adjective invoked was 'martensitic'. If the transformation involved individual and chaotic atom movements, then the process was by diffusion. Presumably they must define 'short-range diffusion' in terms of the progression of the interface, but they were not usually in a position to watch that.

Unfortunately, there seemed to be no positive criterion for the shear transformation: as he had mentioned to Professor Owen, it was perverse of iron–chromium alloys to show surface rumpling at intermediate cooling rates, while at faster rates there was *no* surface effect.[29] (The produced structure was, by X-ray diffraction, the same.) However, while surface rumpling might not be an adequate criterion, he would be content to believe that if a structure showed traces on the surface of what appeared to be sheared planes (Owen and Wilson, Figure 8), then, it had been produced by shear. He did not know to what extent its nucleation might have been controlled by diffusion or, indeed, if diffusion played some part in the transformation: but if they were going to use the word martensitic ever again, surely Figure 8 deserved it.

The more troublesome problem was that an absence of parallel traces was not conclusive evidence *against* a martensitic transformation.

In an attempt to summarize, he would suggest:

(i) the massive transformation was typified by a constant transformation temperature, invariant with cooling rate

(ii) the martensitic transformation occurred at cooling rates at which calculations such as they would perform showed that diffusion could not produce the new phase in the available time; the martensitic structure, produced by cooperative shear, *might* show the effects of the shear; but one could imagine shear processes that might not be manifest by resolvable traces

(iii) the term 'massive martensite' was, if one accepts (i) and (ii), unnecessary

(iv) they still could not unequivocally define either massive or martensitic in terms of a property or a characteristic that was observable or measurable; until they could they were in the same sort of quandary that would arise were they to understand (for example) the mechanism of galvanic electricity but be denied the use of a voltmeter to check for the presence of the potential. He was really concerned about this aspect: they could not continue to debate possible mechanisms of transformations when, in fact, they were unable to state the criterion of any of them.

Professor W. S. Owen (University of Liverpool), in reply to Professor Parr said that he could only repeat the argument in the paper. There was a negative and a positive aspect to the argument. The main reason for wishing to abandon the use of the word massive to describe a transformation was that the word did not identify the physical process by which the transformation occurred unless a special definition of the word was invented. Thus, it was easier and less likely to lead to confusion if an abbreviated form of the definition was used. Hence the suggestion that the transformations with which they were concerned should be classified as either SRO or martensitic transformations; martensitic being a word which meant 'involving a shape change' and which in modern usage had no other meaning. On the positive side, it was argued that the word massive could well be applied to the description of a microstructure. Webster defined massive as 'in mass, not necessarily without a crystalline structure, but having no regular form'. It was in this sense that they had used the word to describe microstructures such as those in Figures 5 and 8. It was only a small extension of these ideas to describe the product of the SRO transformation as ferrite and of any martensitic transformation as martensite. If the appearance of the microstructure of the product was acicular or Widmanstätten it was usual to use these words to complete the description, hence Widmanstätten ferrite was a common description. It seemed to them to be a good idea to use the word massive in the same way where appropriate.

Resisting the temptation to comment upon all of Professor Parr's minor points, he would like to make two points. The transformation which proceeded by the movement of a high-angle interface with diffusional movements of atoms in the vicinity of the interface they had described as an SRO transformation. He thought this was the transformation referred to in Professor Parr's summary. This transformation was not 'typified by a constant transformation temperature'. This could be inferred[5] from the work of Kogin and Entin and had been clearly demonstrated by E. A. Wilson's measurements of the variation of electrical resistance and temperature with time during the quench.[5] Finally, he felt bound to say that he never found the use 'of 'troostite', 'sorbite', and the rest' confusing. They were still useful descriptions of microstructures and he did not know of any words which he could use to replace them.

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Metallography of titanium martensites

W. K. Armitage

SYNOPSIS

Martensites in several titanium alloys were examined by optical and electron metallography. Observations showed that internal twinning occurred very infrequently in titanium martensite plates, but that it should be possible to strengthen alloys containing supersaturated titanium martensites by a tempering treatment.

The orientation relationship and habit plane of acicular martensite was determined, and a unique association between a particular variant of the orientation relationship and its habit plane found. When twinning occurred in a martensite plate, the twin crystallography agreed with that reported for most hexagonal metals. Evidence is given for the isothermal formation of a titanium martensite 2582

INTRODUCTION

AT 882°C pure titanium transforms from the cph α-modification to the high-temperature bcc β-modification. On holding at temperatures near 882°C the transformation $\alpha \rightarrow \beta$ or $\beta \rightarrow \alpha$ is extremely sluggish, indicating that diffusion processes are involved,[1] but on cooling at even moderate rates from the β-phase the transformation becomes a diffusionless shear process. Duwez[2] has shown how the temperature for complete transformation to martensitic α-phase can be reduced from 882°C to 855°C by increasing the cooling rate from 10 deg C to 10 000 deg C/min.

In titanium alloys the martensite transformation generally occurs over a temperature range which increases with increased solute additions, that is, the M_s and M_f temperatures diverge. Duwez[3] has shown that additions of elements (in order) tantalum, niobium, tungsten, vanadium, molybdenum, chromium, manganese, iron progressively depress the M_s temperature of β-stabilized alloys at a greater rate, which corresponds roughly with the rate at which the β-transus temperature is reduced by additions of each element.

Recent reviews[4,5] have outlined the $\beta \rightarrow \alpha$ transformations in titanium and several of its alloys; the orientation relationship most frequently reported has been $(0001)_{\alpha'} \| (110)_{\beta}$ and $[11\bar{2}0]_{\alpha'} \| [\bar{1}11]_{\beta}$ which can be associated with martensite having either $\{334\}_{\beta}$ or $\{344\}_{\beta}$ habit planes; the less prevalent $\{344\}_{\beta}$ habit plane can also be associated with the orientation relationship $(0001)_{\alpha'}$ 14° to $(1\bar{1}0)_{\beta}$ and $[10\bar{1}0]_{\alpha'} \| [110]_{\beta}$. Table I summarizes the habit planes detected in titanium and its binary alloys by several investigators.

Mackenzie and Bowles[12] have extended their geometrical theory of martensite transformations[13,14,15] to account for transformations in titanium and its alloys. They found that the $\{334\}_{\beta}$ habit plane could be explained on the assumption that $\{111\}_{\beta}$ is the operative twinning plane, but no justification for the $\{344\}_{\beta}$ habit plane was predicted.

This paper outlines some recent observations on martensites formed in several commercial titanium alloys. Electron metallography has been supplemented by optical metallography where necessary and some crystallographic details have been evaluated by transmission electron diffraction through thin foil specimens.

EXPERIMENTAL

Thin foil specimens suitable for examination by transmission in the electron microscope were prepared by electropolishing disks (3 mm diameter, ½ mm thick) in a PTFE holder.[16, 17]

TABLE I Habit planes of titanium martensites

Alloy	β habit planes	Comments	Reference
Pure titanium	(8,8,11)		6
Pure titanium	(8,9,12)		7
Pure titanium	(334) and (112)	predicted	8
Ti–Cr	(334)		9
Ti–Fe	(334)		9
Ti–Mn	(334) and (344)		10
Ti–10%Mo	(334)	more prevalent	9
	and		
	(344)	also produced by sub-zero treatment or room-temperature deformation	9
Ti–12·5%Mo	only (344)		11
Ti–11%Mo	(334)	predominant	11
	and		
	(344)	both types formed by stress	11

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MG/Conf/79/65). UDC No.669.295.5: 669.112.227.342

TABLE II Electropolishing conditions for titanium alloys

Electrolyte and conditions	Comments
I 350 ml ethyl alcohol 118 ml perchloric acid 78 ml butoxy ethanol 20–40 V Pt cathode Room temperature Perforation time about 2 min	Polishing voltage depends on alloy composition and heat treatment condition; the current is switched on and off during polishing to prevent build up of a thick oxide film; this electrolyte produces an excellent specimen profile
II 10% perchloric acid 90% acetic acid 25–40 V Pt cathode Room temperature Perforation time about 2 min	Under optimum conditions a thick oxide film should not form and small bubbles should stream from both specimen surfaces; this electrolyte has sometimes been used for perforation after profiling in I

Several electrolytes were used successfully (Table II) but it was usually found necessary to remove an epitaxial oxide, formed during electropolishing, by a short chemical polishing treatment (Table III).

Surface replicas were prepared from optically flat specimens that had been electro-etched or chemically etched, and from specimens which had been ground flat before heat treatment in the β range and quenching. In all cases direct carbon replicas produced better resolution of detail, and in some instances the replicas were shadowed with one of the commonly used shadowing media.

RESULTS

Types of martensite

Martensites have been broadly classified into two types:

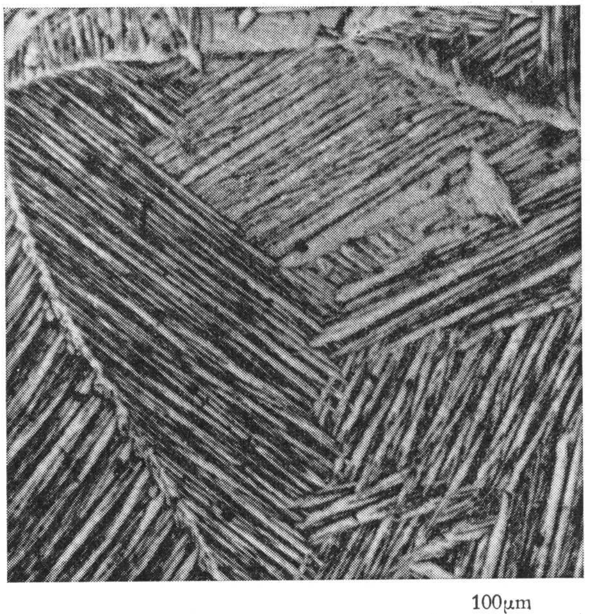
(i) a coarse block structure (massive) which sometimes contains an internal lenticular structure

(ii) acicular martensite which, in the ferrous systems, has again been subdivided into needle, lath, and plate-like forms.

A structure with the appearance of massive martensite is a feature of many titanium alloys. Figure 1 is an optical micrograph showing the colonized arrangement of lenticular region within the outlines of original β-grain boundaries. The alloy used for this micrograph (Alloy *A*, Table IV) was air-cooled from the β range. Further examination by thin-foil electron microscopy showed that there was no retained β-phase in this alloy, therefore a detailed crystallographic interpretation of the transformation would be a difficult proposition.

TABLE III Chemical cleaning solutions for electropolished titanium alloys

Solution	Comments
I 200 ml 30% nitric acid 125 ml 30% fluorosilicic acid 30 g ammonium bifluoride	Reasonably effective for removal of oxide film but tends to etch sample; produces a coloured tarnish on several alloys
II 75 ml conc. nitric acid 25 ml distilled water	Often removes tarnish produced in I
III 30 g anhydrous zinc chloride 25 ml conc. nitric acid 100 ml distilled water	Can be used after I and II to produce excellent clean foils



1 *Alloy A after air cooling from the β range; optical micrograph* ×200

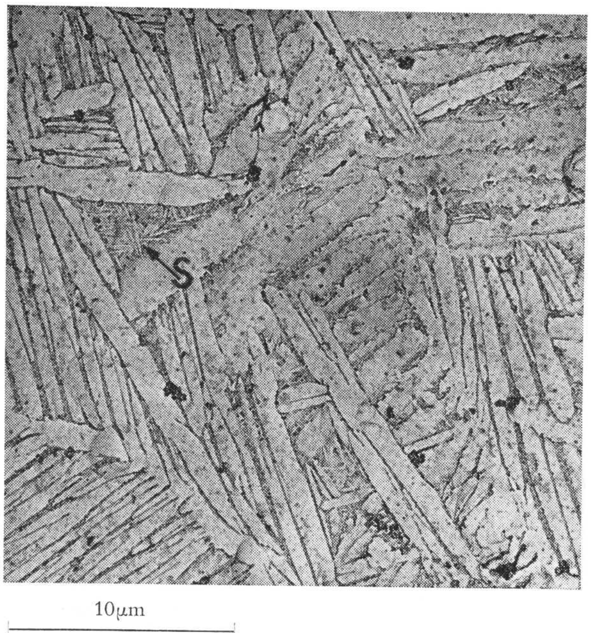
A surface replica from alloy *B* after the same β heat treatment is shown in Figure 2. This micrograph shows smaller lenticular regions in much smaller colonies and many variants within each original β-grain. (The β-grain size was much greater than the area shown in the micrograph.) Retained β-phase is present between each α region, and in the area marked S some has presumably transformed to acicular martensite at a later stage during cooling.

Comparison of the microstructures in these two alloys suggests that β-stabilizing additions which retain β-phase after transformation (2%Mo in this instance) have a pronounced influence on the coarseness of the structure by limiting the sizes of plates and colonies and allowing more frequent nucleation of different variants.

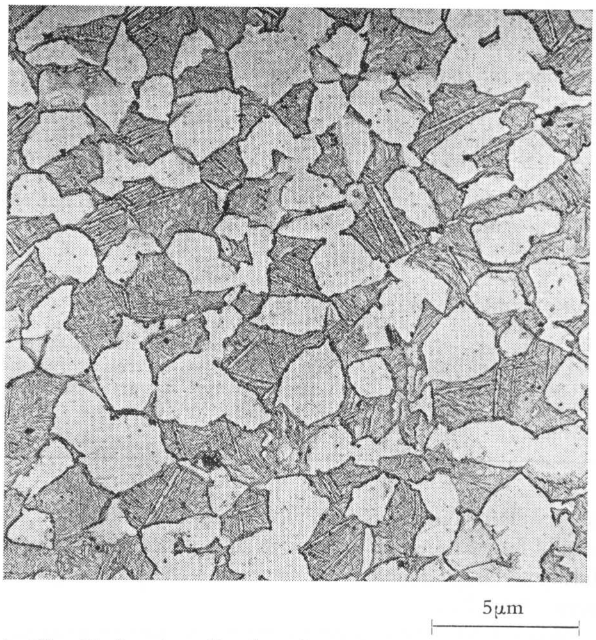
The retained β-phase in alloy *B* has allowed some preliminary determinations of the crystallography for the transformation to form coarse lenticular α regions. These suggest that the orientation relationship is that shown in Figure 9 and the habit plane is $(\bar{1}1\bar{2})_\beta$. This evidence and some information on the nature of surface tilts during similar transformations suggest that the microstructure is probably not formed martensitically.

TABLE IV Compositions of the titanium alloys examined

Alloy identification	Nominal composition, %				
	Al	Sn	Mo	Zr	Cu
A	3	6	...	5	...
B	3	6	2	5	...
C	4	2	4	...	...
D	2	11	1	5	...
E	8	...	...	...	...
F	...	...	...	...	2½
G	...	...	...	...	6
H	...	...	15	...	...



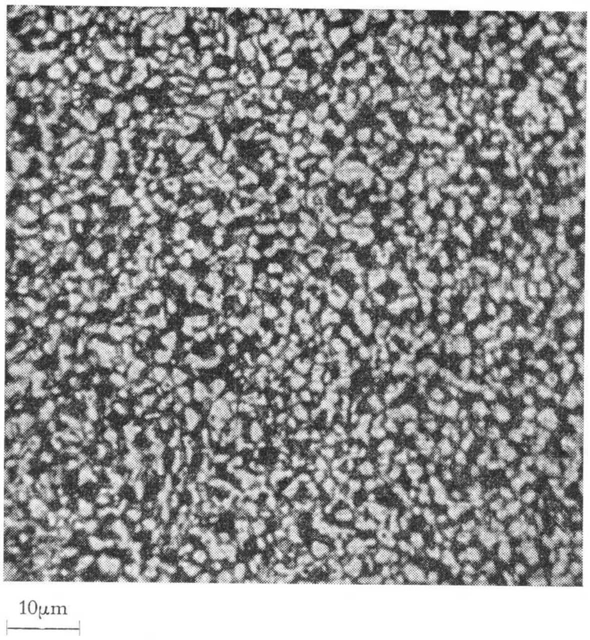
2 *Alloy B after air cooling from the β range; replica electron micrograph* ×3 000



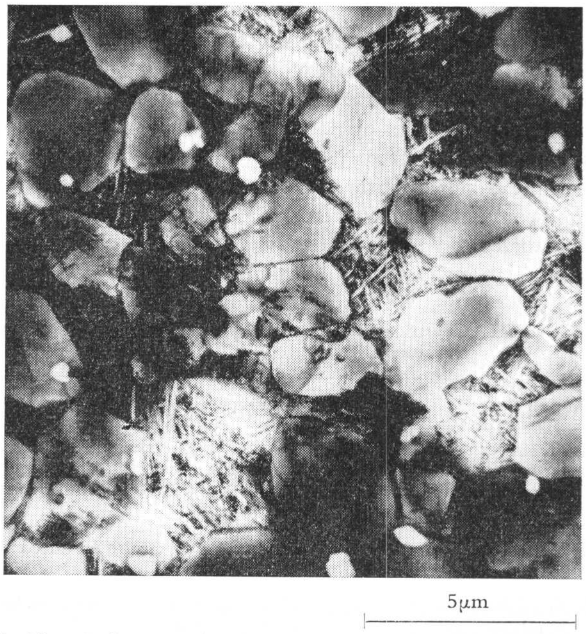
4 *Alloy C after air cooling from the α + β range; replica electron micrograph* ×4 000

Figure 3 is an optical micrograph from alloy *C* after an α+β solution treatment and air cooling. The small clear regions are equiaxed primary α-grains, and the dark honeycombe is a β region in which no evidence of decomposition is resolved. Figure 4 shows this same microstructure taken from a surface replica and Figure 5 from a thin foil by transmission electron microscopy. Both micrographs suggest that the β-regions have partially transformed into acicular martensite of a similar scale to that shown at S in Figure 2. This alloy contains 4%Mo as a β stabilizer that is negligibly soluble in the primary α-phase; therefore, it is concluded again that coarse structures are not easily formed in alloys containing β-retaining additions.

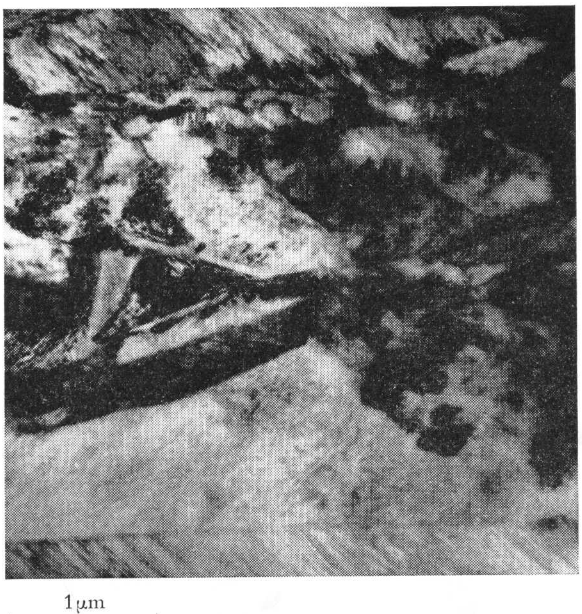
A similar sequence of microstructures were obtained from alloy *D* after α+β solution treatment and air cooling, but in



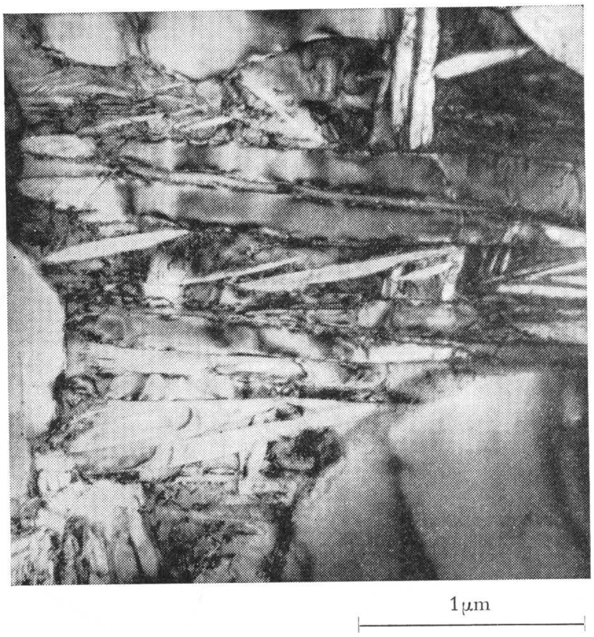
3 *Alloy C after air cooling from the α + β range; optical micrograph* ×1 000



5 *Alloy C after air cooling from the α + β range; thin-foil electron micrograph* ×6 000



6 *Alloy E after air cooling from the β range; thin-foil electron micrograph* ×20 000



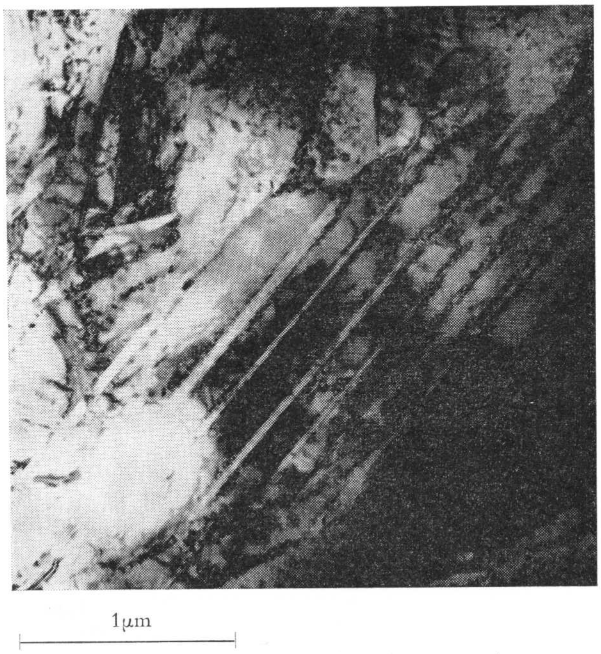
8 *Alloy C after air cooling from the α + β range; thin-foil electron micrograph* ×30 000

this instance there were fewer variants of larger acicular martensite plates in each decomposed β region. This is probably accounted for by the lower β-stabilization (1%Mo).

Internal twinning of titanium martensites

Optical metallography has never positively identified internal twinning of martensites formed in dilute titanium alloys.

During development of electropolishing techniques to produce thin foil specimens many micrographs showed martensite plates which apparently contained very fine twins similar to those observed in ferrous martensites[18] (Figure 6, alloy *E*). Electron diffraction analysis showed that this effect was produced by epitaxy with an oxide film that was difficult to eliminate from the specimen surface, but can now be removed by a short chemical etching treatment to reveal twin free martensite plates (e.g. Figures 8 and 10).



7 *Alloy F after cold water quenching from the β range; thin-foil electron micrograph* ×30 000

Mackenzie and Bowles[12] have shown that, theoretically, the inhomogeneous shear accompanying transformation in pure titanium is 0·0768 of the twinning shear, thus suggesting that twinning would not normally be expected. This prediction has been confirmed in most of the alloys examined; in fact, only one specimen of alloy *F* after cold water quenching from the *β*-phase contained some twinned martensite plates (Figure 7). In this instance the twin crystallography was found to agree with the commonly observed $(10\bar{1}2)\ [10\bar{1}\bar{1}]$ type.

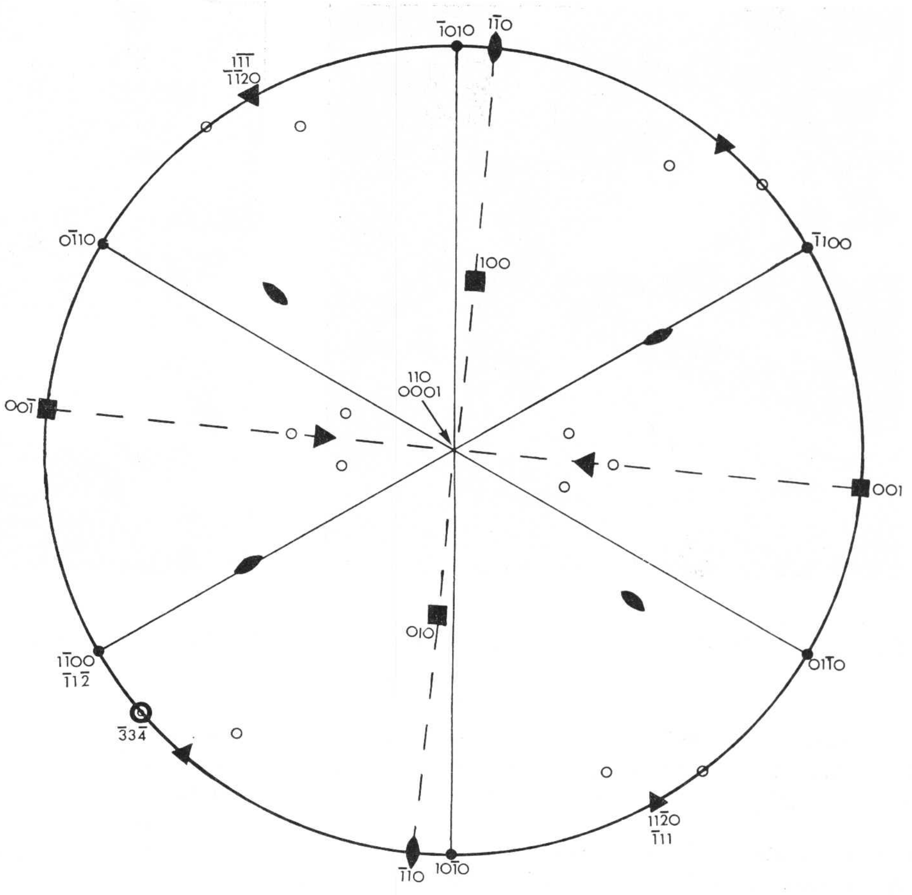
The crystallography of acicular martensite

When acicular martensite is formed in a region of retained β (e.g. alloys *C* and *D*) it is possible to study the detailed crystallography of the transformation by electron diffraction. Figure 8 shows such a region containing four prominent variants of clear martensite plates in alloy *C* after air cooling from the α + β range.

Electron diffraction studies from several similar regions showed that the martensite orientation relationship in both alloys *C* and *D* agrees closely with the previously determined relationship[9,10] for martensite of the $\{334\}_\beta$ habit in binary Ti–Mn, Ti–Mo, Ti–Cr, and Ti–Fe alloys, namely

$$(0001)_{\alpha'} \| (110)_\beta$$
$$[11\bar{2}0]_{\alpha'} \| [\bar{1}11]_\beta$$

The habit plane of the same acicular martensite plates was determined by normal trace analysis and in every case the result was within a few degrees of $\{334\}_\beta$.



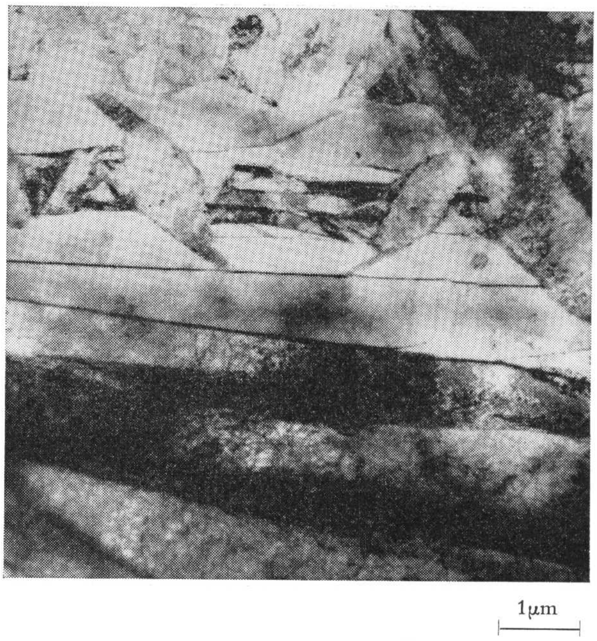
9 *Stereographic projection showing one variant of the orientation relationship for acicular martensite in alloys* C *and* D*; possible variants of the* $\{334\}_\beta$ *habit plane are denoted by open circles and the unique* $(\bar{3}3\bar{4})_\beta$ *habit plane for this variant of the orientation relationship is denoted by concentric open circles*

Previously it has not been possible to determine the unique relationship between a variant of the habit plane and its association with a particular variant of the orientation relationship, but by using selected area diffraction in conjunction with dark field techniques to study only one particular martensite variant, it was calculated that the definite orientation relationship mentioned above is uniquely associated with a $(\bar{3}3\bar{4})_\beta$ habit plane (Figure 9).

Supersaturated martensites in titanium alloys

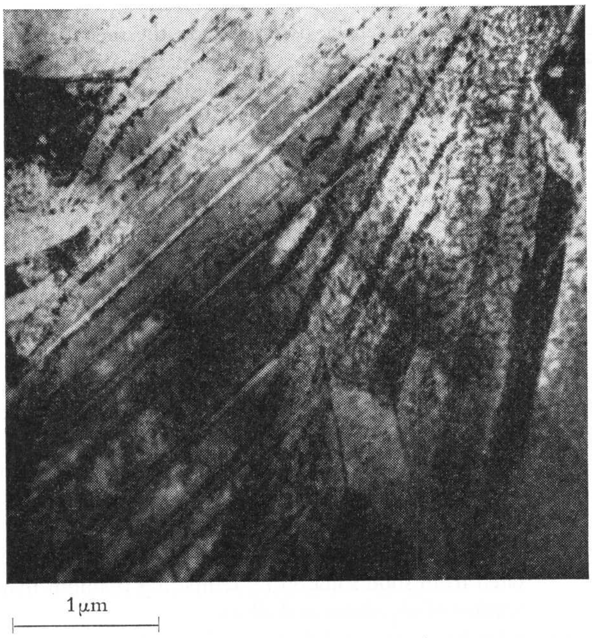
The commercial applications of ferrous materials containing martensite often rely upon a tempering treatment to precipitate an intermetallic phase from supersaturated martensite to produce optimum strength properties. A similar mechanism has been studied by electron metallography and electron diffraction in alloys *F* and *G* which had been cold-water quenched from both the $\alpha+\beta$ and β ranges.

Figure 10 is a micrograph from alloy *F* after quenching to retain the solute in solution in the acicular martensite plates, and Figure 11 the same alloy after tempering at 550°C. This micrograph shows a dispersion of small Ti_2Cu particles precipitated from solid solution in the martensite plates during tempering.



10 *Alloy F after cold-water quenching from the* β *range; thin-foil electron micrograph* ×12 000

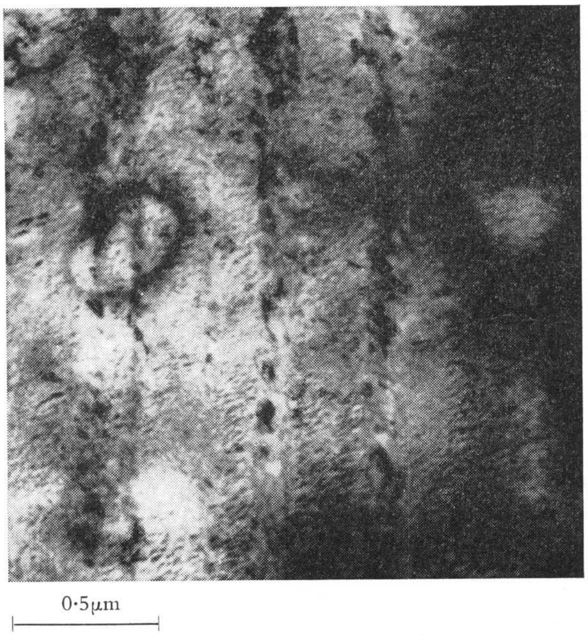
Figure 12 shows a similar dispersion of particles precipitated



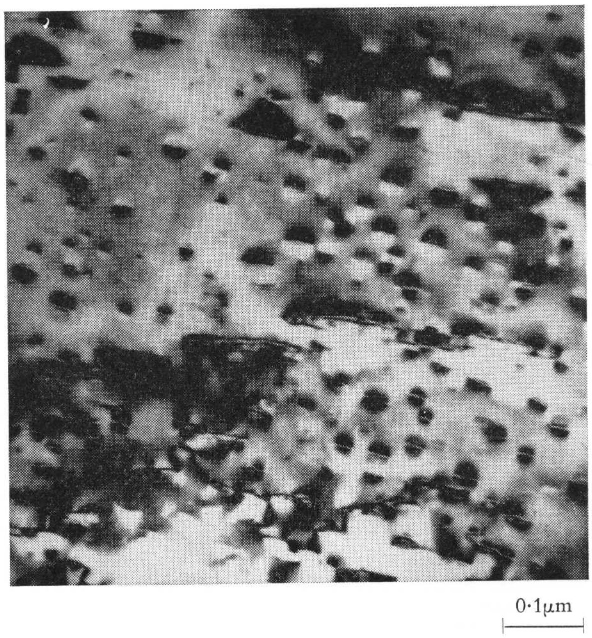
11 *Alloy F after quenching from the β range and tempering at 550°C; thin-foil electron micrograph* ×20 000

from solid solution during tempering martensite formed in alloy *G* by cold-water quenching.

Electron metallography also showed that there is a fine dispersion of plate-like particles in the coarse lenticular regions formed by air cooling alloy *A* (Figure 13). Attempts to eliminate the particles by quenching and attempts to grow the particles by long term aging in order to identify them have been unsuccessful, but their habit plane is known to be $\{0001\}_{\alpha'}$.



12 *Alloy G after quenching from the β range and tempering at 550°C; thin-foil electron micrograph* ×40000

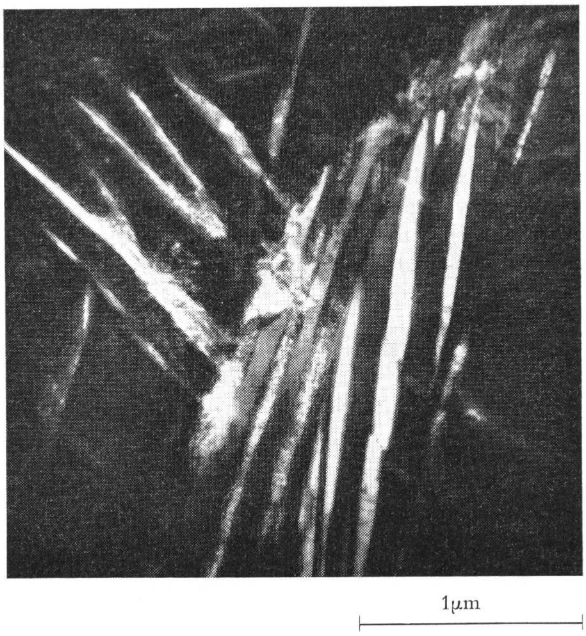


13 *Alloy A after air cooling from the β range; thin-foil electron micrograph* ×120 000

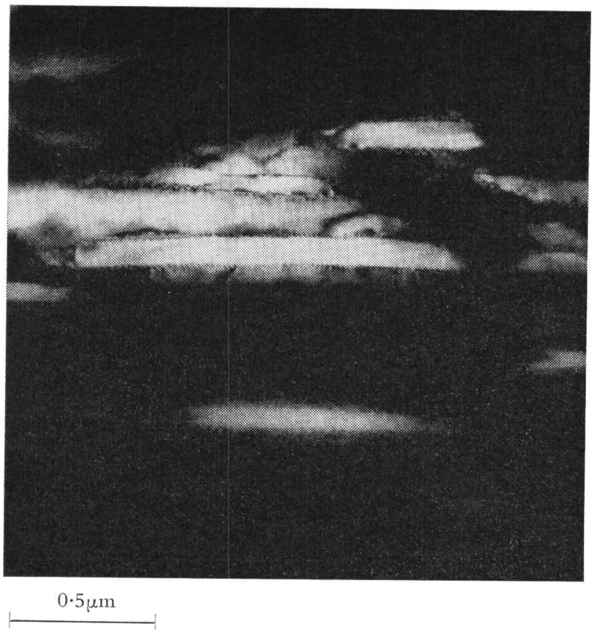
This feature might not strictly be an example of precipitation from a supersaturated solid solution.

Isothermal martensite in titanium alloys

Lenticular plates of α-phase were observed in alloy *H* after isothermally aging the equiaxed β-grain structure of the quenched alloy at 550°C. Figure 14 is a micrograph showing an acicular arrangement of plates and indicating how variants of lenticular



14 *Alloy H after isothermal transformation of the β-phase at 550°C; thin-foil electron micrograph* × 30000



15 *Alloy H after isothermal transformation of the β-phase at 550°C; thin-foil electron micrograph* ×40 000

plates can form in colonies nucleated near the β-grain boundaries. Individual α-plates with coherency dislocations along their interfaces with the β-matrix are shown in Figure 15.

At first sight it does not seem reasonable that martensite should form isothermally at temperatures well above the M_S temperature of the alloy (in this instance M_S is probably well below room temperature), but this alloy forms small dispersed particles of ω-phase even after cold water quenching, which can then be grown by low-temperature aging. Therefore, it seems possible that segregation of β-stabilizing solute element might allow isothermal martensite transformation by increasing the M_S temperature of small solute-depleted regions.

To confirm that this is a martensite transformation it is necessary to determine the detailed crystallographic relationships. Present indications suggest that the orientation relationship could be that described in Figure 9. An electron diffraction pattern showed $(\bar{1}1\bar{2})_\beta || (1\bar{1}00)_\alpha$ for one particular variant which was studied by single-surface normal trace analysis to suggest a unique habit plane near $(\bar{1}1\bar{2})_\beta$ that might possibly be $(\bar{3}3\bar{4})_\beta$. Further study should confirm the nature of this transformation.

CONCLUSIONS

The investigations reported in this paper have shown how the electron microscope can be used to study the metallography and crystallography of phase transformations in titanium alloys. The particular findings of the investigations can be summarized as follows:

(i) both coarse and acicular microstructures have been examined
(ii) the dimensions of transformed α plates appear to be reduced by the presence of greater concentrations of β-stabilizing element in the alloys
(iii) care must be taken when electropolished titanium specimens are examined in the electron microscope; an epitaxial oxide film is often formed which can be confused with internal twinning of the martensite plates
(iv) internal twinning of martensites has only been found to occur very infrequently in one alloy
(v) the unique association between a variant of the martensite orientation relationship and a particular $\{334\}_\beta$ habit plane has been determined
(vi) dispersed particles of intermetallic phase can be precipitated from solid solution by tempering titanium martensites of supersaturated alloys
(vii) it has been suggested that an isothermal transformation which apparently occurs above the M_S temperature of an alloy might be a martensite transformation.

ACNOWLEDGMENTS

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Martensite and bainite transformations in uranium alloys

J. Burke

SYNOPSIS
The evidence relating to the martensite and bainite transformations in uranium and uranium-rich alloys is reviewed and the results of recent kinetic and metallographic studies presented. In uranium alloys the martensite change occurs isothermally by slow growth and has C-curve kinetics. M_S *decreases with chromium content from 600°C in pure uranium to about 200°C in a uranium–1% chromium alloy. The driving force at* M_S *is found to be about 50 cal/mole. The reaction above* M_S *is similar to the bainite reaction in steels and is thought to involve both lattice shear and diffusion of chromium in the* β*-phase.*

INTRODUCTION

IN PURE URANIUM the β-phase is complex tetragonal containing 30 atoms per unit cell and is stable between 668° and 775°C; α, which is orthorhombic with four atoms per unit cell, is stable below 668°C. The $\beta \rightarrow \alpha$ phase change is insuppressible in the pure metal,[1] but in alloys containing about 0·5 at-% or more of certain solutes, notably the transition metals, the rate of the phase change is drastically reduced and the β-phase may be retained to room temperature by moderate quenching rates, thus permitting the isothermal transformation characteristics to be studied over a wide range of sub-critical temperatures. Several systematic investigations of the transformation kinetics have been made in uranium–chromium alloys over a range of chromium contents,[2–6] in a U–1%Pt alloy,[7] together with some general survey work of a range of alloys.[8] Metallographic and crystallographic studies have been carried out on a few selected alloys.[9–11] Out of this work has come the suggestion that three modes of transformation are possible, of which two, the low temperature martensite transformation and the mechanism having certain similarities to the bainite reaction in ferrous alloys, are relevant to this report. In the present paper the state of knowledge concerning these two transformations and some new results are presented.

ISOTHERMAL TTT DIAGRAM

The various reaction mechanisms may be discussed most conveniently with reference to the time–temperature–transformation diagram associated with isothermal sub-critical transformation. Figure 1 is the TTT diagram for the $\beta \rightarrow \alpha$ change in a U–0·85%Cr alloy determined by Townsend and Burke,[4] using a resistivity method. It consists of three *C* curves. The low-temperature *C* curve is well separated from the others by a bay of extended β stability. As the solute concentration is decreased the low-temperature *C* curve shifts to higher temperatures and shorter times and the separation between it and the higher temperature parts of the diagram become less marked. However, even in alloys containing about 0·1% solute there is still a distinct low-temperature *C* curve.[8] Attempts to establish a TTT diagram for pure uranium have so far proved unsuccessful.[5,8] The two high-temperature *C* curves overlap extensively and it requires careful measurement to separate them. Early published diagrams showed only one *C* curve covering this range of temperature, but the division into two overlapping curves is now well established experimentally, at least in alloys containing 0·85%Cr,[4] 1%Cr,[12] and 1%Pt.[7] In more dilute alloys the kinetics of the reaction modes corresponding with these two *C* curves are indistinguishable experimentally. However, metallographic examination of the morphology of the products of transformation suggests that the two modes persist at least down to 0·5%Cr.

The product of transformation in the high-temperature *C* curve is α-uranium plus dispersed particles of chromium.[3,6,13] The X-ray diffraction patterns of the fully transformed alloys consist of sharp, well defined lines of α, indistinguishable from those of well annealed pure uranium. Evidently long-range diffusion is involved in the transformation. This reaction will not be considered further. Transformation in the other two *C* curves will be considered in detail.

LOW-TEMPERATURE MARTENSITE REACTION

Isothermal transformation at temperatures in the range covered by the low-temperature *C* curve has many of the characteristics of a martensite reaction. The product of transformation is supersaturated α with a highly irregular, coarse grain structure (Figure 2). Grains up to 0·5 mm across are frequently observed, indicating that the rate of nucleation is extremely slow. Indi-

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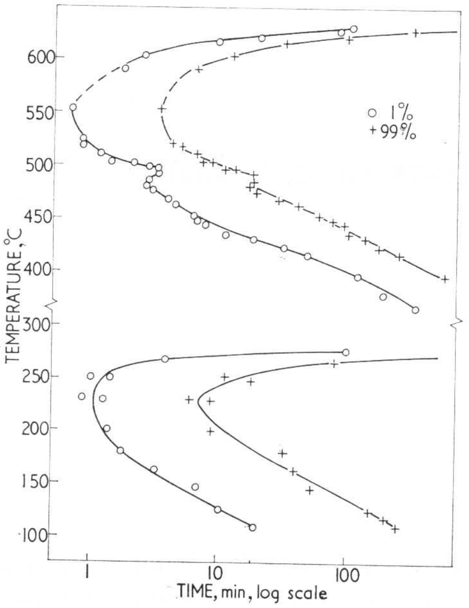


1 *Isothermal TTT diagram for a U–0·85%Cr alloy, determined by a resistivity method; the broken line covers a region in which the sensitivity of the technique is too low to give reliable results*

vidual grains are heavily twinned and show extensive subgraining. The X-ray diffraction pattern corresponds with the usual orthorhombic α-uranium cell but the lines are diffuse and the α_1–α_2 doublets irresolvable at all angles. α formed in this region recrystallizes when annealed just below the eutectoid. Clearly the product is subject to high internal stresses. Pure uranium rapidly cooled from the β-phase shows similar characteristics and presumably transforms athermally by a similar mechanism to that which occurs isothermally in the alloys.

Metallographic examination of partially reacted samples shows that nucleation of α occurs at favoured sites within the β-grains (rarely at grain boundaries) after an incubation period, the length of which varies from a few seconds for a U–0·5%Cr reacting at the nose of the *C* curve to several hours for a U–1%Cr alloy transforming at room temperature.

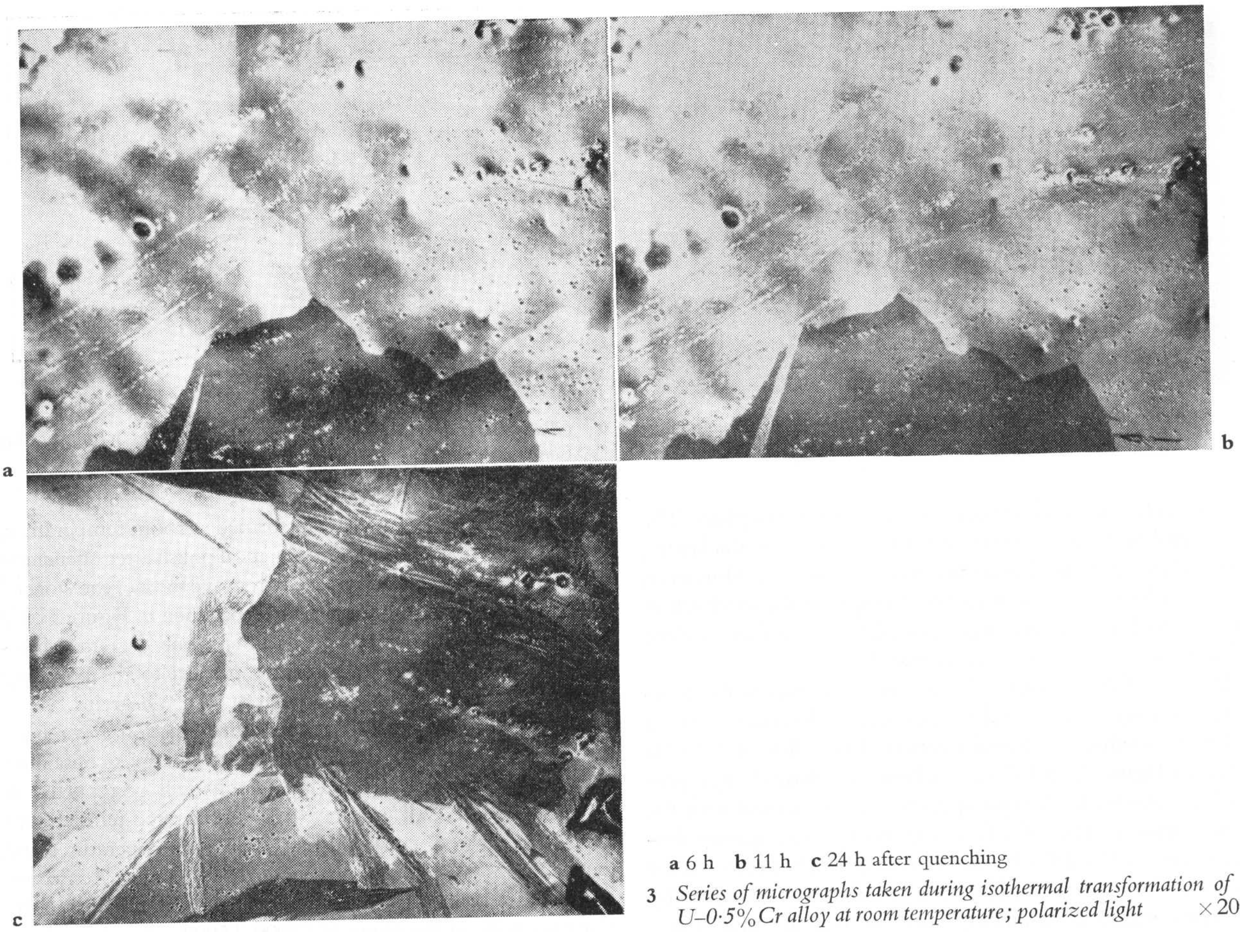
Even at the temperature of maximum transformation rate nucleation is rare compared with reaction in the higher temperature *C* curves. The micrographs in Figure 3 are typical of the mode of transformation at room temperature. These are part of a series taken of a sample of U–0·5%Cr that was polished before heating to, and quenching from, 730°C and then allowed to react on the stage of a microscope. The first crystal of α was observable 3½ h after quenching. After 6 h this had grown to the size shown in Figure 3*a*. It was in the form of a lenticular plate growing along a preferred plane in the parent β-grain. It continued to grow slowly both in length and thickness but the rate of lengthwise growth was very much faster than the increase in thickness. Measurements were made on several different α-plates on this sample and gave widely different values for the rate of lengthwise growth from 10^{-3} cm/h to 10^{-2} cm/h. Holden[10] found values of this same order. It is not clear whether this variation is due to a directional anisotropy of growth along the habit plane, which would be manifest as a variation in values measured on the plane of polish, or whether it is due to a variation in growth rate from grain to grain. Lengthwise growth stops when the plate reaches a grain boundary. Occasional examples have been noted of plates growing straight through small angle boundaries but large angle boundaries appear to be insurmountable obstacles (*see* Figure 3*b*). This implies that the α/β interface is at least partly coherent. It is to be expected that a completely incoherent boundary would propagate regardless of grain boundaries, as in the equiaxed diffusionless transformation in some ferrous alloys.[19] However, it often happens that once a plate is stopped at a grain boundary it induces the nucleation of a new plate in the contiguous β-grain, presumably due to the stress concentration at that point on the boundary. An example is shown in Figure 3*c*.

2 *α-phase (U–0·85%Cr) formed by isothermal reaction at 170°C; polarized light* ×35

Thickening continues after lengthwise growth has stopped. Measurement made on one needle gave a thickening rate of 2×10^{-4} cm/h. Slow isothermal growth is very unusual in martensite transformation but it has been observed in an Fe–28·8%Ni alloy reacting at room temperature by Yeo,[17] who reported growth rates approximately 500 times as fast as those reported here. Another example is the growth of β^1 martensite at room temperature in Cu–Al–Ni alloys.[18]

The α/β interface is usually irregular on a macroscopic scale presumably due to growth being halted at certain points due to some kind of obstacle. An extreme example is to be seen in Figure 3*c* in which the plate in the upper left hand β-grain has thickened locally to produce an inverted L-shaped crystal. Lengthwise growth is sometimes non-uniform over the advancing surface with the result that the plate appears to break up into a number of separate plates propagating along parallel habit planes in the β-grain and joined at a common base. The lathes of β trapped between these plates are ultimately transformed as the plates thicken. Similar observations have been made in the case of martensite in β brass.[15]

In Figure 3*c*, taken 24 h after quenching, a number of new plates have been nucleated, both in the β-grain to produce the first α-plate and in others. Eventually every β-grain produced several non-parallel α crystals; but in any one grain the maximum number of habit directions was three. Other authors[8,9] have reported the same results.



a 6 h **b** 11 h **c** 24 h after quenching

3 *Series of micrographs taken during isothermal transformation of a U–0·5%Cr alloy at room temperature; polarized light* ×200

It is clear that nucleation of α is difficult at room temperature and the reaction rate is determined by the growth rate and the β-grain size, since this determines the ultimate size of the α crystals. This is also unusual in martensite reactions.

The crystallography of the transformation has been studied by Holden[10] in a 1%Cr alloy transforming at room temperature and by Butcher and Rowe[11] in a 1·4%Cr alloy transforming at 90°C. The principal habit plane is $\{321\}_\beta$. The latter authors also found evidence for a $\{441\}_\beta$ habit. Both of these planes are unimportant in the β-lattice which is typical of many martensite reactions. Three orientation relationships between parent and product were found.

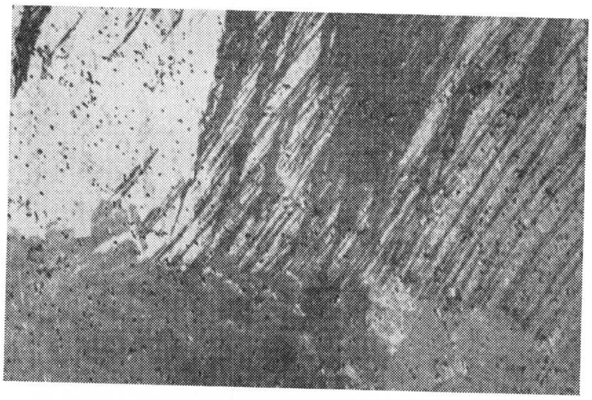
(i) $(001)_\alpha \parallel \{101\}_\beta$
(ii) $(001)_\alpha \parallel \{212\}_\beta$
(iii) $(001)_\alpha \parallel \{410\}_\beta$

Of these (i) and (ii) are by far the most important. Large isolated plates of orientation (iii) were not found and this relationship was deduced from pole figures of fully transformed specimens.

Lomer[13] computed the homogeneous strains associated with a very large number of possible lattice correspondences between the α and β-lattices and only in one case was the change in length of the principal β-lattice vectors less than 10%. The approximate orientation relationship deduced from this correspondence agrees with (i) above. Lomer showed that (ii) and (iii) could be accounted for on the basis of two β unit cells being the basic transforming unit and that the strains associated with (iii) are much greater than the other two. This may explain why crystals of (iii) are found only in the final stage of transformation when high internal stresses have accumulated.

The formation of α at room temperature produces a change in shape of the transformed region, as shown by the relief effects on a pre-polished surface and by the fact that scratches that were straight and parallel before transformation remain parallel after transformation but change direction across the transformed region.[10] Furthermore, the reaction is crystallographically reversible. On up-quenching partly reacted specimens to temperatures below the eutectoid temperature the β is regenerated.[6,9]

The mode of transformation illustrated in Figure 3, involving the nucleation and growth of relatively few isolated plates on non-parallel habit planes in any one β-grain, appears to be characteristic of room temperature transformations in all as-quenched uranium–chromium alloys. Raising the transformation temperature or applying a stress brings about a change in the metallography of the transformation (Figures 4 and 5). Examination of specimens of U–0·85%Cr partly reacted at temperatures near to the nose of the *C* curve showed that transformation proceeds by the simultaneous nucleation of groups of α-plates of similar orientation on parallel habit planes. Figure 4 shows an example of transformation at 211°C. Lengthwise growth is again several times as rapid as thickening



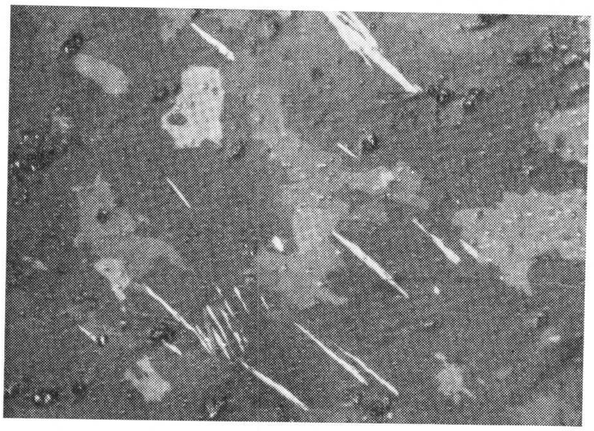
4 *Transformation of a U–0·5%Cr alloy at 211°C showing one principal growth direction; polarized light* ×150

and grain boundaries halt the growth of a group of plates. The individual plates in a group eventually coalesce as thickening proceeds, so that one β-grain produces one α-grain. Moreover, transformation proceeds unevenly throughout the specimen in that individual β-grains may completely transform before adjacent ones start to produce α-crystals.

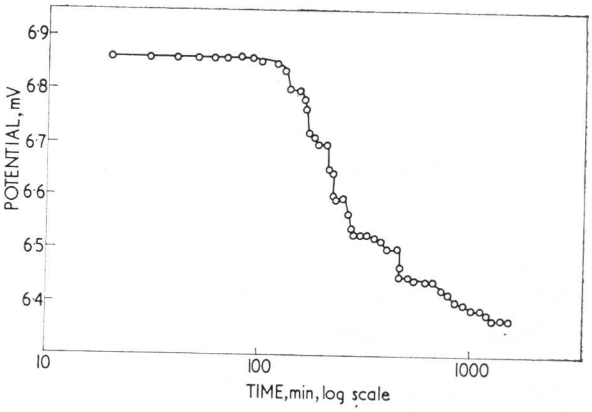
Because of this, isothermal reaction rate curves in this temperature range are irregular. The curve determined by a resistivity method for transformation of the alloy at 274°C is given in Figure 6, and illustrates how the phase change proceeds in 'bursts'. Each burst appears to be associated with the rapid transformation of a few α-grains by the sequence described above. The delay between bursts is the time required for thermal activation, assisted by the internal stresses generated by the transformation, to initiate transformation in other grains. The transformation curves associated with transformation at temperatures around room temperature do not show this 'burst' type behaviour.

The metallographic observations of Jepson *et al.*[8] on the effects of temperature are generally in accord with those reported here.

The effect of stressing is also to reduce the number of habit directions. Figure 5 shows the structure of a specimen similar to that in Figure 3, partially transformed at room temperature, which had been given a light mechanical polish after quenching followed by an electrolytic polish to remove most of the worked layer. In contrast to the as-quenched specimen in Figure 3 only one growth direction is produced in any one β-grain. Moreover, these are all parallel or nearly parallel to the polishing direction, irrespective of the orientation of the β-grains.



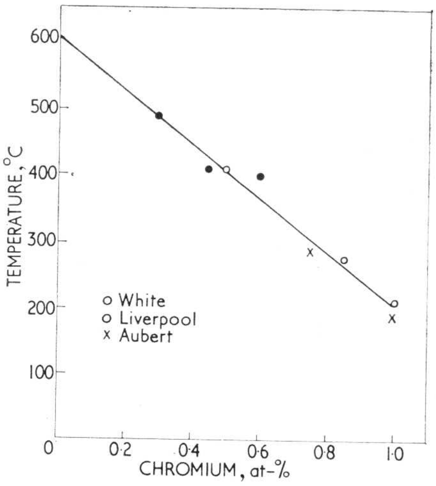
5 *Effect of prior plastic deformation on the habit planes of the β-phase in U–0·5%Cr transforming at room temperature; the specimen was given a light polish after quenching, as shown by the scratch, and then an electrolytic polish; polarized light* ×150



6 *Change in resistance of a specimen of U–0·85%Cr transforming isothermally at 274°C, showing 'bursts' of reaction*

The kinetics of the low-temperature reaction have been examined in a series of uranium–chromium alloys containing between 0·5 and 1·0%Cr. These results will be reported in detail elsewhere. All produce a *C* curve type temperature dependence, the *C* curve shifting to lower temperatures and longer times as the alloy content is increased. Activation energies determined from the low-temperature portion of the *C* curves were in the range of 11 000–15 000 cal/mole with no systematic variation with chromium content. These values are in agreement with those found by other authors.[6,14] In the absence of any detailed model for the transformation no fundamental significance is attached to the activation energy but the numerical value is of interest in so far as it indicates that thermal activation plays some part in the process.

The *C* curve associated with the low-temperature transformation in any given alloy was found to be asymptotic to an



7 *M_s as a function of chromium content in uranium–chromium alloys* upper limiting temperature. This temperature is M_S. The variation of M_S with chromium content is shown in Figure 7. The points plotted in this figure are taken from the Liverpool work carried out using a resistivity method and from other workers who used dilatometric and metallographic techniques. The data suggest that M_S decreases linearly with chromium contents.

The value of M_S in pure uranium is of some interest in relation to the discussion concerning the possible transformation mechanisms in the pure metal. Extrapolation to zero chromium puts M_S for pure uranium at 610±10°C. Several attempts have been made to confirm this by direct measurement. Jepson *et al.*[8] attempted to determine the TTT diagram. Their diagram for technical purity uranium (∽0·1% total metallic impurity) shows two *C* curves, the upper limiting temperature of the lower one being 580°C. This value corresponds with that predicted by the extrapolation shown in Figure 7 for an alloy containing 0·1%Cr. Their diagram for high-purity uranium is of doubtful significance but implies an M_S of ∽600°C. Duwez[1] using a high-speed thermal analysis technique found that the $\beta \rightarrow \alpha$ arrest decreased continuously with cooling rate to about 400°C at 7000 degC/s. There was no indication of achieving a lower limiting transformation temperature. Indeed the rate of depression increased with cooling rate, suggesting that with sufficiently fast cooling the transformation might be suppressed. A careful re-examination of transformation during continuous cooling at cooling rates up to 70 degC/s has been carried out by Townsend and Burke.[22] The results are shown in Figure 8. This figure is important in that it provides the most direct evidence yet obtained that two transformation mechanisms are possible in pure uranium. At cooling rates up to 45 degC/s only one arrest was observed; between 55 degC/s and 65 degC/s two arrests were often noted, separated by about 35 degC; for cooling rates in excess of 65 degC/s only one arrest occurred. The highest temperature of the lower arrest is 590±10°C, which corresponds closely with the M_S obtained by extrapolation of the uranium–chromium data. Since α-uranium produced by fast cooling pure uranium has the same characteristics as that produced by reaction in the low-temperature *C* curve of uranium–chromium alloys it is reasonable to assume that the low-temperature arrest corresponds with transformation by the same mechanism as in the alloys, and this is further supported by the agreement between the value of M_S determined from Figure 8 and that by extrapolation in Figure 7.

With this value it is now possible to estimate the minimum driving force for the reaction in pure uranium. The free energy difference between α and β at any temperature T is given by

$$\Delta G = \Delta H - T\Delta S$$

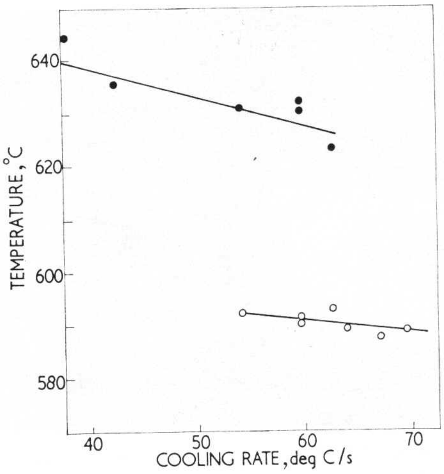
where ΔH is the difference in enthalpy and ΔS the difference in entropy between the two phases. At the temperature T_E at which α and β are in equilibrium

$$\Delta S = \Delta H / T_E$$

Provided that the temperature dependence of the specific heats of the two phases are not very different ΔH and ΔS will vary slowly with temperature and so ΔG may be written

$$\Delta G = \Delta H\,(1 - T/T_E)$$

Taking $\Delta H = 680$ cals/mole and $T_E = 668$°C, ΔG at M_S in pure uranium is approximately 50 cal/mole, which is remarkably low for martensite reactions.



8 *Thermal arrests associated with the $\beta \rightarrow \alpha$ transformation during continuous cooling in pure uranium as a function of cooling rate*

There are no thermodynamic data available for uranium–chromium alloys and so it is impossible to extend this calculation.

REACTION IN THE INTERMEDIATE *C* CURVE

Until the metallographic study of Beaudier *et al.*[16] it was thought that transformation throughout the temperature range covered by the two higher temperature *C* curves in Figure 1 occurred by the same mechanism. These workers showed that in a U–0·6%Cr alloy the morphology of α produced at 450°C was quite different from that produced at higher temperatures, and this work has prompted a re-examination of transformation throughout this temperature range in several laboratories. The cusp in the TTT diagram is now firmly established and is further confirmed by the existence of discontinuities in graphs of resistivity and hardness of transformation product as a function of transformation temperature, which coincide with the cusp in the TTT diagram.

α formed below this cusp but above M_S has an irregular feathery appearance with suggestions of some acicular grains

9 *α-uranium in U–0·5%Cr formed by isothermal transformation at 450°C; polarized light* ×150

10 *Specimen of U–0·5%Cr partially transformed at 450°C; polarized light* ×150

11 *Surface relief produced by partial transformation at 450°C; U–0·85%Cr* ×150

(Figure 9). The grain size is very much smaller than that of α formed below M_S. X-ray diffraction photographs give lines which are broad and diffuse.

Metallographic examination of partially reacted samples suggests that a large number of α-plates or needles are nucleated seemingly at random throughout β-crystals and grow in several different directions, as shown in Figure 10. There are at least five different trace directions in any one β-grain, two of which are mutually perpendicular suggesting growth on $\{100\}_\beta$ or $\{110\}_\beta$. The α-grain crystals produce relief effects on a pre-polished surface as shown in Figure 11, but attempts to observe the behaviour of surface scratches have so far proved unsuccessful. Finally, Aubert[6] up-quenched specimens partially transformed in this region and claimed that the reaction is crystallographically reversible at temperatures above 650°C, which is higher than the temperature required to reverse the low-temperature transformation and is approximately the eutectoid temperature on heating.

The kinetics of isothermal transformation in this range have been measured. The transformation produces smooth sigmoidal curves with no signs of 'bursts'. The activation energy for the reaction is in the order of 40000 cal/mole at 0·85%Cr, increasing to 60000 cal/mole at 1%Cr. As a result of this relatively high activation energy the reaction rate is particularly sensitive to temperature.

DISCUSSION

Martensite reaction

Although the significance of shape changes during a phase change has been questioned, Christian[20] has concluded that an observed shape change indicates a martensitic type of growth process in which the structural change involves the movement of semi-coherent boundaries. Hence the low-temperature reaction in uranium alloys is correctly described as martensitic. It possesses many of the features commonly shown by other martensitic reactions such as irrational habit plane, autocatalysis, crystallographic reversibility, and sensitivity to applied stress. Martensitic reactions in ferrous alloys have been further sub-divided by Owen *et al.*[19] into massive martensite and acicular martensite on the basis of the morphology and fine structure of the product and the transformation habit plane. On this basis uranium martensite is of the massive type in so far as the product is large irregular shaped grains and individual plates often form in packets within one parent grain. Electron microscopy has so far failed to reveal fine twins in uranium martensite. The substructure consists of a high density of irregular dislocations together with many large twins presumably formed to accommodate the transformation dilatation. This again is similar to massive martensite in iron–nickel alloys. One difference, however, is in the magnitude of the driving force which in pure uranium is about one-fifth of that characteristic of massive martensite in iron–nickel.

Two explanations of the slow isothermal growth have been advanced. In the first, due to Mott and Haines[9] and Holden,[10] it is proposed that growth is intrinsically a fast process but that the speed is not realized because of the difficulty of accommodating the shape and volume change. β is almost completely brittle and so accommodation is effected largely by plastic deformation in the α by twinning. Growth should be rapid at first, slowly decreasing as the back stresses build up, ultimately reaching a value sufficient to nucleate twins in the α, which thus yields relieving elastic stresses, and permitting a further period of rapid growth. On this basis the effect of solutes on the phase change is primarily associated with the stiffening of the α-lattice.

Various factors are difficult to reconcile with this theory;

(i) metallographic and kinetic studies in uranium–chromium alloys suggest that the growth rate decreases fairly rapidly with temperature; in pure uranium the fact that the transformation temperature continuously decreases as the cooling rate increases also implies that growth rate is temperature dependent. If growth is not a thermally activated process then it is to be expected that the rate of growth should increase or at least remain virtually constant as the temperature decreases, because the driving force increases more rapidly with undercooling than do the elastic constants

(ii) there is some evidence that molybdenum is one of the least effective β-stabilizers and yet one of the most effective hardening solutes in α.

The alternative explanation due to Lomer[13] is that growth is intrinsically a slow process due to the complexity of the atom movements involved. In the β-lattice only one atom in 30 is sited on a lattice point and in the α-lattice also most atom sites do not correspond with lattice points. Thus the lattice deformation derived by Lomer and found to be consistent with the observed orientation relationship puts only one atom in 30 or 60 onto an actual atom site in the α-lattice, necessitating extensive reshuffling of atoms to accomplish the structural change. On this picture growth involves the migration of a semicoherent interface by means of the thermally activated movement of single atoms through distances comparable with the interatomic spacing.

This theory is preferred to the first one. The *C* curve kinetics of the reaction in uranium alloys and the effect of increased cooling on the reaction in pure uranium indicate strongly that nucleation and growth are thermally activated.

One possible difficulty is the effect of solutes. In pure uranium the growth is comparatively fast, while in alloys containing as little as 0·5% solute the growth is slower by several orders of magnitude, although the addition of one foreign atom in 200 can hardly affect the complexity of the atom movements. It may well be that the role of solutes is to decrease the free energy of β relative to α and so depress M_S to lower temperatures at which growth is retarded due to the necessity for thermal activation.

Reaction at intermediate temperatures

The reaction at intermediate temperatures has some of the characteristics of the martensite reaction: the product is acicular, forms on preferred planes in the parent (although probably different ones than martensitic α), produces a shape change, and is internally stressed. Kinetically it resembles the diffusional reaction found at high temperature; the two *C* curves overlap extensively and they both have high activation energies.

The shape change indicates that the α/β interface is semicoherent and that there is a lattice correspondence. As emphasized by Christian,[20] in principle this does not exclude the possibility that the mechanism of growth involves thermally activated movement of substitutional atoms, but it is extremely unlikely since it should be possible for these same atom movements to destroy the correspondence and relieve the associated strain energy. However, if the minor component diffuses much more rapidly than the substitutional atoms then it is possible for redistribution of the more mobile solute to occur while the main structural change is accomplished martensitically. This type of phase change, of which bainite is the most well known example, is expected to occur in a temperature range above M_S (because the redistribution of solute releases additional free energy relative to a completely martensitic transformation), where the solute is sufficiently mobile to permit migration over several hundred interatomic distances during the time of growth and where the substitutional atoms are able to migrate over one or two spacings at most. Some measurements of the rate of diffusion of chromium in β-uranium have been made by Rothman.[21] The diffusivity of chromium was found to be faster than self-diffusion of the uranium by a factor of 160. This implies that a bainite type reaction is possible. Thus it is suggested that the chromium atoms segregate within the β, allowing plates of α to form martensitically in regions of essentially pure uranium. The rate of growth is governed by the rate of diffusion of chromium. Although there is no value for the activation energy for diffusion of chromium in β-uranium, the observed activation energies for this mode of reaction (40000–60000 cal/mole) are of the right order. According to the theory precipitates of chromium should be found between the α-plates. So far none has been observed but attempts are currently being made using transmission electron microscopy.

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Bainitic transformations in copper–zinc and copper–aluminium alloys

R. D. Garwood

SYNOPSIS

The product that forms during the isothermal decomposition of metastable β-brass below a critical temperature has been described as bainitic because (a) *the transforming region is homogeneously sheared on a macro-scale, and* (b) *the plates adopt the same habit planes as those reported for the sub-zero martensitic transformation. At higher temperatures the α-precipitate is of rod-like form and recent investigations have shown that the upper temperature limit for the plate-like mode of growth varies with the composition in a manner similar to the* M_s *point. This suggests that the transition occurs at a* T_0 *temperature where the α- and β-phases of the same composition are in thermodynamic equilibrium.*

The analogous transformation in copper–aluminium alloys, which takes place during both the isothermal and the continuous cooling modes of decomposition, has been studied using the latter technique. It is shown that the bainitic plates are nucleated and grow primarily in the copper-enriched regions between the domains of the Cu_3Al *superlattice.*

The significance of the morphological changes in both alloy systems is discussed. 2586

INTRODUCTION

THE INCLUSION of a paper on transformations in copper-based alloys in the proceedings of a conference organized by BISRA is an acknowledgement that useful information concerning the mechanism of transformation of austenite in steel may be obtained from a study of analogous transformations in other alloy systems. Since the classical study by Smith and Lindlief in 1933 on copper–aluminium alloys,[1] much attention has been devoted to eutectoid transformations in non-ferrous systems, a topic which has been the subject of a recent comprehensive review.[2] Martensitic transformations of the β-phase, electron compounds in copper alloys have also been studied in some detail,[3] although progress in understanding these reactions has, until recently,[4,5,6] been hampered by the uncertain crystal structure of the β′-martensite in copper–aluminium and copper–zinc alloys. Other factors that detract from the usefulness of transformation studies in copper-based alloys are the lack of thermodynamic and diffusional data, and the complication of an order ⇌ disorder reaction in the parent β-phase.

In spite of these difficulties the study of copper-based alloys has much to recommend it for it gives some insight into those modes of transformation which are least understood in steels, namely the 'massive' and 'bainitic' reactions. Indeed the term 'massive' was first used by Greninger[7] to describe a non-martensitic form of the β→α reaction which takes place without an apparent change of composition in rapidly cooled copper–aluminium alloys. Massive transformations form the subject of another contribution to this conference[8] and will not, therefore, be discussed further in this paper.

BAINITIC REACTION IN COPPER-BASED ALLOYS

The use of the term 'bainitic' to describe the slow isothermal growth of plates of α- from β-brass containing 41·3% Zn between 150° and 400°C was first suggested by the author in 1954.[9] The justification for this description arose from the following observations:

(i) the plates adopt the same habit planes, $\{2.11.12\}_\beta$, as in the martensitic transformation which occurs when metastable β-brass is cooled below room temperature[10]

(ii) the formation of the plates is accompanied by a surface relief effect in which the transformed volume appears to undergo a homogeneous shear

(iii) on transforming below 225°C, the Debye-Scherrer X-ray patterns exhibited by the precipitate contain many extra lines and resemble those shown by the martensite.[11]

It was therefore argued that the interface between the parent and precipitating phase was martensitic in character and that the slow isothermal growth of the plates was controlled by the diffusion of zinc away from the transforming region. The mechanism was analogous to that suggested by Ko and Cottrell[12] for the growth of bainite in steel except that the additional change in chemical free energy, which provides the driving force for the reaction, was due solely to the diffusion of

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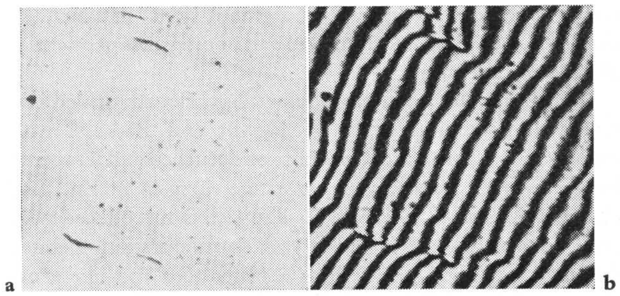
zinc into the matrix and not to the precipitation of a second phase (carbide).

The description of a diffusion controlled, displacive process as 'bainitic' when a single phase precipitates from solid solution may legitimately be criticized on the grounds that in plain carbon steels bainite is a two-phase aggregate of ferrite and carbide. There are also two bainite reactions in steel and a prominent feature that distinguishes upper from lower bainite is the difference in form and distribution of the carbide particles.[13] However, carbide precipitation may be secondary only to the main reaction which involves the transformation of the iron lattice from fcc to bcc. If this is the case the extension of the term to other shear type transformations, where growth at constant temperature is controlled by diffusion, is fully justified.

FERROUS BAINITES

There are conflicting opinions concerning the bainite reaction in steels. In one theory it has been proposed[14] that the basic process responsible for the $\gamma \rightarrow \alpha$ lattice transformation is the same regardless of whether the product is lower bainite, upper bainite, or Widmanstätten ferrite. The justification for this assumption is that surface relief effects of the shear type have been observed to accompany transformation into Widmanstätten ferrite,[15] as well as upper[16] and lower bainite.[12]

As Widmanstätten ferrite may form with as little as 30 degC undercooling below the equilibrium γ/α phase boundary, this view is at variance with an earlier theory[17] in which an upper limit was set for the bainite reaction (B_S) coinciding with the thermodynamic temperature T_0. This is where the free energy of the austenite is equal to that of supersaturated ferrite of the same composition ($\Delta F_{\gamma \rightarrow \alpha} = 0$). Evidence also exists for a discontinuity between the upper and lower bainite reactions and separate *C* curves have been reported.[18] An attractive hypothesis is that lower bainite forms as supersaturated ferrite by a diffusionless reaction of the martensitic type and that carbide subsequently precipitates behind the moving interface.[19] During transformation into upper bainite, on the other hand, a carbon build-up is envisaged in the austenite in front of the moving γ/α interface.[20] This concentration is most efficiently dispersed by diffusion at the sharp edges of a plate, whereas enriched regions of austenite trapped between the sides of parallel plates eventually precipitate carbides.



1 *Light micrograph and interferogram of relief effect accompanying the formation of 'bainitic' α on tempering quenched brass containing 41·3%Zn at 400°C for 120 s; mercury green line, λ=5460Å* ×460

Although the study of the displacive precipitation reaction in brass and its analogue in copper–aluminium alloys is unlikely to clarify discontinuities in the bainite reaction in steel arising from differences in the sites and the nature of carbide precipitates, morphological similarities may exist between the lattice transformations in the two cases which justify further research. This philosophy is accentuated by the recent report that in nickel–chromium steels, at least, upper bainite forms as rods or needles and not as plates.[21] The long-standing evidence of a continuous transition of the bainite habit planes towards the $\{111\}_\gamma$ pole as the transformation temperature is raised must now be in doubt.

Some evidence for a discontinuous change in the morphology of the transformation product in brass already exists.[9] It must also be noted that a duplex reaction similar to upper bainite has been reported in copper–aluminium alloys[22] where the β-phase decomposes into a two-phase, non-lamellar aggregate of α and γ_2.

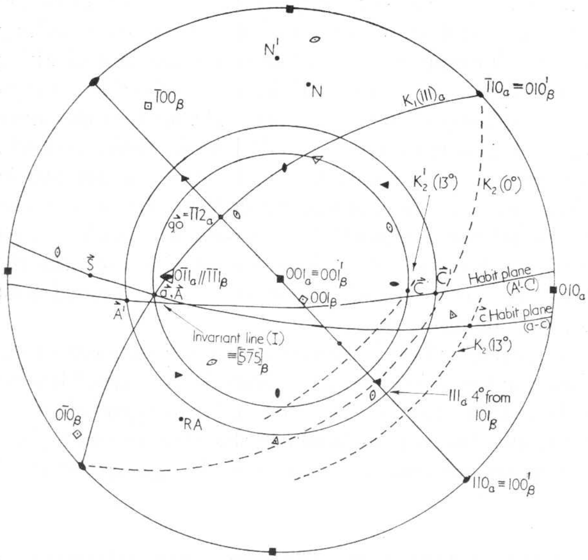
SURFACE RELIEF ACCOMPANYING THE BAINITIC REACTION IN BRASS

Possibly the most characteristic feature of the bainitic reaction in isothermally transformed β-brass is the change in shape of the transforming region. When tilting on a pre-polished surface was first observed[9] no attempt was made to assess the magnitude or the direction of the shear. The distortion in this alloy is so described because the change in volume during transformation is small.

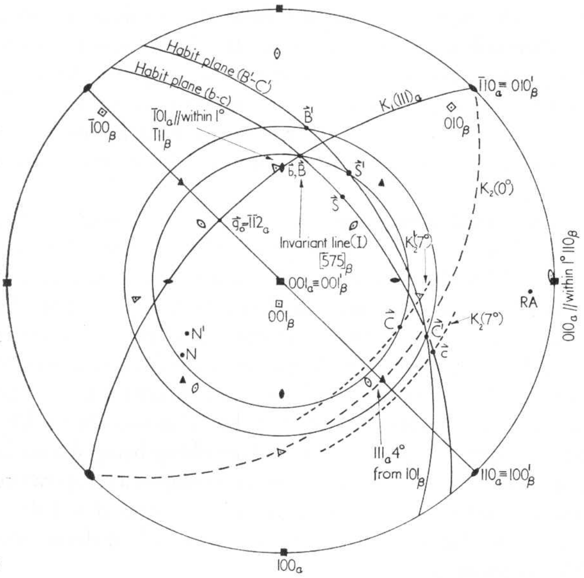
A theoretical appreciation has recently been made of the origin of surface relief effects in phase transformations.[23] It was concluded that shape changes of the shear type would not occur in diffusion-controlled precipitation reactions in which the average distance travelled by the atoms is of the order of the size of the product crystals. As this view conflicts with present observations, more precise information concerning the nature of the surface relief is obviously desirable. This was obtained by interferometry, examples of the surface tilting being shown in Figures 1*a* and *b*. Clearly, even on tempering at a temperature as high as 400°C, the transformed region is sheared and there are accommodation strains in the β-matrix, at least during the initial stages of growth of the plates.

The plates at this temperature were sufficiently wide to allow measurement of the angles of surface tilt. These, of course, vary as the direction and plane of shear change relative to the plane of the polished surface. Nevertheless the values observed should all fall below a maximum not much in excess of the true angle of shear (γ), provided that the latter is reasonably small. As there is a tendency to select plates for measurement showing the largest relief, it is not unreasonable to assume that γ lies within 8–12° range of the observed tilt angles.

This value is in good agreement with the shear angle observed for the sub-zero martensite transformation in brass[24] and also accords with that forecast theoretically by a Lieberman[25] stereographic analysis of a bcc → fcc transformation (Figure 2*a* and *b* and Table I). In making the analysis it was assumed that the atomic volumes did not change from the parent to the product phase so that the results are also applicable to the β′-martensite transformation where the assumption of an fcc product lattice in copper–aluminium alloys has been justified by



a



b

in making the analysis it was assumed that the atomic volumes of both phases are the same and that the inhomogeneous shear occurs on a $(111)_\alpha$ plane and in the $[\bar{1}\bar{1}2]_\alpha$ direction. For convenience the strains were assumed to take place in the sequence *a* inhomogeneous shear, *b* Bain strain, *c* lattice rotation; however, the solution is independent of the order in which these operations are carried out. Poles of the β-lattice are shown as open and those of the α-lattice as closed symbols. The letters *N* and *S* give the positions of the habit plane normal and the direction of shear of the invariant plane strain respectively (*N'* and *S'* are their positions before operation *c*, a rotation about the axis marked *RA*, is carried out.) The *a–c* solution is shown in (**a**) and the *b–c* solution in (**b**)

2 *Stereographic analysis of the bcc→fcc lattice transformation after Lieberman*[25]

Swann and Warlimont.[4] Because an *AB* type superlattice exists in β-brass, it would be more correct to regard the product as face-centred tetragonal (AuCu type I structure), and when this is done[26] the habit plane normal is more accurately forecast. However, the solutions obtained stereographically are in good agreement with the known habit planes of β'-martensite in copper–aluminium alloys, where there is little degeneration of the cubic symmetry due to A_3B type ordering. The two possible solutions predict twin related orientations for the product lattice, in both of which a close-packed plane occurs approximately 60° from the habit plane normal as has been experimentally observed.[7,10,24] This is not the case in the numerical solution reported by Jolley and Hull, whose analysis was based on a product lattice of orthorhombic symmetry.

TABLE I Predictions of the stereographic analysis of the bcc→fcc transformations*

	Solution A directions (*a–c*)	Solution B directions (*b–c*)
Interface plane normal, *N*	$\begin{bmatrix} -0·7254 \\ 0·6561 \\ 0·2079 \end{bmatrix}_\beta$	$\begin{bmatrix} -0·1822 \\ -0·6561 \\ 0·7314 \end{bmatrix}_\beta$
Shear direction *S* in habit plane	$\begin{bmatrix} -0·6361 \\ -0·7547 \\ 0·1736 \end{bmatrix}_\beta$	$\begin{bmatrix} -0·1564 \\ 0·7501 \\ 0·6428 \end{bmatrix}_\beta$
Angle of shear	12°	9·5°
Invariant line of Bain strain+rotation	$\begin{bmatrix} -0·5000 \\ -0·7040 \\ 0·5000 \end{bmatrix}_\beta$	$\begin{bmatrix} -0·5075 \\ 0·7022 \\ 0·4924 \end{bmatrix}_\beta$
Orientation	$0\bar{1}1_\alpha \| \bar{1}\bar{1}1_\beta$	$\bar{1}01_\alpha$ within 1° of $\bar{1}11_\beta$
Relationship	111_α 4° from 101_β	010_α within 1° of 110_β 111_α 4° from 101_β

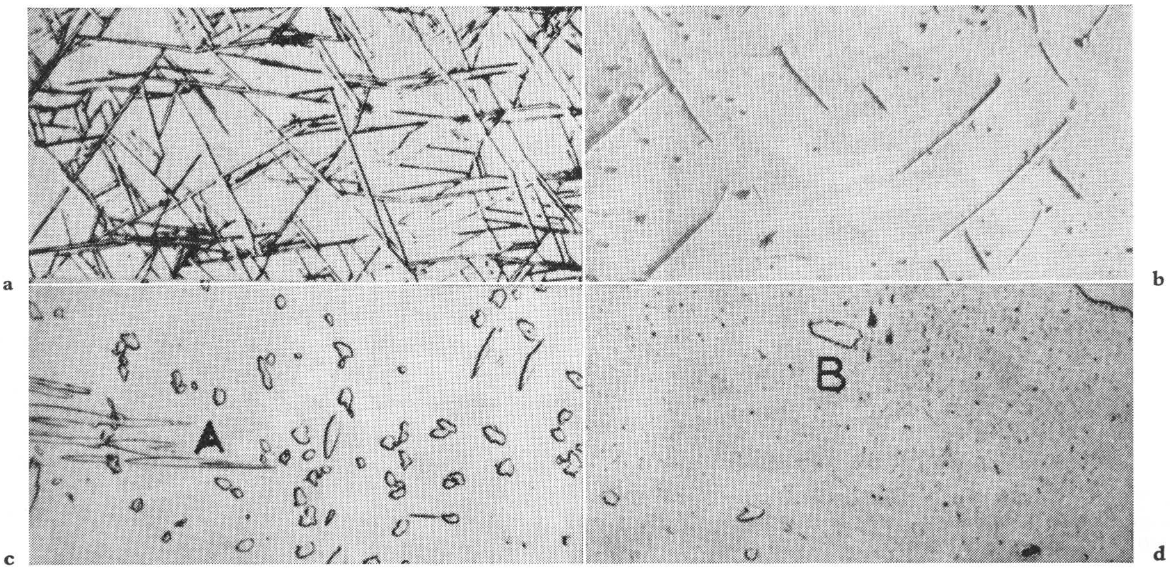
* The α-lattices in solutions A and B when normalized to the same variant of the habit plane are twin-related about the K_1 composition plane, i.e. 111_α in Figure 2*a* and *b*

The existence of a surface relief effect of the shear type in this precipitation reaction, despite the prediction that it should not occur when substitutional diffusion is involved,[23] can probably be traced to the arbitrary assumption that the diffusion process responsible for the change in composition of the precipitate occurs at the same rate as that which relaxes the shear stresses in the matrix. These arise from the displacive nature of the lattice transformation and the existence of a martensitic type coherency at the planar interfaces of the precipitate. This point will be discussed more fully below.

MORPHOLOGY OF THE PRECIPITATE IN BRASS

Unlike the bainite reaction in steel, there is little change in the habit planes adopted by the plates of α-brass during precipitation in the temperature range 150°–400°C.[27] However, above 350°C in the 41·3%Zn alloy the plate-like form of the precipitate disappears and is replaced by a granular one[9] in which the particles are more rounded in shape and possess less geometrically regular interfaces.

This abrupt change in morphology has been confirmed in a recent microscopical study by Flewitt and Bader,[28] who examined the structure of a number of quenched and tempered brasses within the composition range 40·5–44·1%Zn. The change is illustrated in Figure 3*a–d*, which is reproduced with their kind permission. It will be seen that the transition above the critical temperature is from a plate- to a rod-like morphology, although frequently the rods appear as V-shaped pairs separated by an acute angle (*A* in Figure 3*c*). When the incubation periods for visible precipitation are plotted on time/temperature diagrams, e.g. as in Figure 4, discontinuities suggest

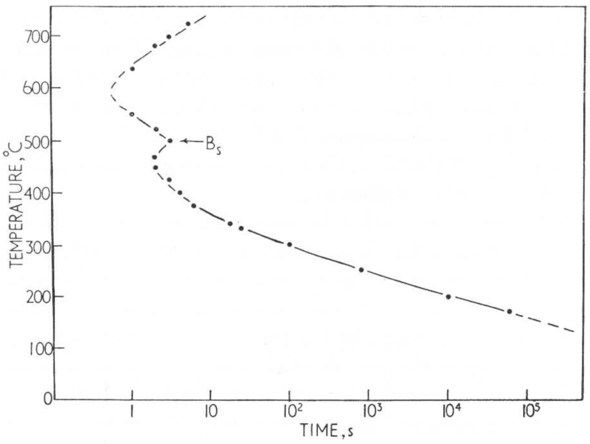


a 40·5%Zn alloy tempered for 10 s at 400°C
b 41·6%Zn alloy tempered for 360 s at 300°C
c 43·2%Zn alloy tempered for 60 s at 400°C
d 44·1%Zn alloy tempered for 100 s at 400°C

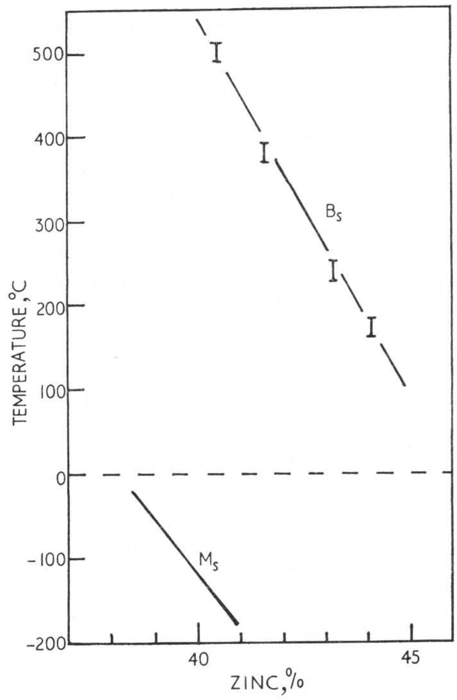
3 *Microstructures of quenched and tempered brasses illustrating the change from plate-like to rod-like morphology (after Flewitt and Bader*[28]*); etched in ammoniacal persulphate* × 1000

that there are two separate reaction curves for the low- and high-temperature forms of precipitation. The one which governs the plate-like mode of growth would appear to suffer a sharp cut off at the upper limiting temperature (B_s) for this type of precipitation. It will be seen from Figure 5 that the transition temperature varies with the composition of the alloys in approximately the same manner as the M_s, although the latter occurs at a much lower temperature.[29]

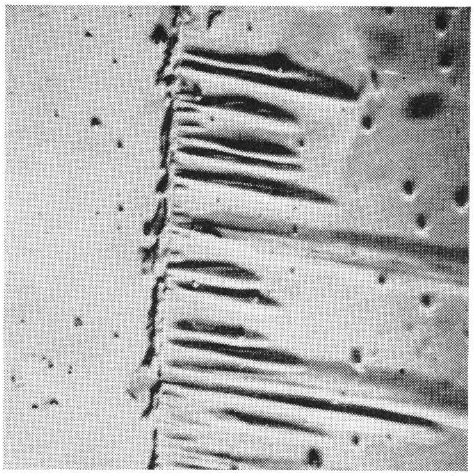
The 44·1%Zn alloy with its low transition temperature is an ideal material for conducting a critical experiment to determine whether the rod-like, high-temperature form of precipitation gives rise to a surface relief effect. This possibility was examined by Flewitt and Bader and a relief effect confirmed (Figure 6). Further investigation is desirable to establish the nature of the strain and whether a relationship exists between this shape change and the flat facets visible in the microstructure when the



4 *Time/temperature diagram showing the incubation period for α precipitation in a brass containing 40·5%Zn; there is a discontinuity when the precipitate morphology changes from plate-like to rod-like (after Flewitt and Bader*[28]*)*



5 *Variation of the upper temperature limit for the plate-like mode of precipitation with composition in brass (after Flewitt and Bader*[28]*); the M_s temperatures*[29] *are also given*



6 *Surface relief associated with rod-like mode of precipitation when a quenched 44·1%Zn brass is tempered* in vacuo *for 3 000 s at 340°C (after Flewitt and Bader)* × 1 000

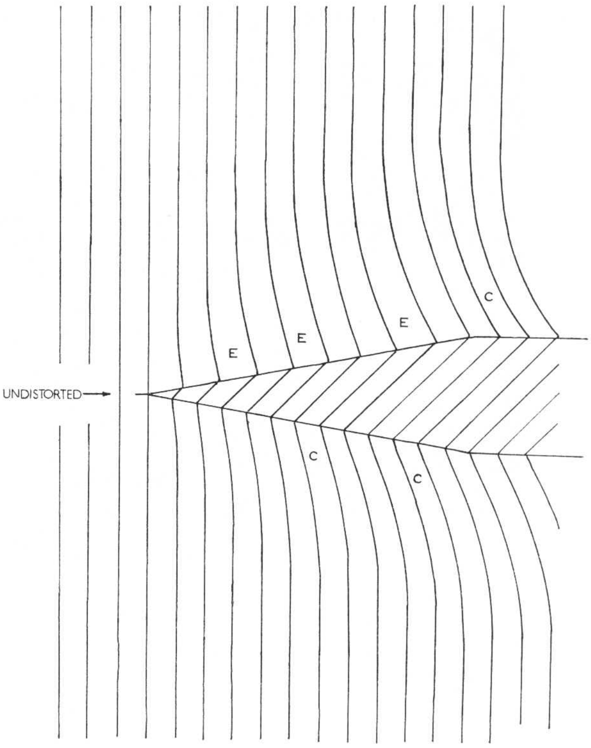
rods are sectioned approximately perpendicular to their axes (*B* in Figure 3*d*).

LOW- AND HIGH-TEMPERATURE MODES OF PRECIPITATION IN BRASS

Plate-like mode of growth

As a similar change from plate-like to rod-like morphology has been reported between lower and upper bainite in steel,[21] it is unlikely that the morphological change in brass is connected with the order $\rightleftharpoons$ disorder reaction in the β-phase. Rather the parallelism of the B_s and M_s lines in Figure 5 suggests that the position of the former is determined by a T_0 temperature, where parent and product phases of the same composition are in thermodynamic equilibrium. If this is the case, the mechanism of growth of the plates seems to involve a stage of transformation in which the symmetry but not the composition of the lattice changes. This most probably occurs in a narrow zone behind the advancing interface in the edgewise direction of growth of the plates.

Consideration of the energy changes involved in the formation of a plate as a whole show that growth above the M_S temperature cannot occur unless extra driving force is made available by the diffusion of zinc away from the product. An incremental increase in this force by loss of zinc from the interior will allow the outer rim of a plate to expand by a martensitic process, and it is envisaged that the movement at this point always outstrips diffusion. Thus, in the bainitic reaction, the habit plane, which is determined by the path taken by the leading edge, is the same as that for the martensite transformation. It is also probable that disordering does not occur in the immediate vicinity of the advancing interface, otherwise the habit plane would alter from $\{2.11.12\}_\beta$ towards that characteristic of a bcc → fcc transformation (Table I, Figure 2, and ref. 26), and this is not observed.



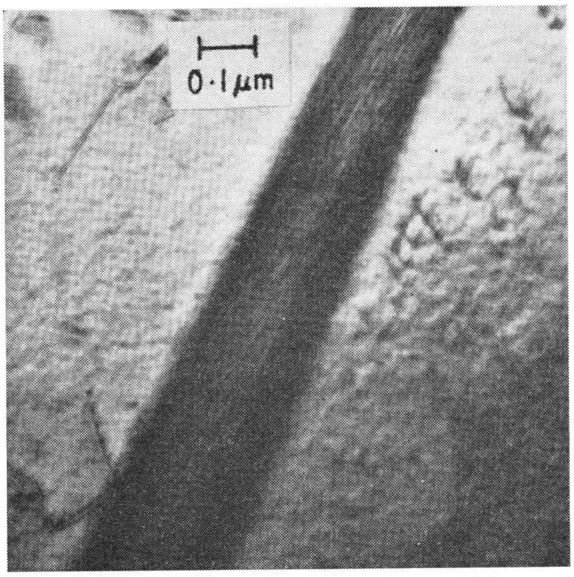
7 *Schematic diagram representing the macro-strain around a martensite plate; lattice planes represented by the vertical lines are compressed in regions marked* C *and expanded in those marked* E

It has been argued that diffusion-controlled precipitation from substitutional solid solution will not be accompanied by a shape change because the atomic migration also destroys the correspondence between the parent and product lattices.[23] A simple model of a semi-coherent interface (Figure 1, ref. 23) was used to justify this reasoning, the shear stresses in the transforming region, i.e. the matrix, being relaxed by atom transport from one face of the crystal to the other. This means that atom planes are created in one locality and destroyed in another.

If the coherency stresses at a martensite type interface in the interior of a crystal of the parent phase are relaxed by a similar process it follows that interstitial and/or vacancy dislocation loops must form where atom planes are respectively expanded and compressed. The situation is illustrated schematically in Figure 7 where the magnitude of the accommodation strain field around a martensite plate may be gauged from the distortion of the vertical lines. Since these may be regarded as the traces of atomic planes, it will be seen that the parent lattice is expanded at *E* and compressed at *C*. The distortion is also least near the tips of the plate, the plane of which is, from a macroscopic viewpoint, undistorted.

It therefore follows that the atom movements responsible for the relaxation of the shear stresses at a bainitic interface differ from those causing the change in composition. The latter may be expected to proceed most rapidly fairly close behind (but not at the advancing edge) without affecting the strain field. At what stage in the growth of a bainite plate the nucleation of dislocations causes the loss of correspondence between the parent and product lattices is not clear. When it occurs, for instance along the planar interface, the mode of sideways growth may be expected to degenerate into the less regular high-temperature form. Such a change has been observed by Flewitt and Bader (Figure 8).

8 *Carbon replica electron micrograph showing the degeneration of the plate-like mode of growth on tempering quenched 40·5%Zn brass for 2 s at 470°C; this is close to the upper temperature limit for the plate-like mode of growth (after Flewitt and Bader[28])*



9 *Thin-foil electron micrograph of a quenched 41·3%Zn brass tempered for $2\frac{1}{2}$ h at 200°C; striations arising from the secondary inhomogeneous shear are visible inside the plate, as are dislocations in the β matrix*

Needle-like mode of growth

Above the critical temperature, which was tentatively identified as a T_0 point in the preceding section, α is precipitated in the form of irregular rods whose axes lie close to $<111>_\beta$.[30] Transformation with a reduction in free energy is now only possible when there is an accompanying change of composition between the parent and product phases. A discontinuous change in composition is presumed to exist at the interface which, in standard models of diffusion-controlled growth,[31] moves at a rate controlled by the downhill diffusion of zinc into the parent (β) phase. In comparison with the low-temperature reaction, decomposition occurs more slowly (Figure 4) so that there is a greater probability of stress relaxation, for example by the nucleation of misfit dislocations, at the interfaces between the two phases.

The existence of a preferred direction of growth may be accounted for by anisotropic diffusion in the β-phase and this explanation is tenable irrespective of the orientation relationship between the lattices of the parent and product phases. However this is unlikely to be random since Sedriks,[32] in a study of the coarse Widmanstätten structure in slowly cooled α/β brass, has shown that the two phases obey lattice orientation relationships that fall between two well defined limits. These, within the ±1° experimental error, are:

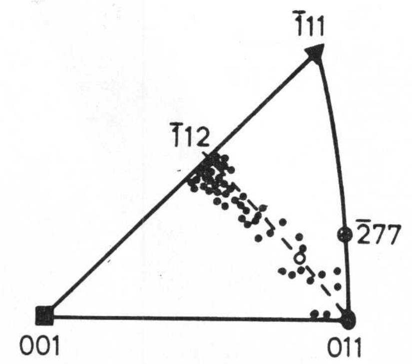
$$\text{A} \quad \begin{array}{l} 011_\alpha \parallel 111_\beta \\ 11\bar{1}_\alpha \parallel 01\bar{1}_\beta \end{array} \quad \text{and B} \quad \begin{array}{l} 011_\alpha \parallel 111_\beta \\ 100_\alpha \parallel 10\bar{1}_\beta \end{array}$$

The former is a variant of the well known Kurdjumov and Sachs relationship, whereas the latter differs from it by a rotation of 5° about an axis delineated by the parallel close-packed directions in the two lattices, i.e. $011_\alpha \parallel 111_\beta$. This was also found to coincide approximately with the long axis of the α-rods in the Widmanstätten structure. Although the latter was coarser than that produced by tempering a quenched brass above B_s (Figure 5) the two structures are essentially of similar appearance.

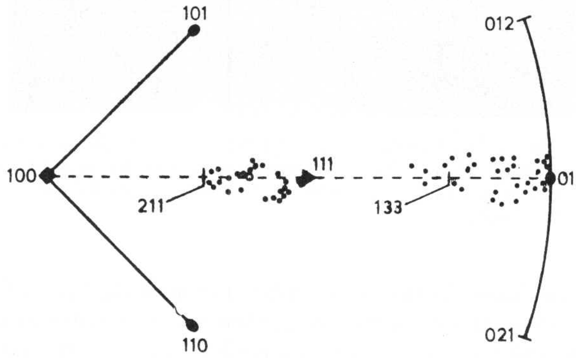
It cannot be fortuitous that these orientation relationships are almost identical with those forecast by the invariant plane strain theory. In the stereographic analysis of the bcc → fcc transformation given in Figure 2, a feature common to the two alternative solutions is the parallelism between an $<011>_\alpha$ and a $<111>_\beta$ type direction. The poles in this zone in solution B (Figure 2*b*) agree with those of Sedrik's limit *B*, whereas in solution *A* there is a difference of 4° between the related $\{111\}_\alpha$ and $\{011_\beta\}$ planes.

The success of the theory in predicting the orientation relationships for the high-temperature form of precipitation suggests that even in this transformation the mechanism of the early stages of growth (nucleation) may be martensitic in character. The low nucleation rate compared with systems in which homogeneous nucleation is known to occur, for example the formation of α′-plates in aluminium–zinc alloys,[33] is an indication that nucleation in this instance is heterogeneous. Segregation of zinc atoms away from a region where a shear strain field exists, for instance in the vicinity of a screw dislocation, may permit the change in lattice symmetry to occur locally under essentially martensitic conditions. This implies that there is an inhomogeneous shear in this region, just as there must be during the growth of the plate-like product along $\{2.11.12\}_\beta$ invariant planes at lower transformation temperatures. Evidence for the occurrence of a strain of this nature during transformation at 200°C in a 41·3%Zn alloy is given in Figure 9, where fine, closely-spaced striations are visible in an α-plate. Similar striations have been observed in this alloy on tempering at 350°C.

However, this type of substructure is not likely to exist in the high-temperature form of α-precipitate for, as indicated by the external form, the subsequent growth of the nucleus occurs by less regular atom movements. Nevertheless, since the orientation relationships persist during growth, the basic atomic rearrangements in the transformation may be thought of as a Bain strain plus a lattice rotation as defined by either Figure 2*a*



a referred to the β-lattice (the open circle is the position given by Hu and Smith for a low-energy interface[34])



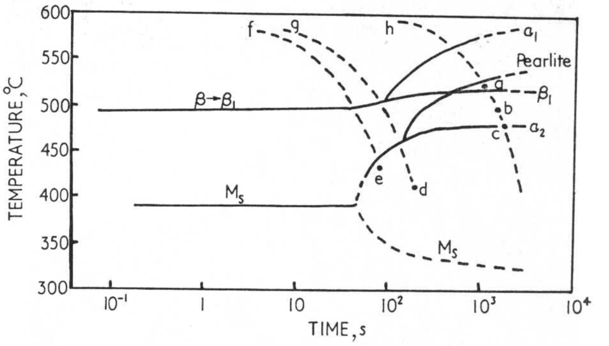
b referred to the α-lattice

10 *Poles of the flat facets on the interfaces of the coarse α-rods precipitated from β-brass during slow cooling*

or *b*. This follows because the inhomogeneous shear does not affect either the symmetry or the orientation of the product. A significant property of the pure lattice strain is that it possesses an invariant line. This is marked with the index letter I in Figure 2*a* and *b* and is close to the $<557>_{\beta}$ direction. It represents that undistorted direction of the Bain final cone which is returned to its original position by the lattice rotation. It is seen to be close to the common $<111>_{\beta} \parallel <011>_{\alpha}$ direction and it is probable that the existence of this invariant line rather than anisotropic diffusion determines the preferred direction of growth. The needle axes are therefore irrational as had been realized in the original crystallographic study, when Mehl and Marzke[30] reported that the α-rods were parallel to $<556>_{\beta}$.

When a unit sphere of the β-lattice is converted into α by a Bain strain, one of the principal strains is an expansion while the two others are compressions. The surface relief effects observed by Flewitt and Bader[28] may be due to these volume changes, for the continuous creation during growth of misfit dislocations, either in the matrix or in the precipitate, only relieves the coherency stresses at the interface. Their presence does not alter the strain but merely changes its character from elastic to plastic.

The development of flat interfaces or facets on the sides of the α-rods requires some final comment. These can be particularly prominent if a specimen is slowly cooled from the β-phase field and held at a temperature in the α/β region for some hours.



11 *Continuous cooling transformation diagram constructed by thermal analysis for a Cu–11·7%Al alloy; typical cooling curves are shown by the broken lines*

This suggests that they are interfaces of low energy similar to those described by Hu and Smith.[34] Using a serial sectioning technique,[35] Sedriks has attempted to determine the crystallography of the facets.[32] He was unable to identify a unique habit plane and reported that the interface poles were distributed in a more or less random fashion in the $<111>_{\beta}$ zone (Figure 10*a*). This disproves a suggestion made by Otte and Massalski[26] that the position of low-energy interfaces could be predicted by the application of invariant plane theory.

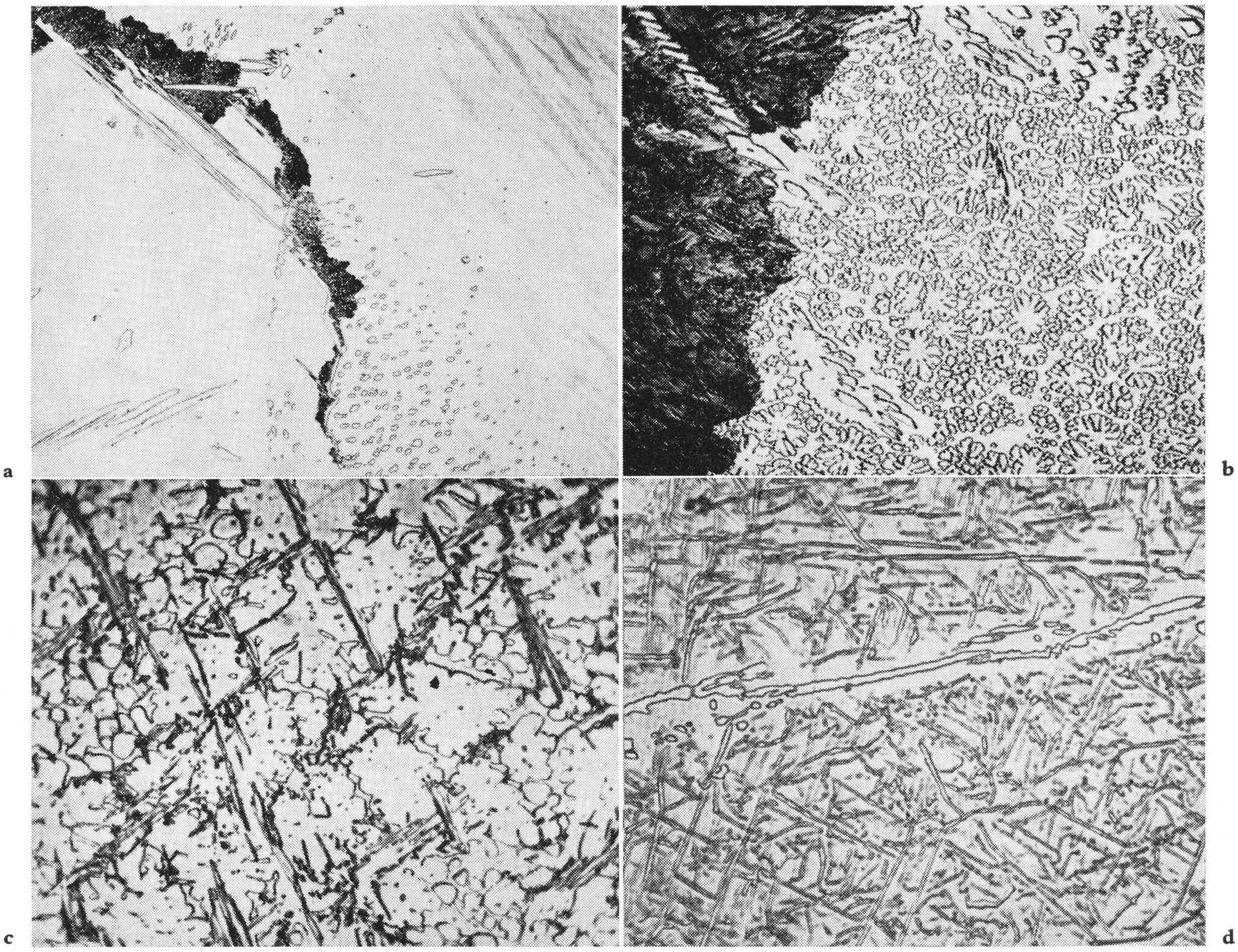
However, when the results were referred to an α-lattice basis (and this was possible since the orientation relations were determined at the same time), it was found that the poles of the facets occurred only in certain regions of the $<011>_{\alpha}$ zone (Figure 10*b*). It will be seen that the majority of the solutions fall in a cluster close to $\{112\}_{\alpha}$.

The significance of these results have yet to be satisfactorily explained. It is possible that Frank's two-dimensional lattice matching theory is applicable.[36] Dislocation boundaries are undoubtedly involved, for it has been found that when specimens with this Widmanstätten structure are up-quenched into the β-field, a network of sub-boundaries is formed when the α dissolves.[37]

MORPHOLOGY OF ALPHA PRECIPITATION IN COPPER–ALUMINIUM ALLOYS

The distinct change in the morphology of α between 500° and 475°C in isothermally transformed copper–aluminium alloys of eutectoid composition has been previously noted.[27] The rather irregular particles precipitated at higher temperatures are replaced by obtuse angled V-shaped plate formations characteristic of the bainitic reaction in brass.

However, the temperature at which the transition occurs is determined by more complex factors than is the case for the analogous transition in brass. Both the mode and the rate of α-precipitation are markedly affected by the formation of a superlattice based on Cu_3Al in the parent β-phase. The influence of this reaction ($\beta \rightarrow \beta_1$) is demonstrated in Figure 11, which shows a continuous cooling transformation diagram for an alloy containing 11·7%Al. The diagram, which covers a wide range of cooling speeds, was constructed[38] by the thermal analysis method. The highest speeds employed, which were achieved by quenching small specimens in a blast of helium gas, exceeded 4 000 degC/s.



a rods of pro-eutectoid α (labelled α_1 in Figure 11) and the start of the pearlite reaction × 100
b matrix ordering is taking place and 'rosettes', i.e. domains of the aluminium-enriched Cu_3Al superlattice, are visible × 500
c fine plates of α nucleated and growing from the aluminium-deficient regions between the rosettes (α_2) × 1 000
d typically bainitic structure in which many pairs of plates intersecting at an obtuse angle may be seen × 1 500

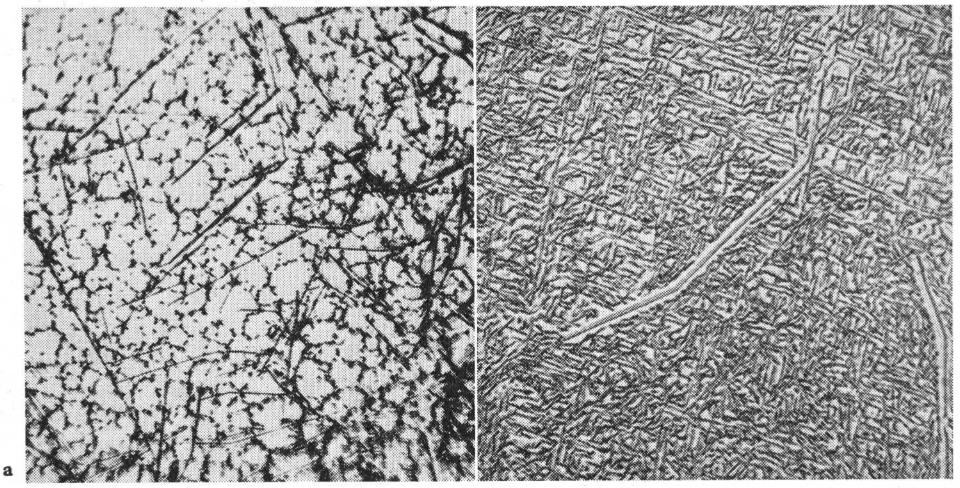
12 *Microstructures of samples of a Cu–11·7%Al alloy cooled at rates indicated by the broken curves in Figure 11; in each case transformation was arrested at the lettered points by quenching into water; etched in dichromate/sulphuric acid mixture*

It will be seen that above a critical cooling velocity (line *f–e*) the temperature at which the $\beta \rightarrow \beta_1$ change starts is independent of the cooling speed, as also is the Ms point. Ordering cannot be suppressed by drastic quenching although the size of the domains progressively decreases. At quenching rates greater than 1 000 degC/s the domains are too small to be seen with an optical microscope and it has been reported[4] that they are only of the order of hundreds of angstrom units in diameter in specimens of 4 mm thickness quenched into cold water.

At lower cooling speeds the $\beta \rightarrow \beta_1$ reaction is responsible for pronounced segregation of aluminium in the β-grains on a scale that is easily visible in the optical microscope. The effect is demonstrated in Figure 12*a–c* which represents the structures of specimens cooled at a rate corresponding to cooling curve *h–a–b–c*. At point *a*, proeutectoid α (α_1 in Figure 11) is present in the form of rods, the cross-sections of which can be seen in the right hand grain of Figure 12*a*, together with small colonies of the ($\alpha + \gamma_2$) pearlite. At the lower temperature *b*, aluminium-rich rosettes, i.e. domains of the Cu_3Al superlattice, appear in the untransformed β with a concomitant decrease in the aluminium content of the disordered matrix. The segregation is in accordance with the metastable diagram proposed by Thomas.[39]

A pronounced arrest then appears on the cooling curve at *c*, this point marking the nucleation of fine platelets of α (α_2 in Figure 11) in the aluminium-deficient regions between the rosettes. However, the platelets grow across the domains to give a final structure similar to that shown in Figure 12*d*, which represents the structure of a specimen cooled at a faster rate to point *d* (cooling curve *g–d*, Figure 11) before transformation was arrested by quenching into water. Many plates intersecting at an obtuse angle are visible in this structure, a feature characteristic of the bainitic reactions in brass.

The untransformed matrix of specimens containing the network of fine, post-ordering α-plates eventually transforms into martensite, but the temperatures at which this occurs were difficult to determine accurately because thermal analysis becomes increasingly insensitive at low temperatures. For this



13 **a** *Microstructure of a copper – 11·7% aluminium alloy in which transformation was arrested at point (e) in Figure 11* × 1000
b *Structure of a Cu–11·2%Al alloy in which the pre- and post-ordering* α *is plate-like in form; the latter constituent is much finer than the former; etched in dichromate/sulphuric acid mixture* × 1000

reason the modified M_s temperature is shown as a broken line. However, positive evidence for the depression of the M_s was obtained by completing the final stages of cooling, for example from point *d*, by gas quenching. The depression may be partly due to the partitioning of the matrix by the α-plates and partly to the further enrichment of the matrix in aluminium. The latter effect was confirmed by the detection of γ'- as well as β'-martensite in the Debye-Scherrer X-ray spectra of specimens heat treated in this manner.

Three interesting microstructural features in these alloys deserve some final comment. Firstly, in regions where closely-spaced bundles of α_1-rods are formed (as in Figure 12*a*), γ_2 tends to precipitate at a lower temperature to give a product resembling upper bainite[22] in steel. Secondly, at rates of cooling close to the critical for the appearance of the post-ordering α-reaction (i.e. α_2 in Figure 11), the plates take on a very long and thin appearance. This is shown in Figure 13*a*, which represents the structure of a specimen cooled according to curve *f–e* (Figure 11) before transformation was arrested by water quenching. It is probable that nucleation again occurs in the aluminium-deficient regions between the domains but that very little diffusion of the solute away from the transforming region is required to permit the edgewise growth of the plates at temperatures close to the M_s point.

Lastly in an alloy of lower aluminium content (11·2%Al) bainitic plates of two distinct sizes have been observed at certain cooling speeds (Figure 13*b*). The effect may be readily understood when it is realized that on decreasing the aluminium content of the alloy the T_0 temperature for the bcc → fcc transition is raised whereas the critical temperature for ordering is lowered.[39] In the alloy of eutectoid composition these temperatures are approximately coincident. The large bainitic plates visible in Figure 13*b* are thus formed when the temperature falls below the T_0 temperature for the 11·2% Al alloy, i.e. where disordered β is in thermodynamic equilibrium with disordered α of the same composition, whereas the finer plates precipitate at a lower temperature after ordering in the β-matrix has caused a depletion of aluminium in the regions between the domains.

ACKNOWLEDGMENTS

The author wishes to thank P. E. J. Flewitt and M. G. Bader of the Battersea College of Advanced Technology (proposed University of Surrey) for making available the results of their investigation before publication; also the DSIR who provided financial support for A. J. Sedriks and J. R. Moon, whose results, obtained when they were postgraduate students at the Department of Metallurgy, University College, Cardiff, are also quoted.

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Discussion 4

Chairman: Dr T. Broom (CEGB)

Dr P. M. Kelly (University of Leeds) asked Dr Armitage whether ω-phase was present in the Ti–15%Mo alloy on quenching to room temperature.

Dr W. K. Armitage (Aeon Laboratories) replied that both metallography and electron diffraction showed a fine dispersion of ω-phase on quenching to room temperature from 725°C. If the solution temperature was raised, however, he believed that ω might not be present on quenching to room temperature.

Dr H. Warlimont (Max-Planck-Institut für Metallforschung) commented that it was quite remarkable to have thin-foil pictures of uranium and he wondered how the foils had been made.

Dr J. Burke (University of Liverpool) replied that the polishing solution used contained 133 ml glacial acetic acid, 7 ml water, and 25 g chromic trioxide. An open circuit voltage of 30V was used at a current density of 0·1/0·2 A/cm^2. Foils were then cleaned in a solution due to Westmacott containing 75% sulphuric acid, 18% glycerol, and 7% water.

Professor R. F. Hehemann (Case Institute of Technology) speaking also on behalf of **Mr P. E. Repas** (US Steel Corporation) commented that isothermal transformations in β-brass containing 38·5–44·5 at-%Zn had been under study in their laboratory using hot stage metallography and other techniques. In general, their results agreed with those presented by Mr Garwood. Specifically, they also examined the needle to plate transition observed by Flewitt and Bader and reported by Mr Garwood. Their results on the temperature for the transition were compared with those of Flewitt and Bader in Figure *A*. Although, at zinc contents above 41% the two studies were in good agreement on the upper temperature limit for the formation of plates, they deviated substantially at lower zinc concentrations. The B_s temperature did not remain parallel to M_s at low zinc concentrations.

As pointed out by Mr Garwood, both needle and plate morphologies occurred over a narrow temperature range below B_s. In this range, the high-temperature form (needles) grew from the plates as well as independently from nuclei located primarily, but not exclusively, at grain boundaries. Both forms exhibited surface relief and linear growth in length. However, in contrast to bainite in steels, the plates did not grow significantly in thickness.

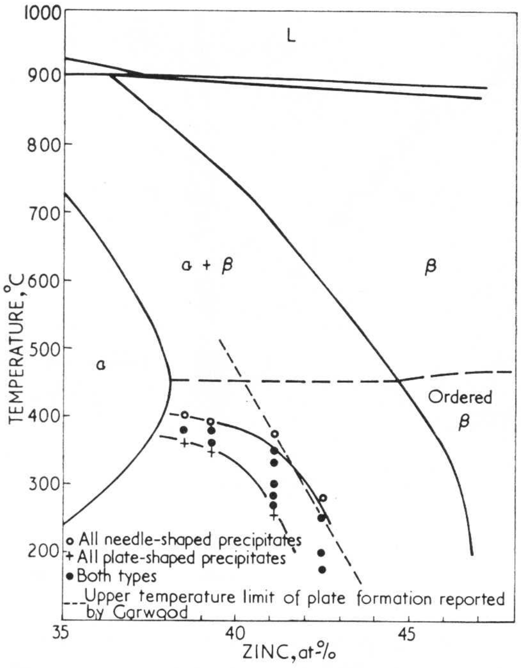
The plates frequently arose in V-shaped pairs constituting two variants of the $\{2\ 11\ 12\}_\beta$ habit. Apparently, during growth, the edge of the plates advancing in an approximate $<111>_\beta$ direction became unstable and dissociated into a series of needles. This could be observed most clearly when the plane of polish was parallel to a $\{110\}_\beta$ plane. Figure *B* illustrated schematically the microstructural arrangement on $(101)_\beta$ that resulted from the intersection of plates with $(11\ \bar{2}\ 12)_\beta$ and $(11\ 2\ 12)_\beta$ habits. Needles grew from the edges of these plates at equal angles to their line of intersection – $[101]_\beta$. When this structure was sectioned parallel to $(101)_\beta$, needles would be observed growing off a broad central midrib consisting of the two variants of the plates. On the other hand, sectioning the structure on $(\bar{1}01)_\beta$ would reveal a cross-section of the composite structure consisting of the central V-shaped plates and adjoining needle cross-sections. The latter structures were observed by Mehl and Marzke[1,2] and described as the coalescence of needles into plates. Examples of both morphological variants were evident in Figure *C* which presented a grain sectioned parallel to $(101)_\beta$. The cross-section of the composite structure growing on $(\bar{1}01)_\beta$ was illustrated at A in Figure *C*.

Mr R. D. Garwood (University College, Cardiff) said that he ought to make it clear that the results he had been quoting recently had been obtained by Mr Flewitt and were not his own results, but he thought Mr Flewitt had found that, if one transformed at a temperature close to the transition temperature, the reaction began by the formation of a pair of plates and subsequently the ragged edges described by Professor Hehemann formed. The precipitation process degenerated from the regular plate-like reaction into the other involving the growth of rods.

Mr L. Delaey (Max-Planck-Institut für Metallforschung) said that, from micrographs, Mr Garwood concluded that the nucleation of bainite occurred in the copper-rich regions between the Cu_3Al domains. The same effect had been observed in the electron microscope by Mr Debondt at the University of Leuven in Belgium. Thin foils of a copper–tin alloy with nearly γ-eutectoid concentration had been heated inside the microscope up to the γ-region and then rapidly cooled to obtain the ordered δ-phase. The δ-phase had the γ-brass structure and appeared in the form of rosettes (Figure *D*). The foil was then reheated to a lower temperature to obtain bainite. During the reheating treatment Mr Debondt observed that the nucleation of bainite in this copper–tin alloy occurred in the copper-rich regions between the δ domains (Figure *E*).

Dr Warlimont said that he and Dr Hornbogen had recently been interested in investigating the precipitation of α- from β-brass from the standpoint of the mechanism of nucleation and of the crystallographic characteristics of the bainitic transformation.

They had worked with an alloy containing 41·0 at-%Zn which was quenched from the β-range to room temperature and held at 250°C. In the as-quenched condition the dislocations



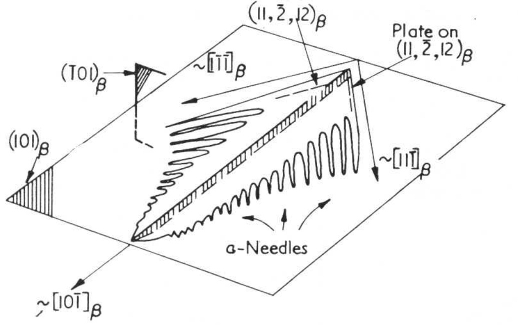
A *Copper–zinc equilibrium diagram from 35 to 48% Zn*

originally present in the material at high temperature had acted as sinks for vacancies. The dislocations were wrinkled up quite strongly but not in such an orderly manner as that which had been observed in aluminium where dislocations with screw components were formed into helices.

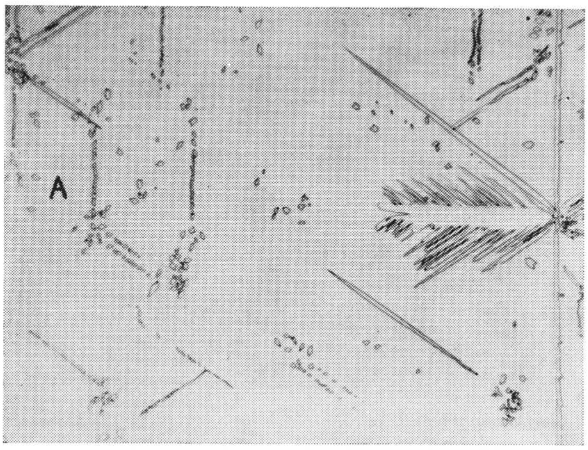
After aging for about 30 min the dislocations in general had straightened out. When contrast experiments were made, one found that the contrast of some straight dark lines in certain directions was much narrower than the contrast of ordinary dislocations. Something seemed to have been seen here which might be embryos of the precipitating phase. But he did not want to imply that they were saying that these striations had positively been identified as embryos of the precipitate.

Figure *F* showed an early growth stage. He drew attention to coherency strains showing up in contrast along the boundary. The background striations in the β-brass were possibly due to some surface effect or an effect of ordering. He was not sure about this but both interpretations appeared possible.

Figure *G* showed a progressed stage of growth. What was shown here was that, besides the main kinks in a plate, there were even more kinks in parts of one of the bainitic plates, and it was thought that these were nucleated in a similar way to various phenomena in martensites, namely that the strain conditions near the tip of a plate were favourable for the operation of another variant of the shear.



B *Schematic drawing of composite plate and needle structure*



C *Growth of needles from the edges of plates in a 42·5% Zn alloy aged 320 h at 200°C; grain sectioned parallel to (101)$_\beta$* ×750

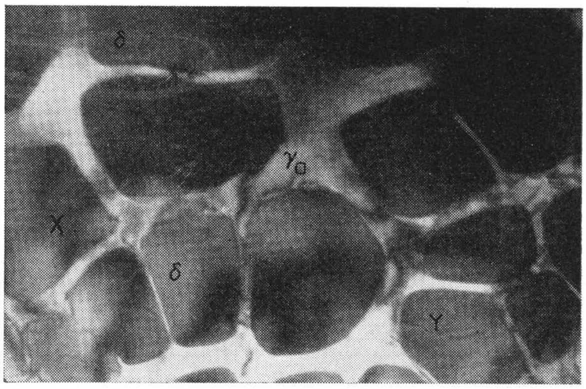
Figure *H* showed a fully grown plate. In fact, it was slightly over-aged already. The striations could be seen to be very dense in one part of the plate and it was from this part that the diffraction pattern shown had been taken. From analysis of the maxima in the diffraction pattern, the internal structure of the plate could conclusively be shown to consist of stacking faults.

In fact the metastable precipitate exhibited the same crystal structure as that of copper–zinc martensite of the respective composition.

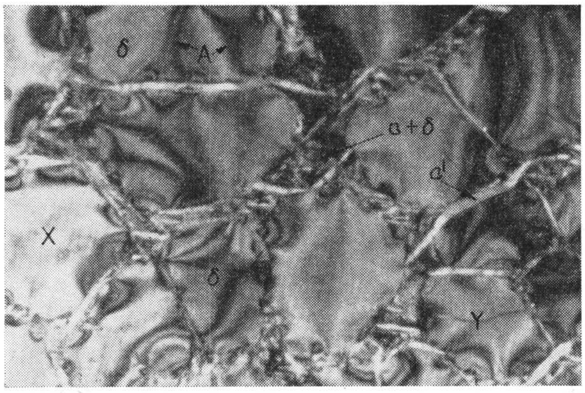
The beginning of overaging was shown more clearly in Figure *I*. It could be seen that the stacking faults were annealed out, and where they were so, there was a bowing out of the interface of the martensite plates due to the higher solubility of zinc in metastable α-phase than in the stable α-phase.

Figure *J* showed an additional characteristic precipitate and might supplement the survey Dr Garwood had presented. Besides the really bainitic plates and the rod-shaped variant there was another plate-like structure which actually consisted of two parallel plates adjoining along a straight boundary. He did not yet know whether they were twin related but he did know that one of the halves was related to the matrix by a variant of the Kurdyumov–Sachs relationship. This work was still in progress.

The Chairman asked Dr Warlimont whether, with observations of fairly simple systems such as the one described and



D *Rosette form of δ-phase; micrograph from the work of M. De Bondt and A. Deruyttere of Leuven University, Belgium*



E *Nucleation of bainite in copper-rich regions between the δ-domains in a copper–tin alloy; micrograph from the work of M. De Bondt and A. Deruyttere of Leuven University, Belgium*

supposing the straightened-out dislocations were embryos, he could start putting numbers in that might give some agreement with the observed *C* curves, because, surely, this was one of the merits of looking at the non-ferrous systems, that the situation might be rather simple and one might develop models using them.

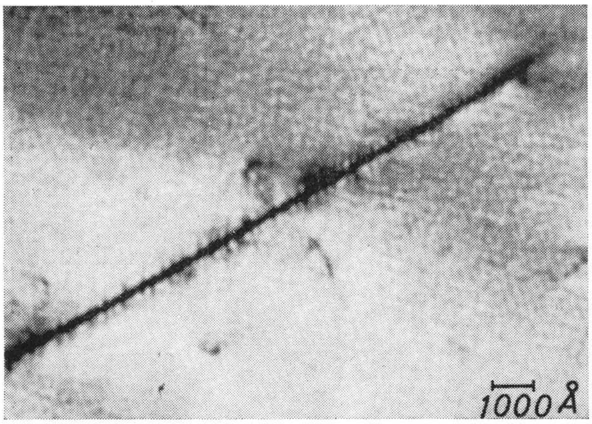
Dr Warlimont said that this might be done in the long run. No kinetic measurements had been made yet except for hardness measurements which, of course, would not give quite enough succinctness in what data one wished to obtain.

Mr J. A. Klostermann (Stichting voor Fundamenteel Onderzoek der Materie) said that the name 'butterfly martensite' for the martensite with an angle-profile habit had only been chosen at first when the right morphology for this martensite was not known. He proposed to call this martensite form 'angle-profile martensite'.

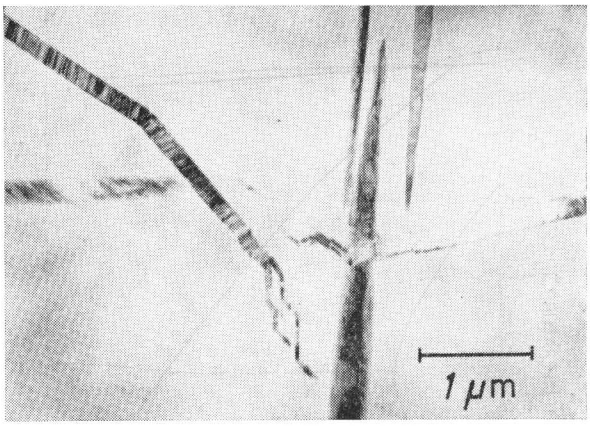
He asked Professor Hehemann what was the habit of the angle profiles in Cu–40·8%Zn.

Professor Hehemann said that it was (101).

Dr G. T. Higgins and **Mr E. Banks** (University of Liverpool) pointed out that observations had been made upon the martensite transformation in (a) iodide–zirconium; (b) Zr–2·5 wt-%Nb–780 ppm O_2; and (c) Zr–5 wt-%Nb–250 ppm O_2. Encapsulated sheet specimens 0·009in thick were water quenched after annealing at 1050°C in the bcc β-range. Thin foils were prepared for examination by transmission in the electron microscope by chemically polishing in a hydrofluoric acid–nitric acid–water solution, and electropolishing in a perchloric–acetic acid solution.



F *Bainitic α-phase formed in a Cu–41·0 at–% Zn alloy, quenched from 870°C, on aging at 250°C; early growth stage exhibiting coherency strain contrast in the matrix at the interface; aged 10 min*



G *Alloy as for Figure F; intermediate growth stage exhibiting characteristic internal striations and kinking of the plates; aged 50 min*

In the case of the iodide–zirconium the plates of the transformation product showed no evidence of internal twinning. In both the 2·5 and 5 wt-%Nb alloys, however, the martensite plates were internally twinned (Figures *K* and *L*). Selected area diffraction had shown these to be of the $\{10\bar{1}1\}$ type. The absence of areas of retained β had so far prevented a full evaluation of the crystallographic features of the twinned martensite plates.

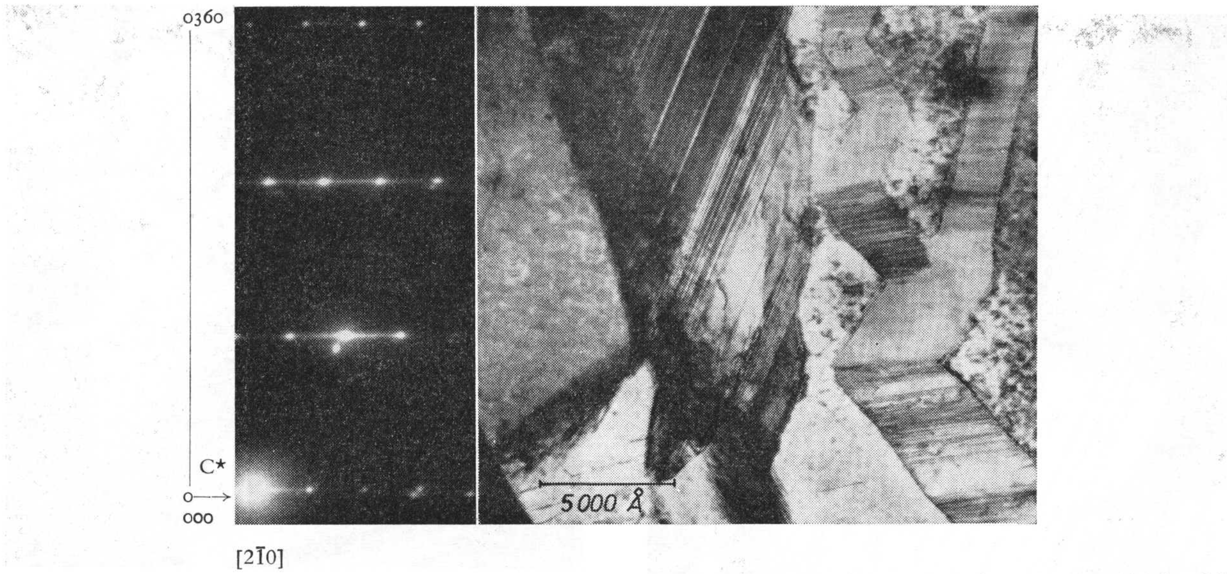
This observation of $\{10\bar{1}1\}$ type twins was contrary to the isolated observation of the $\{10\bar{1}2\}$ type by Armitage,[3] but agreed with the observed twins in the comparable bcc→cph (γ') martensitic transformation in the Cu–Al system.[4,5] On the basis of the correspondence derived from the accepted orientation relationship for titanium and zirconium, $(011)_\beta \parallel (0001)_\alpha$, $[11\bar{1}]_\beta \parallel [11\bar{2}0]_\alpha$, the $\{10\bar{1}1\}$ twinning planes were derived from the $(1\bar{1}0)_\beta$ mirror plane. This was consistent with the observations that twinning planes derived from the $(1\bar{1}0)_\beta$ mirror plane also arose in the martensitic bcc→orthorhombic transformation in gold–cadmium[6] and β-brass.[7]

Employing the Weschler *et al.* analysis[6] for a bcc→orthohexagonal transformation the ratios of the two twin orientations necessary to satisfy the inhomogeneous shear had been calculated. These values together with the lattice parameters employed were given in Table 1. The addition of niobium radically depressed the M_s temperature and the value of 650°C obtained from thermal arrest data had been employed in the calculation.

The results showed a marked variation in the inhomogeneous shear for zirconium as against titanium. Though small the inhomogeneous shear obtained for titanium was greater than the

TABLE I Lattice parameters for zirconium-niobium alloys

Material	M_s temperature employed in fixing values of lattice parameters	Lattice α-Zr *a*	*c*	Parameter β-Zr a_0	Ratio of twin orientations
Iodide Zr	850°C	3·248	5·198	3·609	3·9:1
Zr–2·5 wt-%Nb	650°C	3·2345	5·179	3·596	3·0:1
Iodide Ti	900°C	2·9654	4·7333	3·3065	8·6:1



H *Alloy as for Figure F; late stage of bainitic growth with partial over-aging. The diffraction pattern is characteristic of a fully faulted area of the bainitic plate in the upper left of the micrograph with the fault normal parallel to the plane of the foil; aged 200 min*

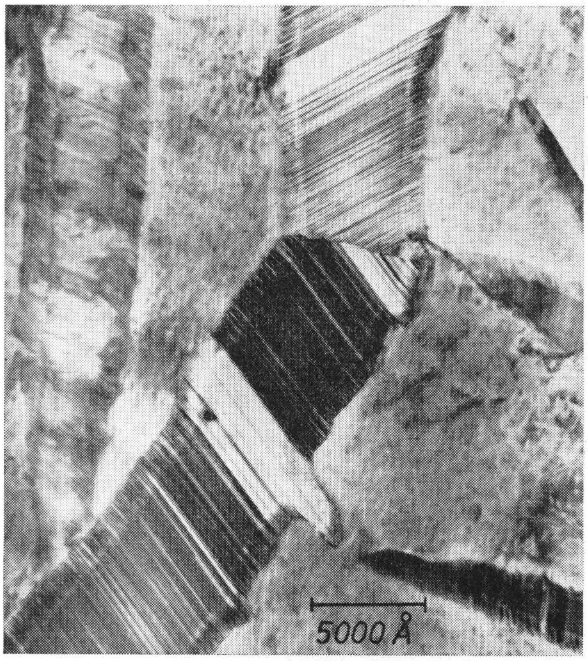
value of 0·07680 of the twinning shear predicted by Bowles and Mackenzie.[8] Values from both theories were in keeping with the results of Armitage[3] and those of Williams *et al.*[9] that internally twinned martensite plates were not normally observed in titanium and its dilute alloys.

In the case of the zirconium–niobium alloys the internally twinned martensite was in keeping with the large fraction of the twinning shear necessary to satisfy the inhomogeneous shear. The theoretical ratio of the two twin orientations of 3·0 : 1 was in good agreement with the experimental value of 3·7 : 1. This large inhomogeneous shear in the case of zirconium compared with titanium also explained the diffuse X-ray reflections observed in the current work and previously reported by Gaunt and Christian.[10]

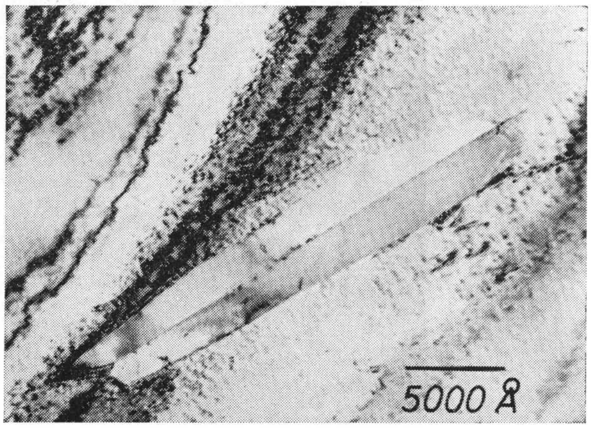
The absence of an internally twinned substructure in the quenched iodide zirconium might be due to a number of factors. In the first instance there was no direct evidence that the product examined was martensitic, though by comparison with previous workers the quenching conditions employed would be expected to produce martensite. In the alloys the lower M_s temperature might be an important factor in promoting twinning as against slip in the pure metal. Finally, it was possible that niobium might vary the stacking fault energy of α-zirconium, but no information was available on this point.

Dr J. W. Christian (University of Oxford) asked if Dr Higgins had used lattice parameters at the M_s temperature.

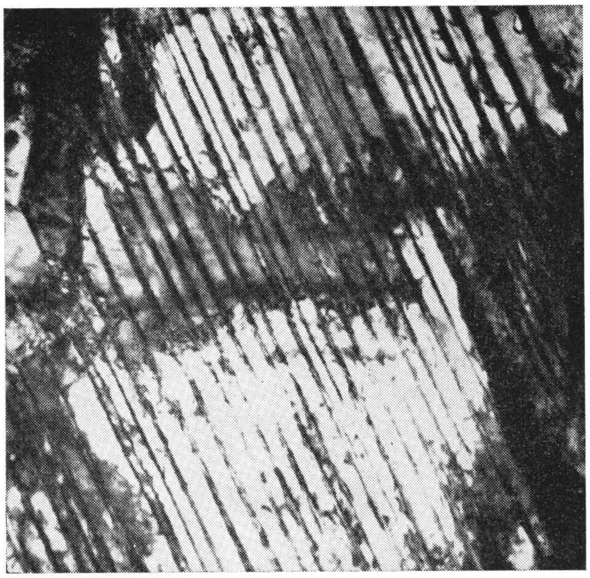
Dr Higgins replied that he had, assuming 850°C for pure zirconium and 650°C for the alloy. The 650°C had been experimentally determined in the alloy by the thermal arrest technique.



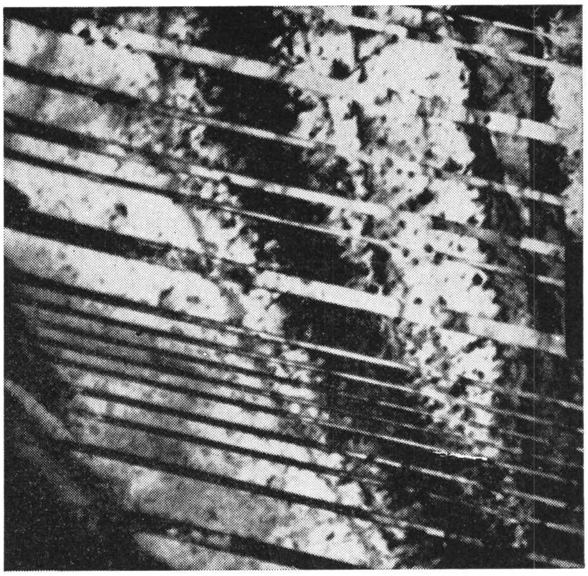
I *Alloy as for Fig F; characteristic effects of over-aging: annealing-out of stacking faults and localized growth protrusions of the bainitic precipitate; aged for 200 min*



J *Alloy as for Figure F; precipitate plates without internal faulting; aged 50 min*



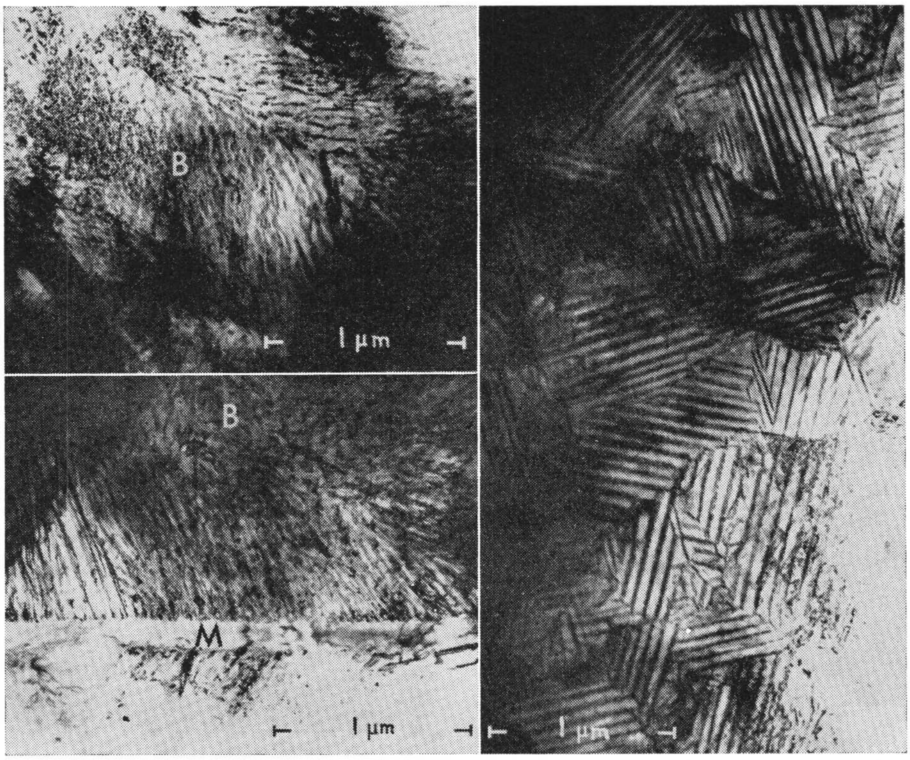
K *Internally twinned martensite plates in 2wt-%Nb alloy*



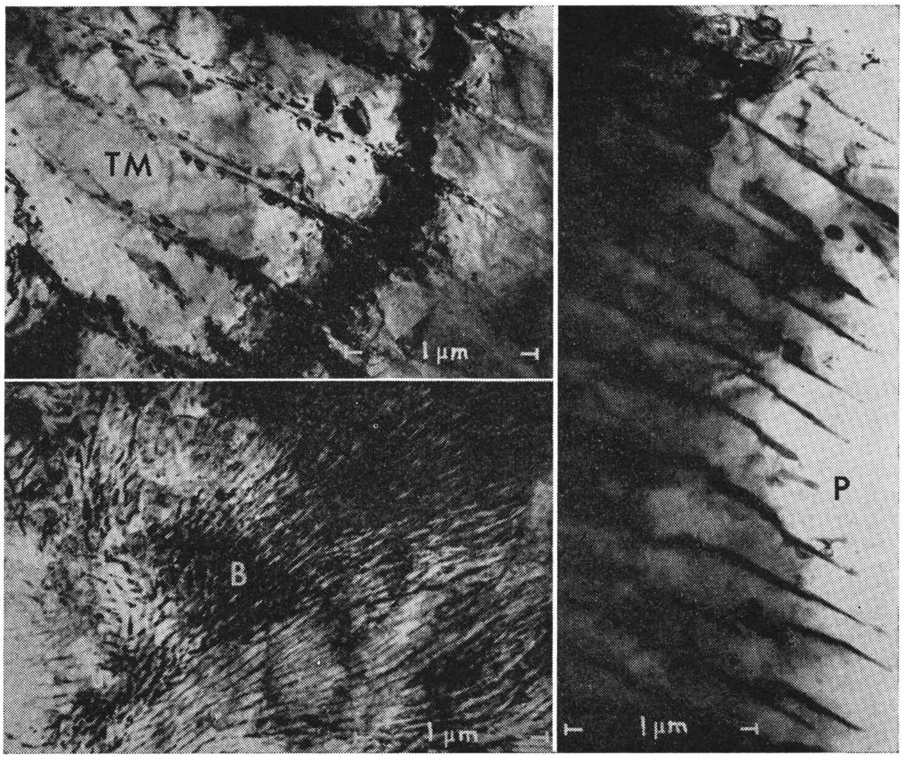
L *Internally twinned martensite plates in 5wt-%Nb alloy*

Dr L. Kaufman (ManLabs Inc.) said that he wished to make several comments on what was known about thermodynamics in the non-ferrous systems. His department had carried out a calculation on the lattice stability of titanium and zirconium and this information was used to calculate the driving force at M_s for both elements with β formers.[11] They had developed a method for carrying out an approximate calculation by T_0, and at the time, collected the data to evaluate ΔF at M_s. They had found that the driving force at M_s was roughtly 50 cal/mole in both cases, substantially less than in iron base alloys at low temperature.[11]

Subsequently Huang measured M_s and A_s in titanium base alloys using heating rates of about 10degC/s. He found that A_s on heating lay about 50 cal/mole above T_0, so the driving force in both the forward and reverse transformation in titanium and zirconium base alloys appeared to be of the order of 50 cal/mole.[12] This might be an additional case in which to compare the elastic constant along the lines indicated by Professor Robertson earlier.



M *Alloy G after quenching from the β-range; thin-foil electron micrographs* ×32000

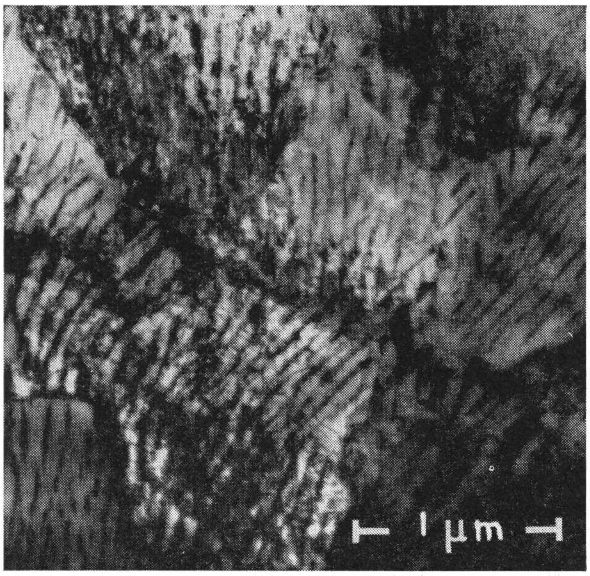


N *Alloy G after quenching from β-range and aging at 550°C; thin-foil electron micrographs* ×32000

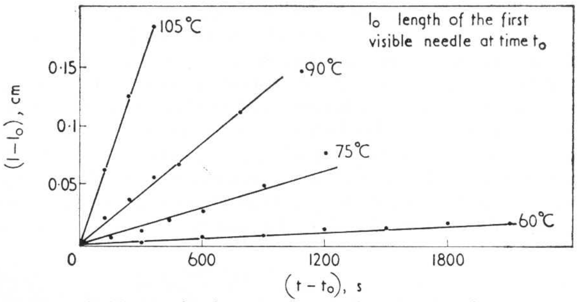
Another interesting fact which related to the body centred/hexagonal transition was that recently there had been high pressure investigations on the ω-phase and the temperature–pressure diagrams for titanium[13–15] and zirconium.[13,14,16] In these cases there were bcc, hcp, and ω-phases, the latter being similar to that which appeared in titanium base alloys as a metastable or transitional phase.

At low temperatures, the *T–P* line for the $\beta \rightarrow \omega$ reaction intersected the 1 atm temperature axis at about 400°C, which was the temperature below which β-titanium base alloys had to be cooled before the ω-phase formed.[15]

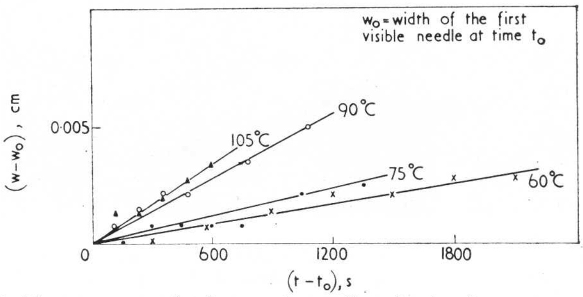
Dr A. G. Crocker (Battersea College of Technology) said that he and Professor Bilby had performed extensive calculations some six years ago[17] on the crystallography of the transformations in titanium, zirconium, and uranium–chromium alloys.



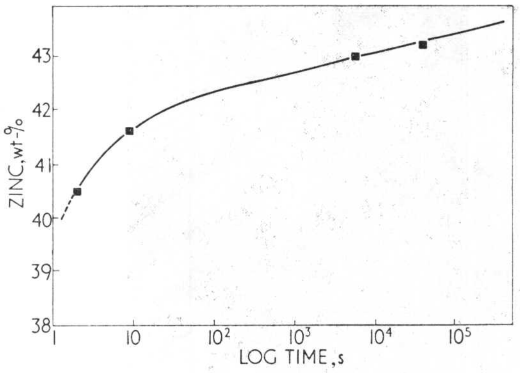
O *Alloy G after quenching from the β-range to 630°C and transforming or 2 h; thin-foil electron micrograph* ×27000



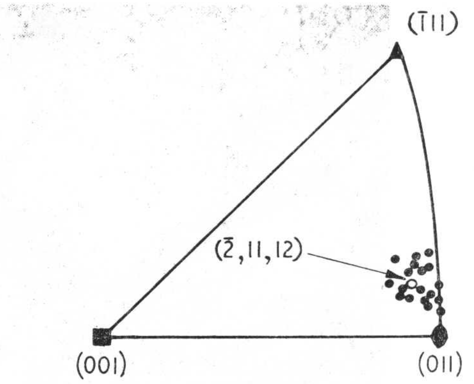
P *Longitudinal growth of martensite needles related to heat treatment*



Q *Transverse growth of martensite needles related to heat treatment*



R *Variation of the incubation period of the bainitic nose with composition, showing rapid reaction rates below 40% Zn*



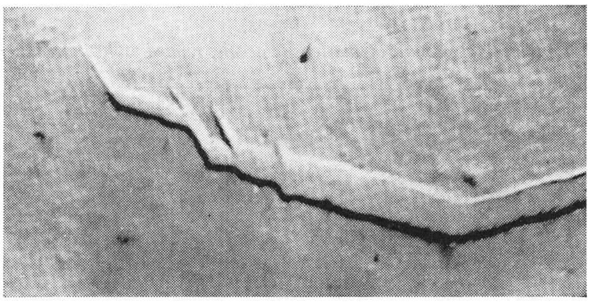
T *Experimental habit planes for alloys 40·5 wt-% Zn at 350°C and 200°C, also 43·0 wt-% Zn at 230°C*

Since then very little work seemed to have been done on these transformations and it was therefore encouraging to see this new experimental work being reported. Previously there had been very few observations with which to compare their predictions. For the titanium and zirconium transformations their results showed that reasonable agreement between the theory and some of the observations could be obtained by postulating several different types of inhomogeneous deformation. The possible shear strains associated with these mechanisms were, however, extremely small compared with the shears involved in the martensite reaction in steel, of the order of 0·05 rather than 0·25. This certainly explained why very little transformation twinning, and possibly no twinning at all, was observed in the thin foils of titanium and zirconium.

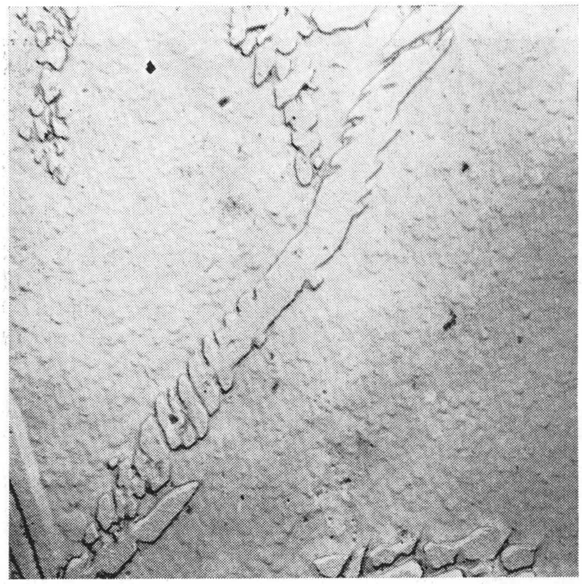
He congratulated Dr Armitage on obtaining the specific variant of the orientation relationship associated with the (334) habit plane in titanium, but said it would be even more useful to know whether the exact location of this habit was near (8,9,12) or (9,8,12). He attributed the differences between the predictions of Mackenzie and Bowles,[8] for the titanium transformations, and those of Dr Higgins, for the zirconium transformation (using the Weschler–Lieberman–Read theory), to the inclusion in the former analysis of a uniform strain in the interface. Mackenzie and Bowles had postulated a large dilatation of about $\frac{3}{4}\%$. This he considered questionable as it was difficult to see how this strain could be accommodated. It was also unnecessary as the volume change associated with the transformation was negligible. However in the calculations of Gaunt and Christian[10] for zirconium an even larger dilatation of about $1\frac{1}{2}\%$ was used. This again resulted in a different set of predictions. However, the small differences in the lattice parameters of zirconium and titanium gave rise to only a negligible difference in the results of the theories. He did not feel that a satisfactory correlation had yet been obtained between the observations and the predictions of the crystallographic theories. To achieve this more detailed experimental information on surface tilts, and hence shape deformations, orientation relationships and operative modes of inhomogeneous deformation were necessary.

Finally, he said that the transformations in uranium–chromium alloys were particularly interesting because of the large number of possible correspondences, involving small strains, between the parent and product structures. Lomer[18] had considered three of these but there were many more which seemed equally feasible. This contrasted very markedly with the situation in steels, in which only the Bain correspondence was satisfactory. Additional experimental information on these transformations with which to compare their predictions was again needed. The theoretical results did indicate, however, that the shear strain involved in the inhomogeneous deformation was small, of the order of 0·02, so that very little twinning or slip was likely to be found.

Dr J. W. Christian, in amplification of Dr Crocker's remarks, said that he would agree with him about the dilatation parameter. The dilatation had been chosen in order to get the best fit between observed and theoretical habit planes, rather than taking a simple prediction on the basis of an invariant plane



S *41·6% Zn alloy heat treated at 200°C for 10 h, showing small plates nucleated in the matrix ahead of the growing major plate; subsequent growth allows link up; carbon/platinum replica* ×8000



U *40·5% Zn alloy heat treated at 450°C for 8 s, showing degeneration of plates crystallographically; carbon/platinum replica* ×3000