PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Discussion

I. J. Polmear, G. B. Brook, E. D. Hondros, L. M. Wyatt, H. Y. Hunsicker, P. G. Partridge, G. Cooper, W. M. Imrie, H. Tyrer, P. H. Morton, R. B. Nicholson, W. E. Duckworth, D. E. Miles, J. E. Restall, D. R. Holmes, C. A. Stubbington and E. W. Skerrey

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KEYNOTE SPEECH

By R. W. K. Honeycombe (*Department of Metallurgy and Materials Science, University of Cambridge*)

1. Introduction

The papers in this session cover large areas of ferrous and non-ferrous physical metallurgy, so it would be inappropriate in the time available even to attempt to summarize the contents. Instead I shall be very selective, and in doing so try to establish some of the contributions of physical metallurgy already made to successful alloy development and some which can be anticipated. Physical metallurgy, while it is a coherent discipline, can be said to exist at a number of different levels which interact with each other. The original impetus came from the study of microstructure in the optical microscope pioneered by Sorby, combined with the concept of equilibrium diagrams which defined relations between chemical composition and structure, the latter being more precisely defined at a later stage by X-ray diffraction studies.

2. High strength aluminium alloys

The gradual development of aluminium alloys over the period 1920–1940, and in particular the Al–Zn–Mg–Cu alloys discussed by Hunsicker (3.6), owed much to the approach referred to above, which by 1939 had produced alloys with strengths up to 450–550 N mm^{-2}. However, while these alloys relied on precipitation hardening for much of their strength, detailed study of the dispersed phases responsible was not yet possible, indeed the high resolution electron microscopy needed was not available until after 1945. This illustrates that alloy development can go a substantial distance using only the 'surface layers' of physical metallurgy as a guide. The word 'guide' is used advisedly, because although by this time most relevant binary and ternary equilibrium diagrams were known at least in broad outline, they could not be precisely applied to complex alloys with four or five deliberate alloying additions, nor did they describe the metastable structures obtained by most strengthening heat treatments. In 1940 stress corrosion in these alloys was already a serious problem which could only be dealt with by an empirical search for the alloy with maximum resistance to stress corrosion cracking, together with the desirable strength level and reasonable workability. Precise scientific analysis of this phenomenon had to wait until well after World War II. In the decade immediately following World War II, deeper layers of physical metallurgy began to be penetrated; in particular the basic principles underlying the strength of metals and alloys were established by extensive development of dislocation theory and related experiments. At the same time the increased resolution of electron microscopes led to the detailed examination of the various stages of precipitation in alloys and eventually to the direct observation of dislocations in thin foils. These major developments in basic physical metallurgy made it much easier to understand the frequently complex behaviour of aluminium alloys, but unfortunately the basic work which was usually done for good reason on simple binary aluminium alloys, was not always extended with the same zeal to commercial alloys. The consequence was that, while the fine microstructure of commercial alloys became easier to study, the complexities of behaviour, for example on ageing, ensured that empirical development would continue. However it is, I believe, fair to say that empirical development carried out with an increased background knowledge is a great improvement on unaided empiricism.

It is clear from Hunsicker's paper that the improvement of the Al–Zn–Mg–Cu alloys in the period 1960 until the present day had not led to increased strength levels for the optimum strengths had almost been reached in the previous decade. Indeed, the emphasis in recent years has been in the combination of the appropriate strength level with resistance to corrosion, in particular stress corrosion cracking. Alloys have now been developed with virtual immunity to stress corrosion, but it must be said that the basic principles behind the empirical solutions have not yet been fully spelt out. This arises from the fact that it has not been possible to study grain boundaries, frequently the sites of stress corrosion cracking, in sufficient detail until comparatively recently. It is now possible, for example by use of electron energy analysis combined with electron microscopy, to study the solute depletion profiles in aluminium alloys

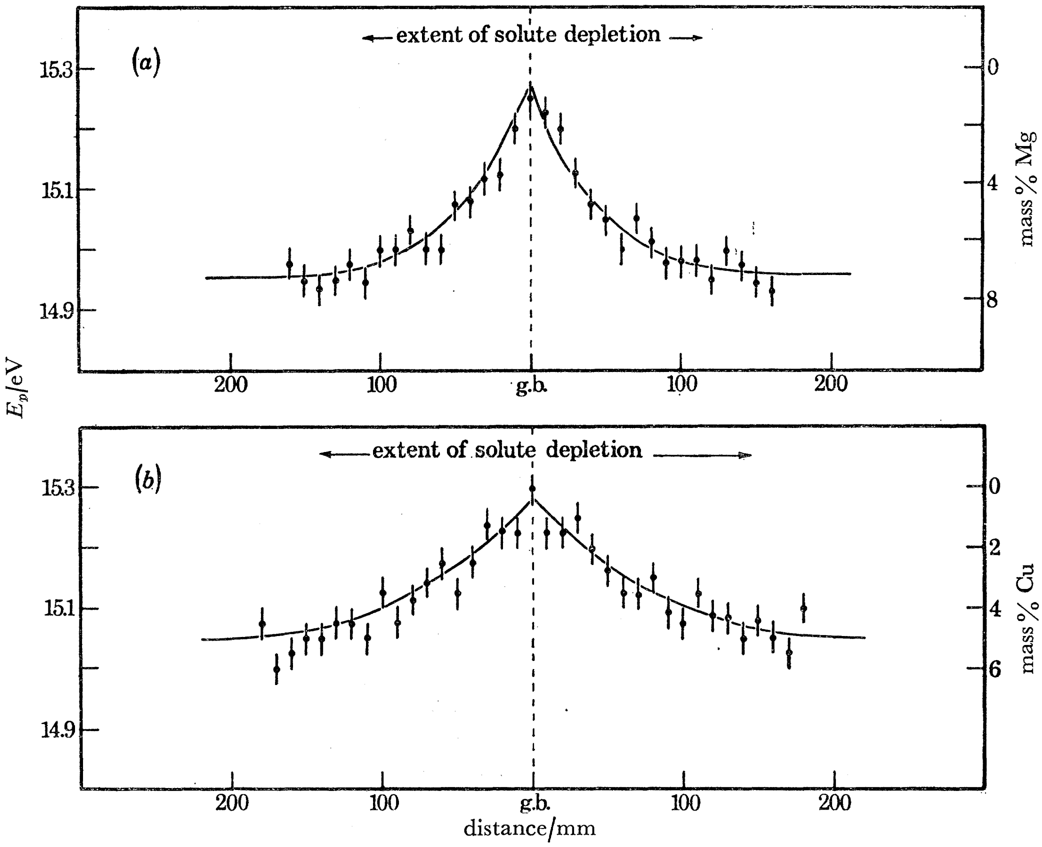

FIGURE 2. Typical energy loss/composition profiles across a grain boundary in (*a*) Al–7.2 mass % Mg aged 200 h at 125 °C, (*b*) Al–4.4 mass % Cu aged 100 min. at 220 °C (Doig & Edington).

sensitive to stress corrosion (Doig & Edington 1974). Figure 1, plate 29 shows the grain boundary precipitation of β' in an Al–7 mass % Mg alloy which leads to s.c.c. sensitivity, while figure 2 shows the electron energy loss profiles in two alloys which can be directly related to solute depletion. So far only binary and ternary aluminium alloys have been studied in this way, but further work on complex commercial alloys should be done, and in my view would be very useful.

The other over-riding requirement of many modern high strength aluminium alloys is that they should have good fracture toughness at high static stress levels – this applies in the

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DESCRIPTION OF PLATE 29

FIGURE 1. A typical grain boundary in an aged Al–7.2 mass % Mg alloy showing β' Al_3Mg_2 precipitates (Doig & Edington).

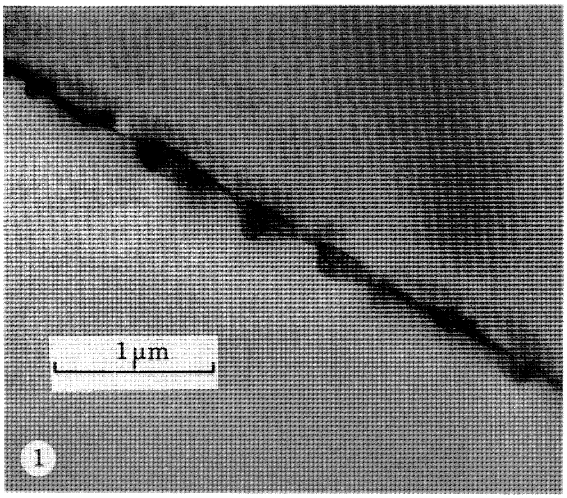
FIGURE 5. A unidirectionally grown lead-silver eutectic (*a*) as grown, (*b*) isothermal treatment for 120 h at 558 K, (*c*) 94 hours in gradient of 4 K mm^{-1} at less than 554 K. Optical micrograph transverse sections (magn. × 500), (*d*) etched, same as (*c*) scanning electron micrograph (magn. × 1000) (Jones).

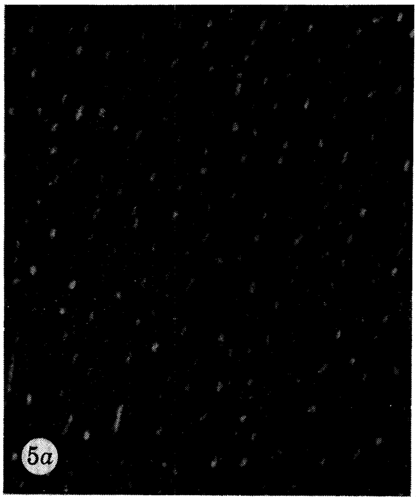
FIGURE 6. The dispersion of vanadium carbide in an Fe–V–C alloy after isothermal transformation and ageing at 725 °C for (*a*) 5 min, (*b*) 15 min showing coarsening on dislocation network. (Dunlop & Honeycombe.)

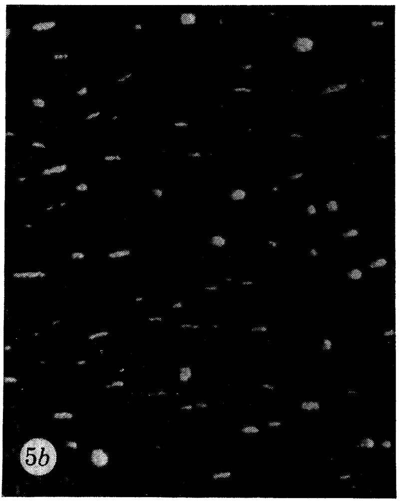
FIGURE 7. An iron–0.04 mass % carbon alloy with 680 ppm antimony. Cracking at the iron carbide/ferrite interface. (Rellick and McMahon.)

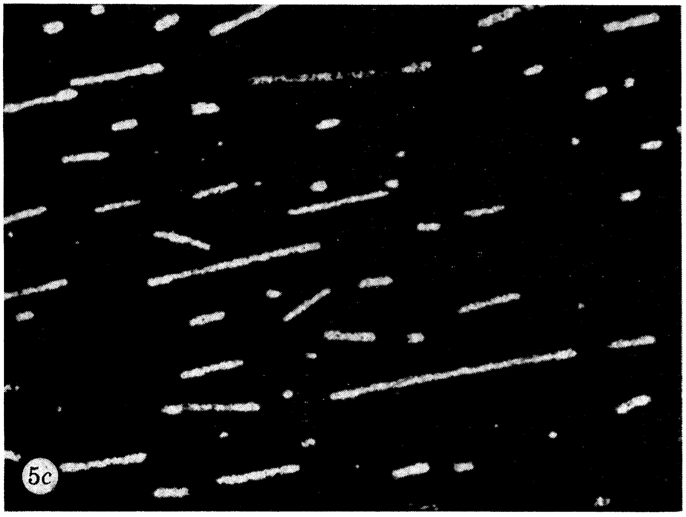
FIGURE 8. Beginning of isothermal transformation of a Ti–7 mass % Ni alloy at 640 °C. Optical micrograph × 300. (Chatfield.)

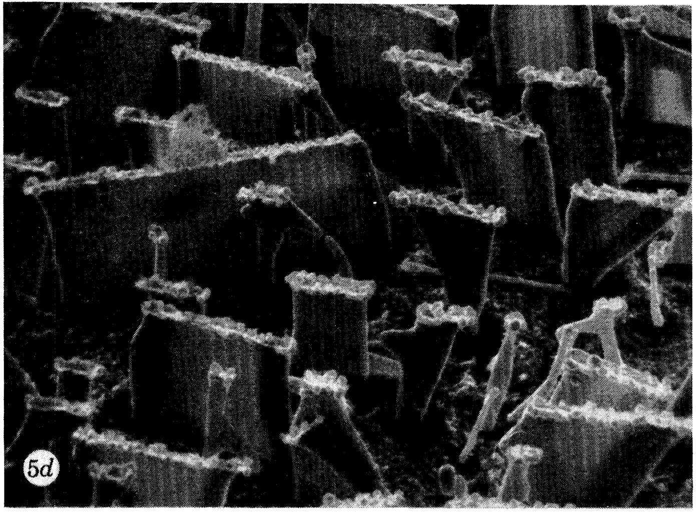
FIGURE 10. Intergranular cavities in a failed Calder Hall fuel element. (Magn. × 45 (Eldred).)

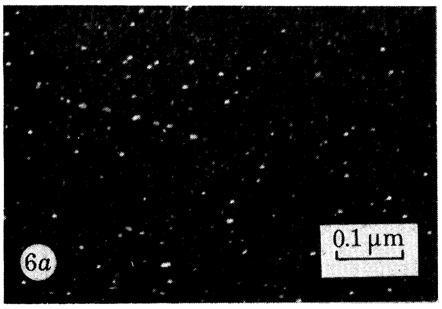


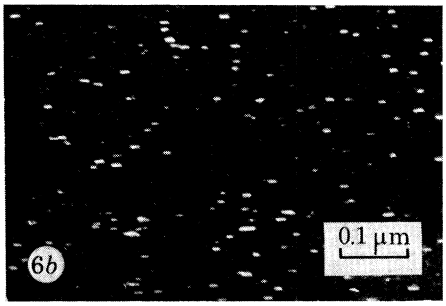


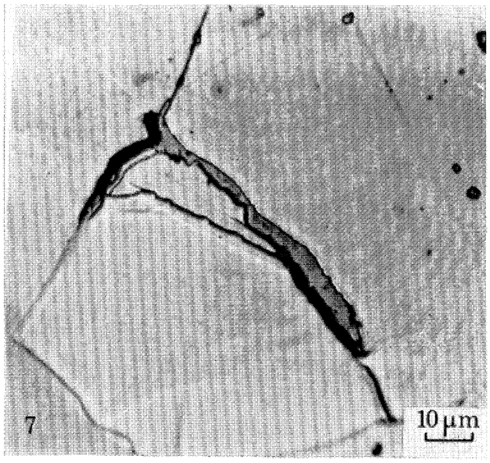


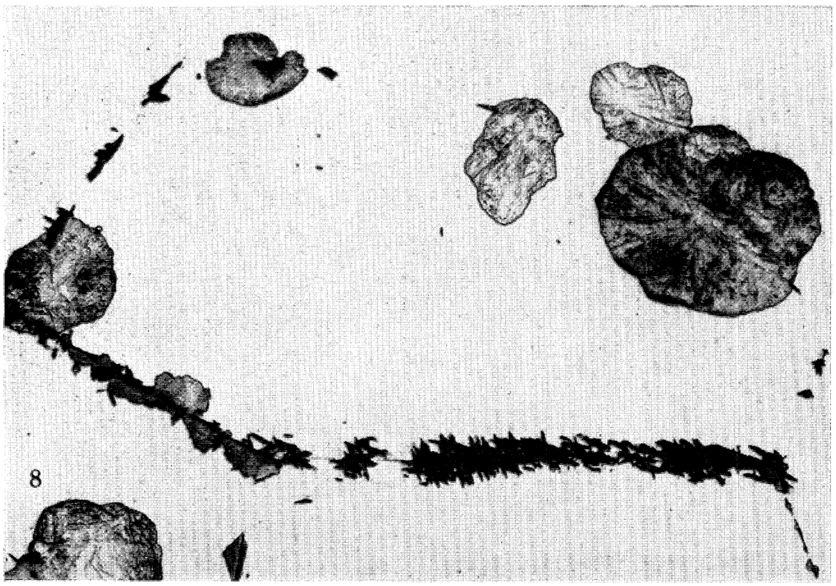


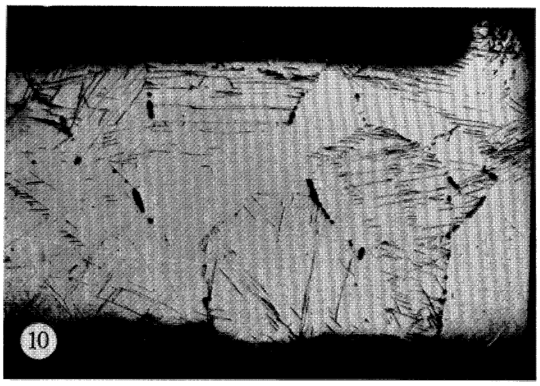












FIGURES 1, 5*a*–*d*, 6*a*, *b*, 7, 8 and 10. For description see opposite.

presence of stress corrosion cracking which is essentially a brittle crack propagation, and even in the absence of this phenomenon when frequently inadequate resistance to crack propagation occurs. In the latter case, the harmful role of coarse particles of intermetallic compounds is now fully understood, and a positive effort is made both by control of composition and heat treatment to minimize their occurrence. The 7474 alloy referred to by Hunsicker has thus close limits imposed on impurity elements such as iron and silicon, and also much attention is paid to control both of chemical homogeneity and of grain size, together with careful particle size control of the strengthening precipitate phase ($Al_{12}Mg_2Cr$).

Finally the aluminium alloy scene would not be complete without some reference to fatigue failure. While it might be thought intuitively that high fracture toughness and fatigue resistance should go hand in hand, Hunsicker throws some doubt on this view, and clearly there is room for more work in this area. Nevertheless the use of thermomechanical treatments (pioneered in the alloy steel field) have shown promise of simultaneously increasing ductility, fracture toughness and fatigue resistance.

3. Nickel-base alloys – high temperature properties

While many basic investigations carried out on aluminium alloys have provided a good scientific framework for future alloy development, it is, I think, fair to say that the use of scientific principles has found fullest scope in the development of precipitation-strengthened nickel-base alloys for use under stress at high temperatures. Moreover it is in this type of application that the metallurgist and engineer work in closest contact, for the technical rewards to be gained by raising the operating temperatures of a gas turbine by only a few degrees are easily worth an intensive programme of alloy development to meet the challenge.

The use of age hardened alloys at high temperatures brings up the important question of stability of microstructure, because the particular creep properties of an alloy can only be maintained at the operating temperature if the microstructure does not alter markedly during the service life of the part. Put the other way around, the service life of the part will be determined to a substantial degree by the ability of the microstructure to resist significant changes. Nicholson (3.8) has discussed the γ' hardening phase in nickel-base alloys and pointed out that its stability at high temperatures is dependent on the close lattice matching between γ' and the nickel-base solid solution matrix. The resulting low energy interfaces do not provide a high driving force for coarsening. The idea of deliberately matching crystal lattices to each other arises from well-defined concepts concerning phase transformations in alloys, and it is indeed satisfying that such concepts can be used along with more empirical methods to improve, for example, the creep properties of an important group of high temperature alloys.

Stability of microstructure is important in another related field, that of the directional solidification of alloys in particular eutectic alloys for possible applications as turbine blades. As Nicholson has pointed out, the growth of single crystal turbine blades has now been shown to be technically achievable, with obvious advantages in the elimination of grain boundaries which play such an important role in creep failure. Brook & Duckworth (3.10) have also emphasized the use of directionally solidified eutectics for similar applications (their figure 11). There is however some reason for concern about the thermal stability of some eutectic structures, not so much at constant high temperatures, but in particular, when the alloy is subjected to a temperature gradient which is the normal circumstance in practice.

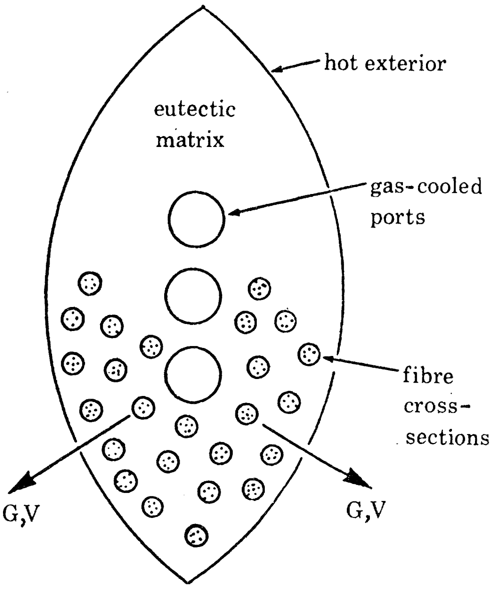


Figure 3. Schematic cross-section of a unidirectionally solidified fibrous turbine blade in service (Jones).

It is now well established (Barnes & Mazey 1963; Shewman 1964; Ho 1970) that inclusions can migrate along a temperature gradient as a result of the driving force provided by thermal diffusion. In the case of two mutually insoluble metals A and B, A forming the inclusions and B the matrix, the motions of the inclusions are limited entirely by diffusivity of B atoms; this has been fully described theoretically (Ho 1970). Jones (1974*a*) has applied the theory to the turbine blade situation where the temperature gradient G is normal to the fibre axis (figure 3), and the rate controlling process is the diffusivity D_i. The velocity of migration of the fibre V_{fibre}, can be written as

$$V_{(\text{fibre})} = D_i \delta Q G / 2RT^2 r, \tag{1}$$

where δ is the thickness of high diffusivity layer, D_i the diffusivity of matrix metal B in the interphase boundary, Q the heat of transport of B, r the fibre radius, R the gas constant, and T the absolute temperature.

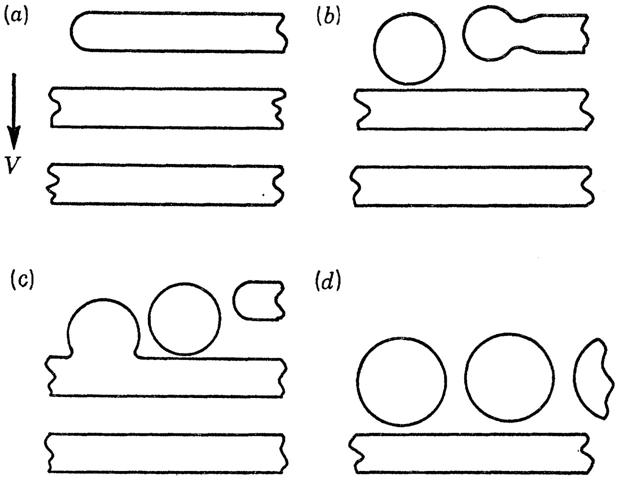


Figure 4. Sequence illustrating how in a temperature gradient a spheroidized eutectic rod can catalyse the spheroidization of its neighbours (Jones).

Jones shows, by use of typical metallic values that the fibres will migrate a distance of 1–5 μm in 10 h at 1000 K in a gradient of 100 K mm^{-1}, which is comparable to the inter-rod or lamellar spacing of a typical eutectic alloy. Such an effect would be expected to lead to a rapid break-down of the aligned structure. This break-down is accelerated by irregularities in r, the fibre radius, but even if it is constant, variation in interfacial kinetics e.g. due to anisotropy, impurities, etc., can readily lead to the degeneration of eutectic rods. The process of progressive spheroidization is shown schematically in figure 4*a–d*. Experiments have been carried out on directionally solidified Al–$\mathrm{Al_3Ni}$ (Jones & May 1975) and lead–silver eutectics (Jones 1974*b*) and in both cases a dramatic effect of temperature gradient on structural stability was shown. In the former case, increases in coarsening rate of up to twenty times were measured in the temperature range 868–883 K. The coarsening of the lead–silver eutectic is illustrated in figure 5*a–d*, plate 29, in which a transverse section of the original directionally grown eutectic (figure 5*d*) is compared with an isothermally heated specimen and one in a gradient as low as 4 K mm^{-1}. Such data would appear to call into question the use of directionally solidified eutectics for turbine blade use, and give some comfort to those who have produced sophisticated nickel-base alloys with very stable dispersed precipitates. Even in these circumstances the stability of finely dispersed phases needs close attention, a problem not only in nickel-base alloys, but also alloy steels and other alloys employed under stress at elevated temperatures.

Particle coarsening at elevated temperatures is defined to some degree by the Lifshitz–Wagner theory which assumes diffusion control:

$$(r_t^3 - r_0^3) = (K/RT)\,V^2\,CD\gamma t, \tag{2}$$

where r_0 and r_t are the mean particle radii at zero time and time t, D is the diffusivity of solute in matrix, γ the particle interface interfacial energy, C the conc. of solution in equilibrium with a particle of infinite size, V the molar volume of precipitate, and K a constant.

However, this theory gives only rough agreement with experiments for various reasons, of which the most relevant are connected with the acceleration of growth beyond that predicted. At least two types of sites in crystals provide for this.

(*a*) Grain boundaries and interphase boundaries: Precipitate particles nucleate at grain and interphase boundaries because they are energetically favourable sites, but having done so, the accelerated diffusion of solute along such interfaces leads to more rapid coarsening than within the grains.

(*b*) Matrix dislocations: Recent work (Dunlop & Honeycombe 1975) on low alloy steels has shown that very fine carbide dispersions within grains coarsen predominantly by selective growth of those particles lying on dislocation lines (figure 6, plate 29). It has been found that a relatively low dislocation density can significantly increase coarsening rates, because of the ability of dislocations to climb, and for their strain fields to interact with those of coherent precipitates. The result is a much broader size distribution of particles than predicted by the Lifshitz–Wagner theory. This theory gives a linear relation between r^3, the mean particle radius, and time for volume diffusion controlled growth, and between r^2 and time for interface reaction control. However a linear relation between r^5 and time was obtained in the case of vanadium carbide coarsening in ferrite, as predicted by Kreye (1970) for coarsening of particles lying on dislocations:

$$(r_t^5 - r_0^5) = (K'/RT)\,V^2\,CD_{\mathrm{d}}\,q\delta Nt, \tag{3}$$

where D_{d} is the diffusion coefficient for dislocation pipe diffusion, q the effective cross-sectional area of the dislocation pipe diffusion path, N the no. of dislocations intersecting each particle, and K′ constant.

So we are now aware of at least some of the important principles determining the stability of microstructure. The application of these principles to industrial alloys is often very difficult, consequently the empirical approach is still necessary; however it now has substantial backing from basic physical metallurgy.

4. HIGH STRENGTH STEELS

As May and colleagues have pointed out in their paper, achievement of very high strength in steels is no longer the real challenge. Today the interest is in high strength steels with great resistance to crack propagation under static load, under cyclic load and often in corrosive environments. This goal of a satisfactory combination of diverse properties is much more difficult to achieve, and calls for extensive basic knowledge often in new fields, in combination with a sensible empirical approach. Steel metallurgists have perhaps clung rather too long to the traditional 'quench and temper' approach to high strength alloy steels. The martensite transformation which occurs on quenching is a valuable way of raising the dislocation density (as high as 10^{11}–10^{12} cm^{-2}), but the high interstitial hardening due to carbon in solid solution brings with it brittleness. The tempering treatment precipitates most of the carbon as iron carbides or alloy carbides, to a large extent on to what is left of the quenched-in dislocations which now form an effective strengthening network in a ferrite matrix. The result is a strong and frequently (but not always) tough material.

One of the dangers of this route to high strength is temper embrittlement which is induced in some steels by tempering in a critical temperature range (500–600 °C), or by cooling at critical rates through this temperature range. It is known that impurity elements, in particular the elements Sn, Sb, As and P are responsible for the embrittlement, and recent work by Rellick & McMahon (1974) has shown that this can be due to the rejection of these elements during carbide formation and growth. Figure 7, plate 29, shows an example of intergranular cracking along a carbide-ferrite interface in a simple iron–0.04 % carbon alloy doped with antimony (680 parts/10^6). If the temperature is low enough to avoid much diffusion, then the elements remain at or near the carbide matrix interface and nearby ferrite/ferrite interfaces. In plain carbon steels such embrittlement is transient, being removed by tempering for long times, however in certain alloy steels, e.g. containing nickel and chromium, the effect is not readily removed in this way. Auger spectroscopy of intergranular fracture surfaces leaves no doubt that the embrittling agents are elements such as antimony and arsenic. In this connection it is interesting to note that a recent survey by the C.E.G.B. has revealed that elements such as As, P, Sn, Pb and Sb are the main contributors to cracking in heat affected zones around welds in steels commonly used in power plant (Townsend 1975). The best solution to such problems in the long run is the use of purer steels with the harmful impurities below certain very low limits. However this trend at present runs contrary to efforts to increase use of scrap with the consequential build up in the resulting steels of harmful impurity elements. The risks in allowing this trend to continue should be fully realized and prompt action taken.

As May and co-authors (3.7) have pointed out, several alternative ways to high strength involve modification either of the austenitic structure or of the martensite resulting from low temperature transformation. The austenitic condition can be retained to room temperature by suitable alloying, and then high strength with good ductility is obtained simply by heavy cold work. A refinement of this approach involves the warm working of austenite of carefully balanced composition to give a high strength deformation structure. Cooling to room temperature retains the austenite, but this phase is now metastable; under the action of plastic deformation it undergoes strain-induced transformation to martensite leading to high strength levels, good ductility and resistance to crack propagation. However these methods involve very close control of composition, working and heat treatment. The maraging steels provide an alternative solution where carbon is eliminated from the steel so that a low carbon martensite can be formed by air cooling; at the same time the composition is adjusted to allow the precipitation of intermetallic compound dispersions on subsequent ageing. Again high strength and toughness are achieved, but high concentrations of expensive alloying elements are needed. The ausforming process provides yet another alternative route in which metastable austenite (in the TTT curve 'bay') is heavily deformed prior to transformation to martensite followed by tempering in the normal way. The undoubted success of this process in achieving high strength, together with toughness in a range of alloy steels is not yet fully explained, and the method places severe limitations on the applications for which it can be used.

All the above processes are tedious, difficult to control and/or use high concentrations of expensive alloying elements. They provide solutions to the strength with toughness problem but at a price that cannot always be paid, except in critical applications. There are clearly needed easier and cheaper routes to strong, tough steels. An obvious approach which should be further explored is the direct decomposition of austenite to a fine-grained dispersion strengthened ferrite without going via martensite. The change in carbide solubility as the γ–α transformation takes place can lead to very fine dispersions of alloy carbides formed as the ferrite grains form in the austenite (Davenport & Honeycombe 1971). This direct transformation approach has been shown to be successful in low alloy steels where, when it is combined with controlled rolling which achieves extremely fine grain sizes, is capable of reaching yield stresses in excess of $500\ \mathrm{N\ mm^{-2}}$. It seems likely that yield stresses very substantially in excess of this will be achieved when the physical metallurgy of direct transformation of austenite is better understood.

It is tempting at this stage to define the ideal type of structure of a high strength steel, but as yet we can only do this in part. It is of course impossible to avoid sulphide and oxide inclusions in commercial steels and their control is of great importance, however we shall concentrate on the basic steel structure. In normal circumstances the matrix should consist of ferrite with as fine a grain size as possible (around 1 μm), equi-axed, containing a fine uniform dispersion of carbide or intermetallic phases with no large grain boundary or other carbide particles. In addition a dislocation-network should exist within the grains stabilized by some of the fine particles to provide sub-grain strengthening. Finally the grain boundaries should be as free as possible of certain impurity elements already referred to. It is clear that such structures can be approached in several different ways, but the ideal approach does not yet exist.

In this section the alternative methods to high strength and toughness in steels have been briefly referred to. Several of these approaches could well find effective application in non-ferrous alloys, but it must be admitted that research in thermo-mechanical treatment of alloys has concentrated mainly on steels.

5. Titanium alloys

Titanium alloys share with many steels the occurrence of a phase change which allows the structure of the alloys to be varied over wide limits, though it is clear that the ramifications of the γ–α transformation in iron have been studied in very much greater detail than the β–α transformation in titanium. This is not surprising since the developments in titanium alloys have occurred primarily since 1950, but it has meant that the titanium alloys have not yet exploited fully the available strengthening routes. For example, there are very few precipitation hardened titanium alloys available, and only one is made commercially. It is a little disappointing that the development of titanium alloys has contained a large empirical element, but this is still inevitable today when most alloys finally chosen for applications are complex in composition, and represent delicate balances between desirable properties. However a close examination of the development to date shows that broad physical metallurgical principles have been widely used, but these relate mainly to the surface levels of understanding rather than the more profound details e.g. of alloy theory in alloy design, or of dislocation theory in the optimization of mechanical properties.

Indeed it would appear to be a valid point that progress may well have been more rapid had a little more attention been given to the fine microstructure and its relationship to mechanical properties, in particular fatigue resistance and fracture toughness. It is surprising that more work has not been done on TTT diagrams or on the structures resulting from isothermal decomposition of β titanium. Recent work on the titanium–nickel alloys indicates that there are many analogies with ferrous structures, but the structures are extremely complex. Figure 8, plate 29, shows the beginning of transformation from metastable β at 640 °C in a Ti–7 % Ni alloy; both pearlitic and bainitic-type structures are already evident in the microstructure.

6. The future in non-ferrous metallurgy

In their paper, Brook & Duckworth have examined some of the more exciting recent developments in physical metallurgy such as memory alloys and superplasticity, and have also bravely tried to predict future trends in such fields as well as the modes of processing which may be extensively used. While it is impossible to review all of their paper it is perhaps worth emphasizing the criteria which may become more commonplace in deciding development trends.

We have all rather suddenly become more energy conscious and appreciative of many other aspects of conservation. One result of this increased sensitivity is that more positive efforts will be made to use expensive metals sparingly, and to replace increasingly rare metals by other materials. In the past and still today we are often profligate with our metallic resources. In ferrous metallurgy clear steps have been taken towards the use of steels leaner in alloying elements, but just as strong as the older alloys they have replaced. To do this has meant an awareness of several important principles in physical metallurgy such as the grain size dependence of the yield stress and the effect of the γ/α phase transformation on the dispersion of carbides. Without limiting consideration to non-ferrous metallurgy I think that several approaches to alloy development and improvement can be mentioned as compatible with the new technological climate, and thus we would expect them to be increasingly employed in future.

(*a*) *Grain refinement*

Physical metallurgical research has clearly underlined the importance of grain refinement as a strengthening mechanism, which has the added advantages of also increasing toughness in alloys which show ductile brittle transitions. While the non-ferrous industry has in some areas used grain refinement very effectively, it is probably in the steel field, in particular in control-rolled micro-alloyed steel, that the most spectacular advances have been made. Yet there is a big challenge still in both ferrous and non-ferrous metals and alloys where grain refinement could be much more widely practiced with resultant improvement in mechanical properties at relatively small cost.

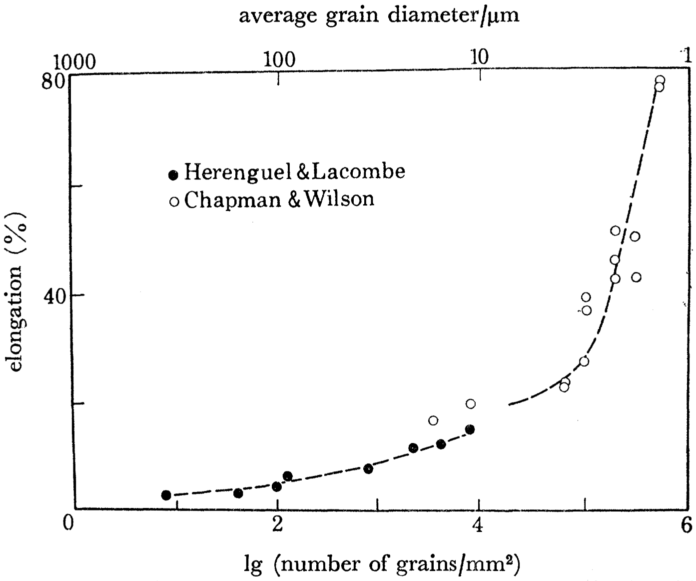


FIGURE 9. Ductility of pure magnesium as a function of grain size. (Emley.)

Brook & Duckworth have referred to new ingenious casting processes, such as rheocasting (Flemings & Mehradian 1973) which result in substantial structural refinement. I share their conviction that this is an important field for development, because refinement of the primary grain structure and minimization of segregation provides a cheap way of upgrading existing alloys to higher levels of strength and general reliability. Another aspect of grain size control is the prevention of grain growth in the solid state, a frequent cause of degradation of mechanical properties. The great benefit to room temperature ductility in refining the grain size of pure magnesium is illustrated in figure 9. In nuclear reactors for power generation, serious problems have arisen in Magnox fuel cans due to excessive grain growth of the magnesium solid solution (Pugh *et al.*). At the operating temperatures, marked cavitation can take place at the boundaries (figure 10, plate 29) and eventually lead to intergranular failure with resultant leaking of radioactive material into the cooling gas. This problem has now been largely overcome by semi-empirical means, but the challenge of maintaining in many alloys a fine grain size under stress at elevated temperatures still remains. Some basic theory exists, for example Gladman (1966), but each alloy still needs a separate detailed approach to provide a satisfactory practical solution to the problem.

(*b*) *Texture control*

Preferred orientation of grains in alloys can have both detrimental and advantageous effects on mechanical properties. In non-ferrous metallurgy, particularly in copper and aluminium-base alloys, control of texture is now commonplace, but there are important aspects yet to be fully exploited, e.g. texture strengthening which is particularly effective in hexagonal materials such as titanium and magnesium alloys. Turning to the ferrous field, I think it is fair to say that it is only recently that deliberate control of texture has been accepted as a method of upgrading mechanical properties (Mintz, Morrison, Morris & Davies 1975). This belated exploitation arises partly from the complexity of textural changes where a phase change is superimposed on the effects of deformation and annealing. This is clearly a field where physical metallurgy must give a lead to the process side in achieving new levels of textural control which will bring benefits in, for example, deep drawing performance, where high *R* values can be obtained with the appropriate types of texture.

(*c*) *Trace elements*

In some alloys, trace elements can have beneficial effects out of all proportion to their concentration on such properties as hardenability, mechanical properties, and stability of microstructure. Examples of successful use of trace elements can be found in all the areas covered by the papers in this session, but perhaps the most familiar examples are those in the aluminium alloys in particular the addition of 0.05–0.1 mass % of cadmium, indium or tin to aluminium–copper alloys which greatly accelerates and accentuates ageing primarily by encouraging the formation of a very fine dispersion of the θ' precipitate rather than g.p. zones 1 and 2. (Hardy, Silcock *et al.* 1956). Similar effects were observed in ternary and more complex commercial alloys (Polmear 1960–1). A second effect is found when silver is added to Al–Zn–Mg–Cu alloys when, in contrast, the g.p. zones are stabilized, enabling higher ageing temperatures to be used, with the result that better resistance to stress corrosion is obtained. More recently it has been found that small additions of germanium to Al–Cu–Mg alloys leads to segregation of germanium at the precipitate interfaces thus reducing the rate of coarsening, and as a result improving the elevated temperature creep properties (Brook & Hatt 1969; Brook 1975). An important but complicating factor is that germanium is only effective if small amounts of magnesium are also present.

In his paper, Nicholson has emphasized, for nickel alloys, the importance of trace elements at grain boundaries, e.g. the effect of boron and zirconium on the morphology and stability of grain boundary carbides. Similar effects result from boron additions to stainless steels. However trace element segregation occurs also to interphase boundaries where the impurity atoms alter interfacial energies and also interact with interface dislocations. These effects play a most important part in controlling the scale of the microstructure, its stability at elevated temperatures, and hence in determining the mechanical properties both at room and high temperatures.

While some of the above phenomena have been known for many years, new trace element effects continue to be found in both high purity and in commercial alloys. Fortunately we are now just at the stage when the techniques capable of resolving the various trace element phenomena are becoming available, e.g. Auger spectroscopy, atom probe, electron energy analysis and scanning transmission electron microscopy. We can thus look forward to a better understanding of trace element phenomena, and to hopefully a less empirical approach to their exploitation in industrial alloys.

The author is grateful to several of his colleagues whose work is referred to in this paper, and who have provided illustrations.

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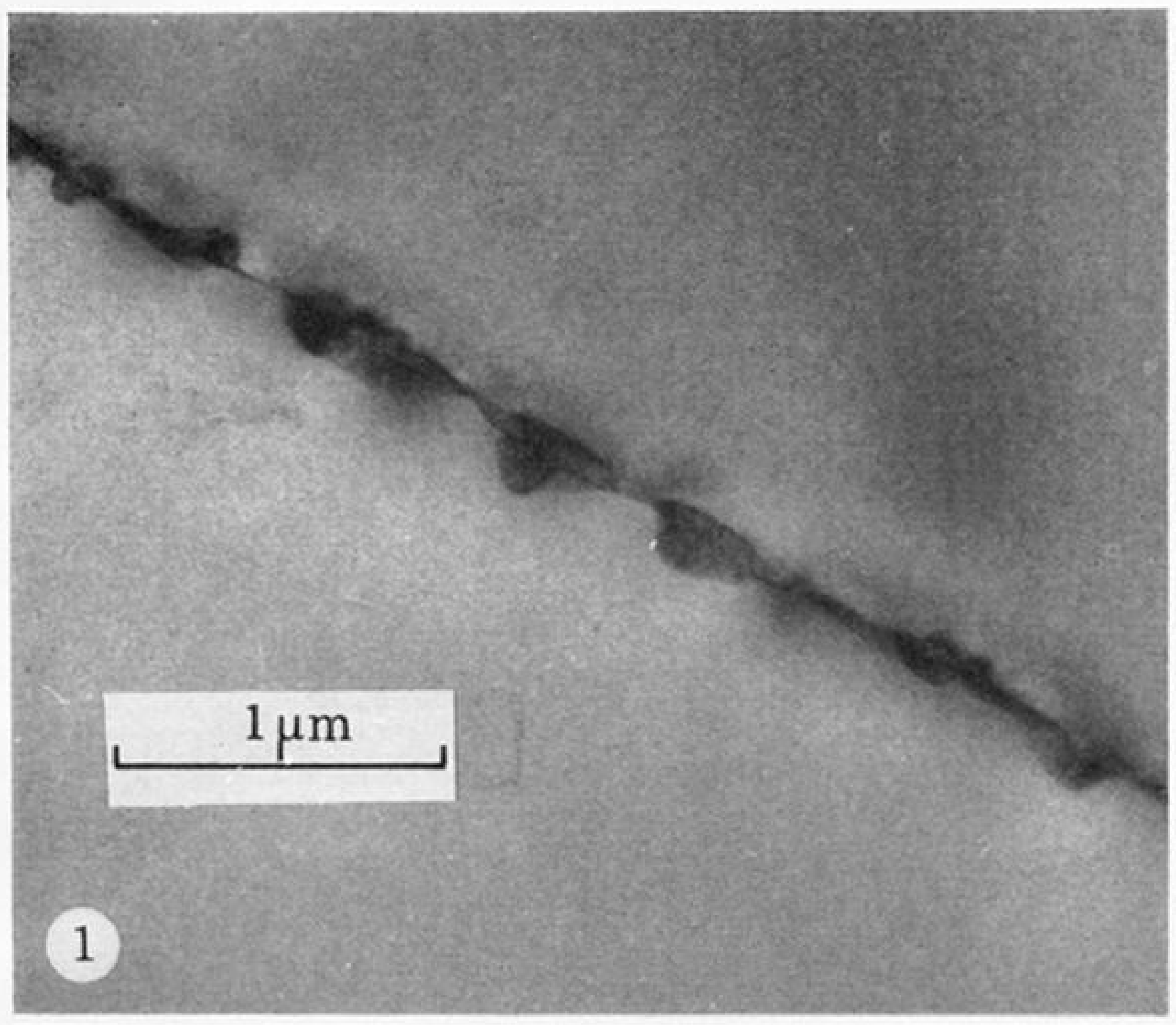
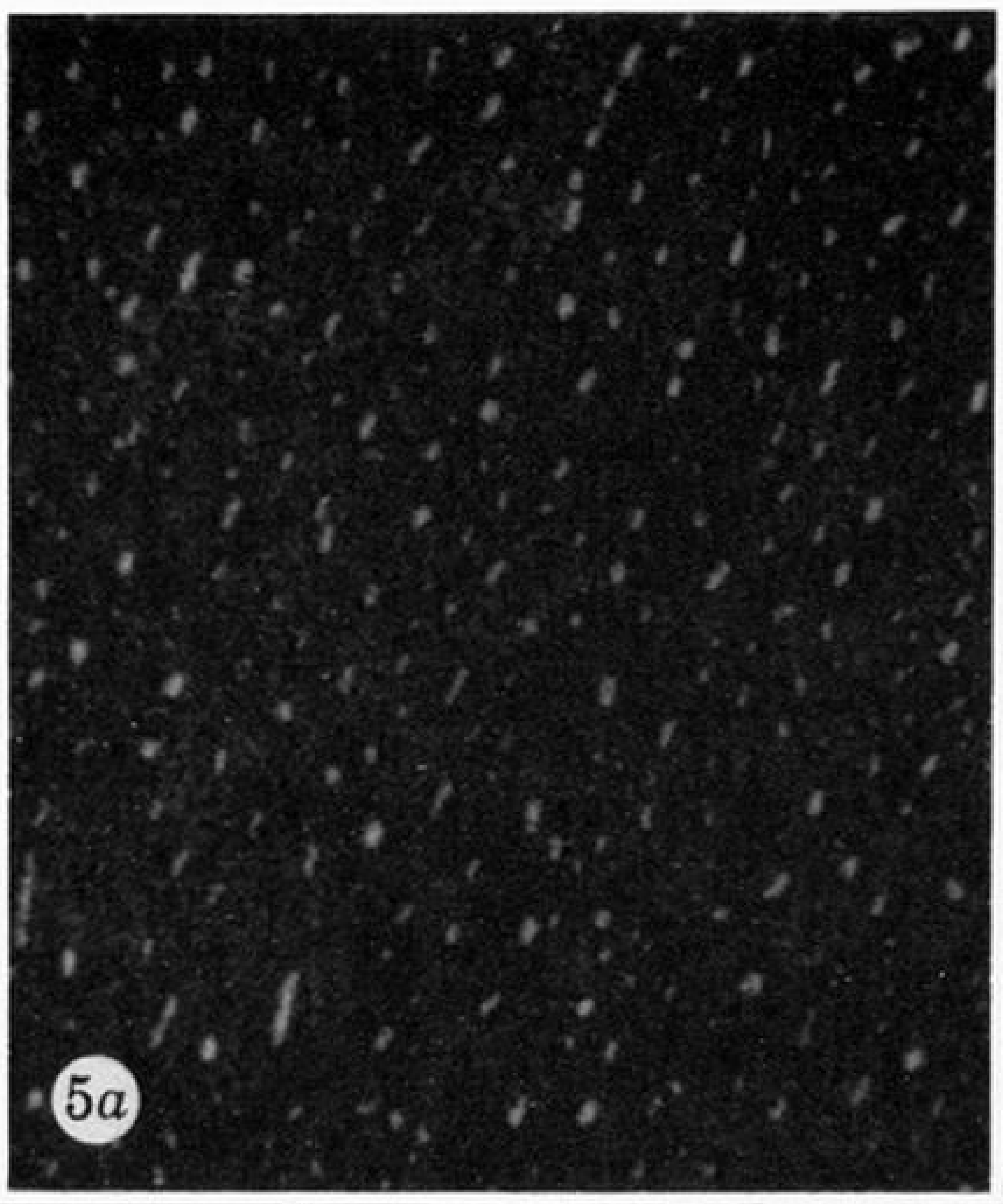
Discussion (Chairman I. J. Polmear (*University of Monash*))

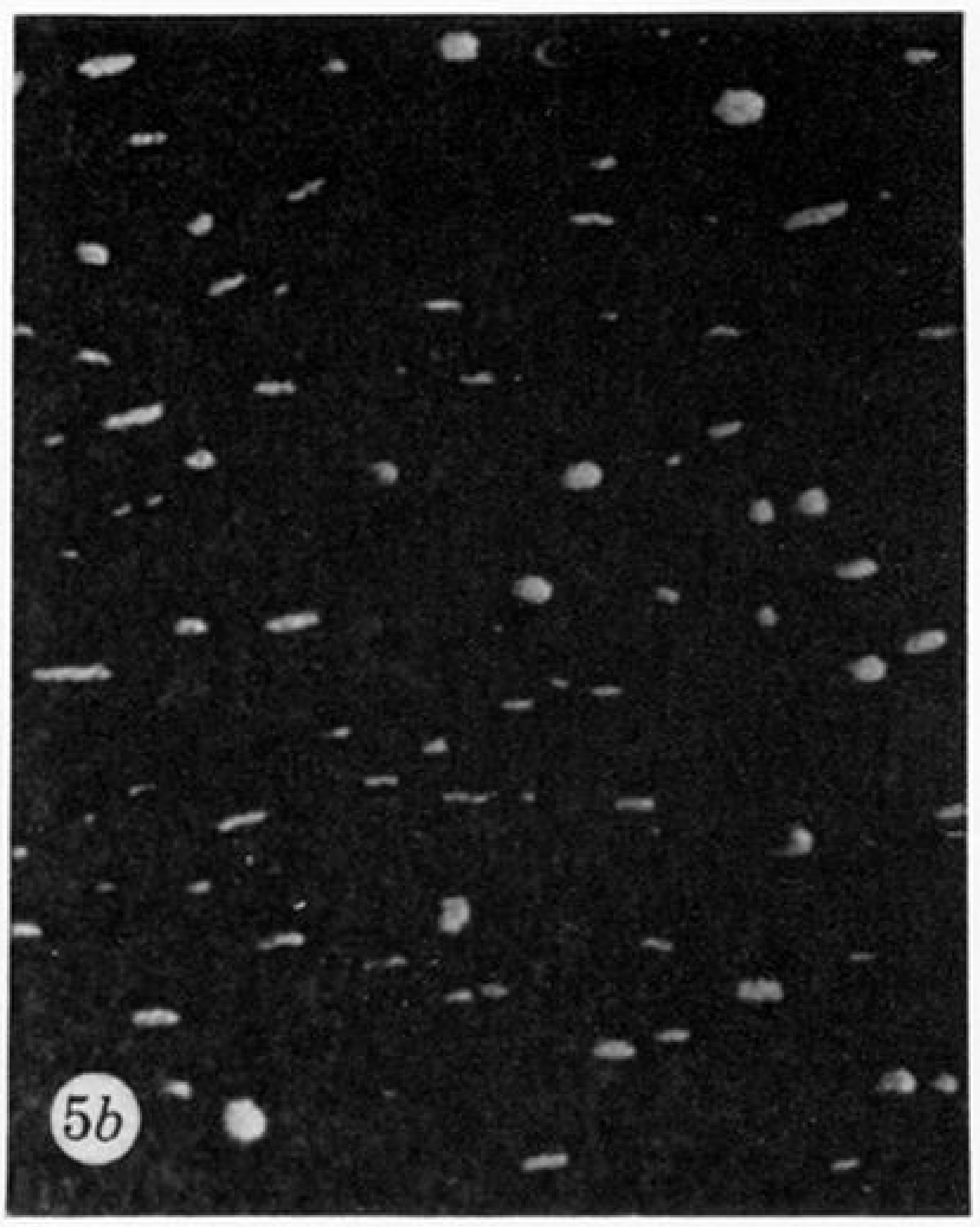
G. B. Brook (*Fulmer Research Institute*)

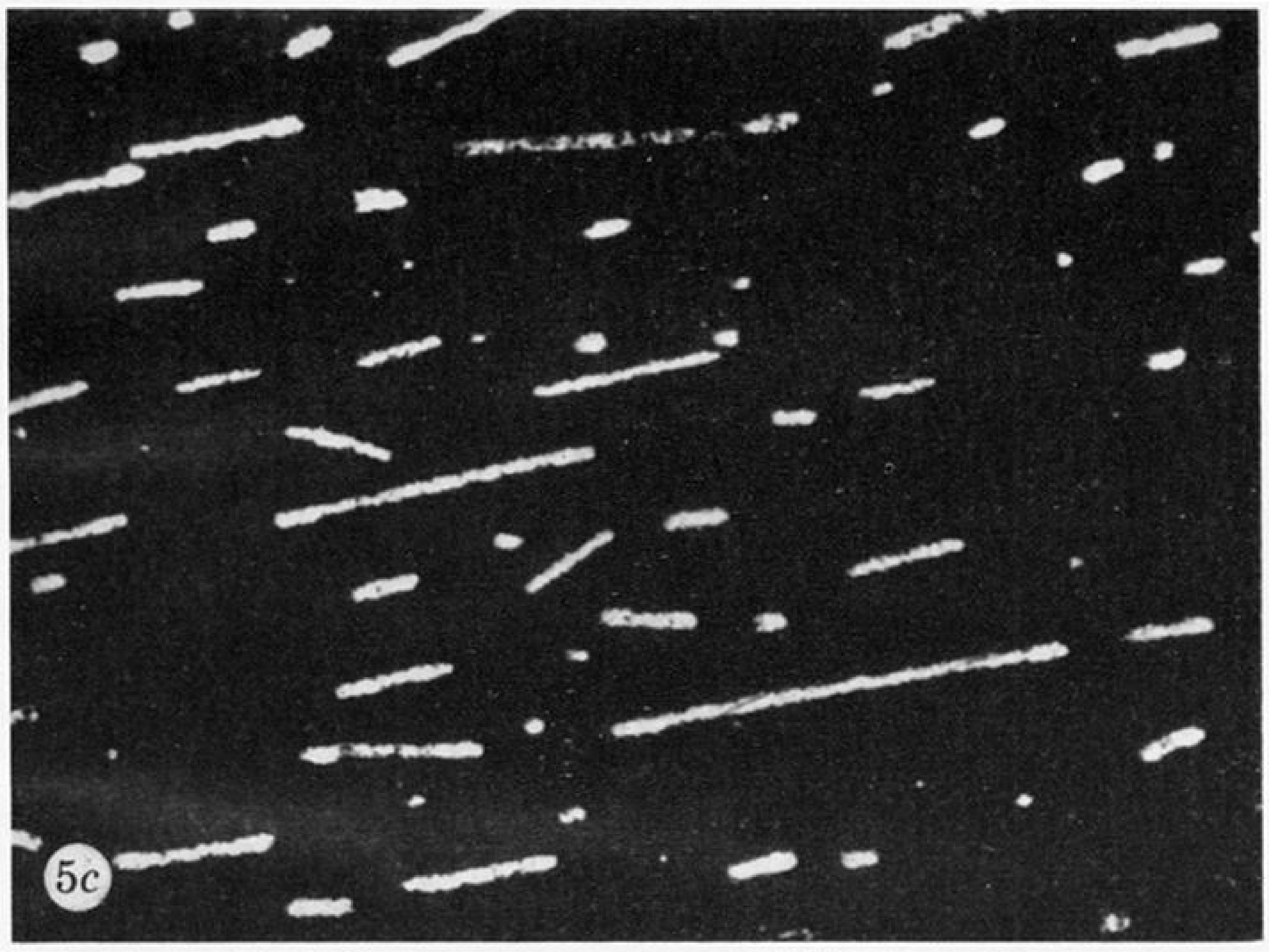
I should like to enlarge on the part of our paper (3.10) in which we considered the effect of trace additions of specific elements on precipitation and on methods of controlling precipitate size. By the term 'trace elements' I differ from those working with steel and mean deliberate additions of specific elements in amounts from a few hundreths to about one tenth of an atomic percentage. The atoms of these elements tend to be different in size from those of the matrix and so it is natural that they should seek some site in the lattice at which they can reduce their energy. This they do by segregating preferentially to defects and interfaces and this is how their effects can be utilized. There are four typical sites:

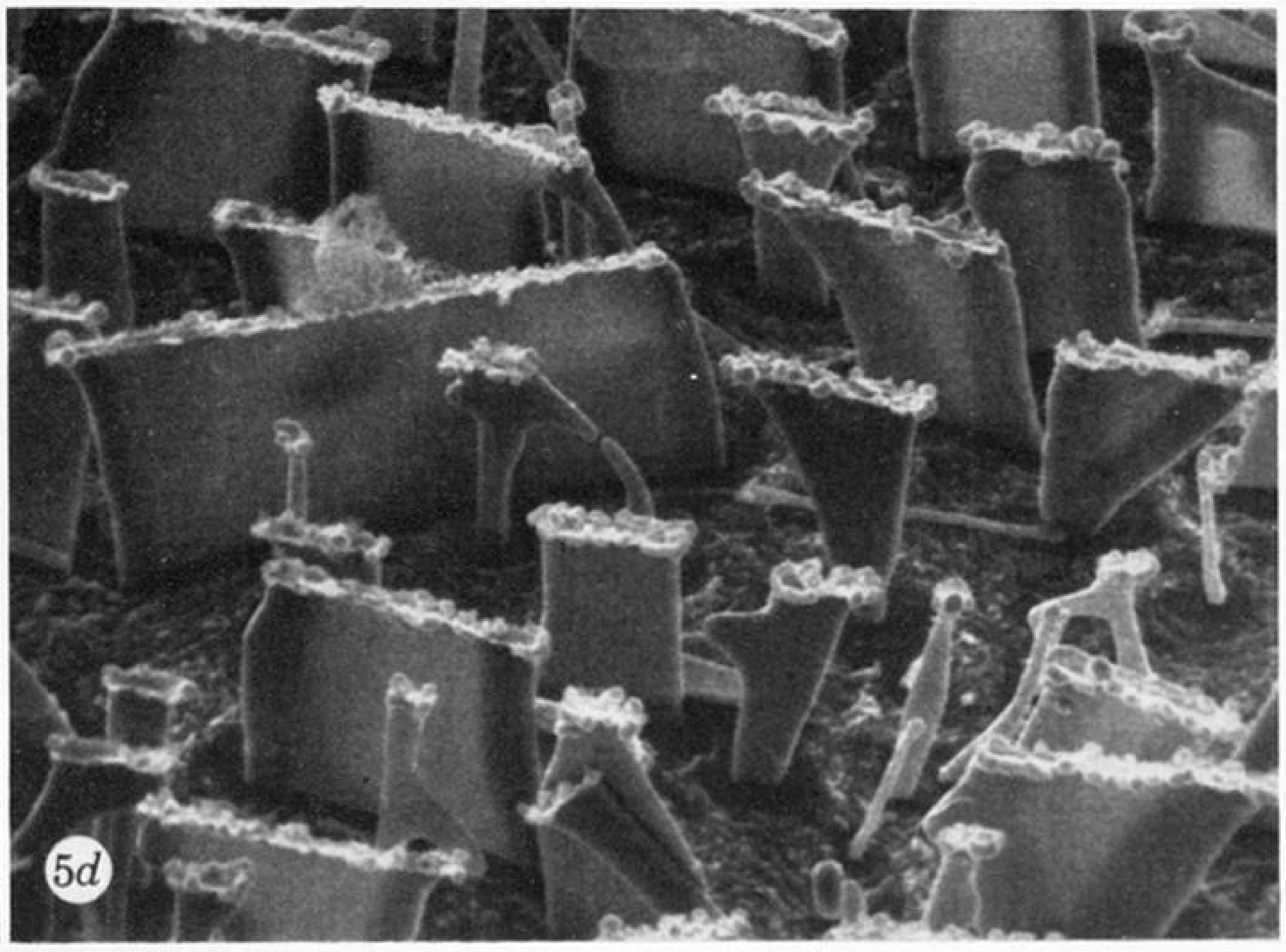
1. Grain boundaries which have recieved most attention. Here trace elements can be used to control the rate at which boundaries can migrate. This can be at higher or lower rates than the normal migration rate of the boundaries in a pure alloy depending on the nature of the trace element. Thus they can cause grain refinement or at the other extreme, they can introduce a property akin to superplasticity for which only about 0.1 atomic percentage is needed. Unwanted trace additions can cause embrittlement but intentional additions can replace detrimental elements at boundaries and thus increase ductility. Embrittlement is often caused by discontinuous precipitation which is a consequence of grain boundary migration. The use of boron in steel to increase the depth of hardening is an example of a trace element effect at grain boundaries. By reducing boundary migration, the formation of pearlite is inhibited.

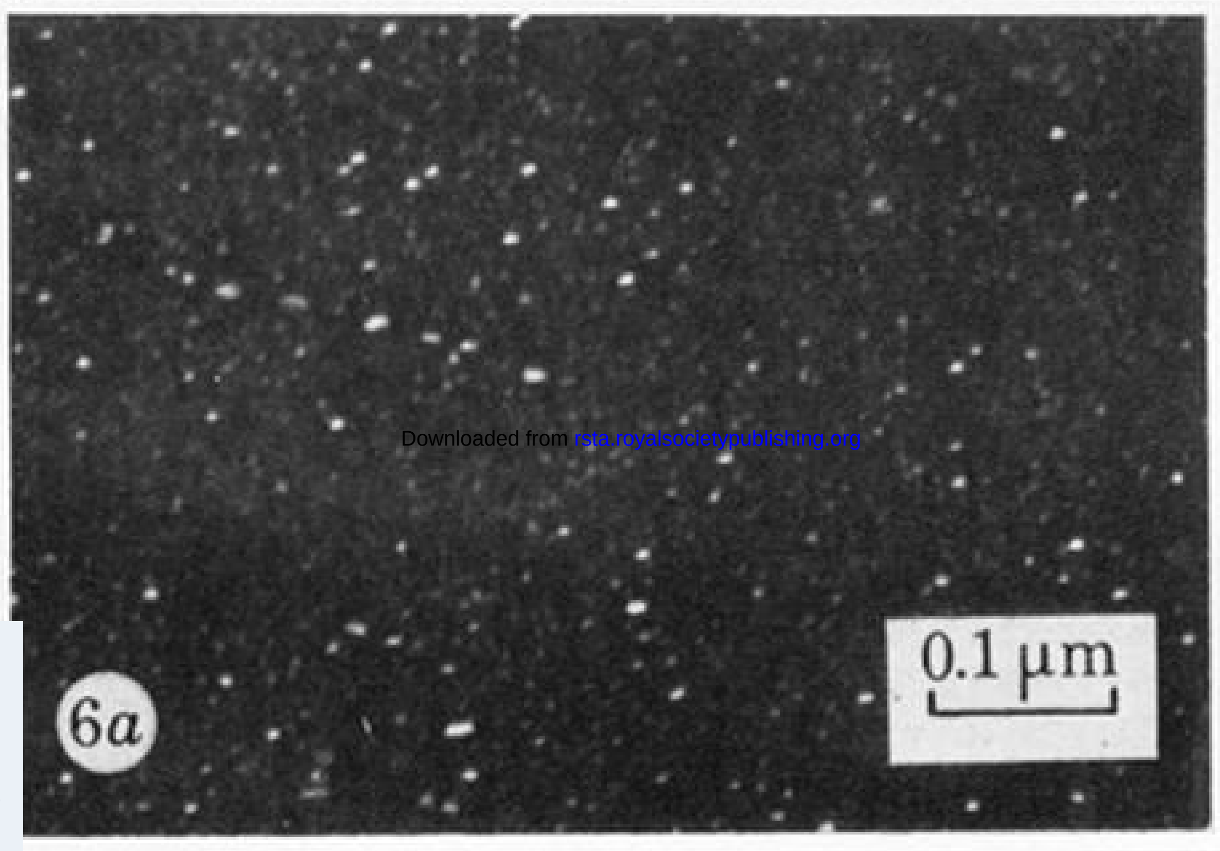


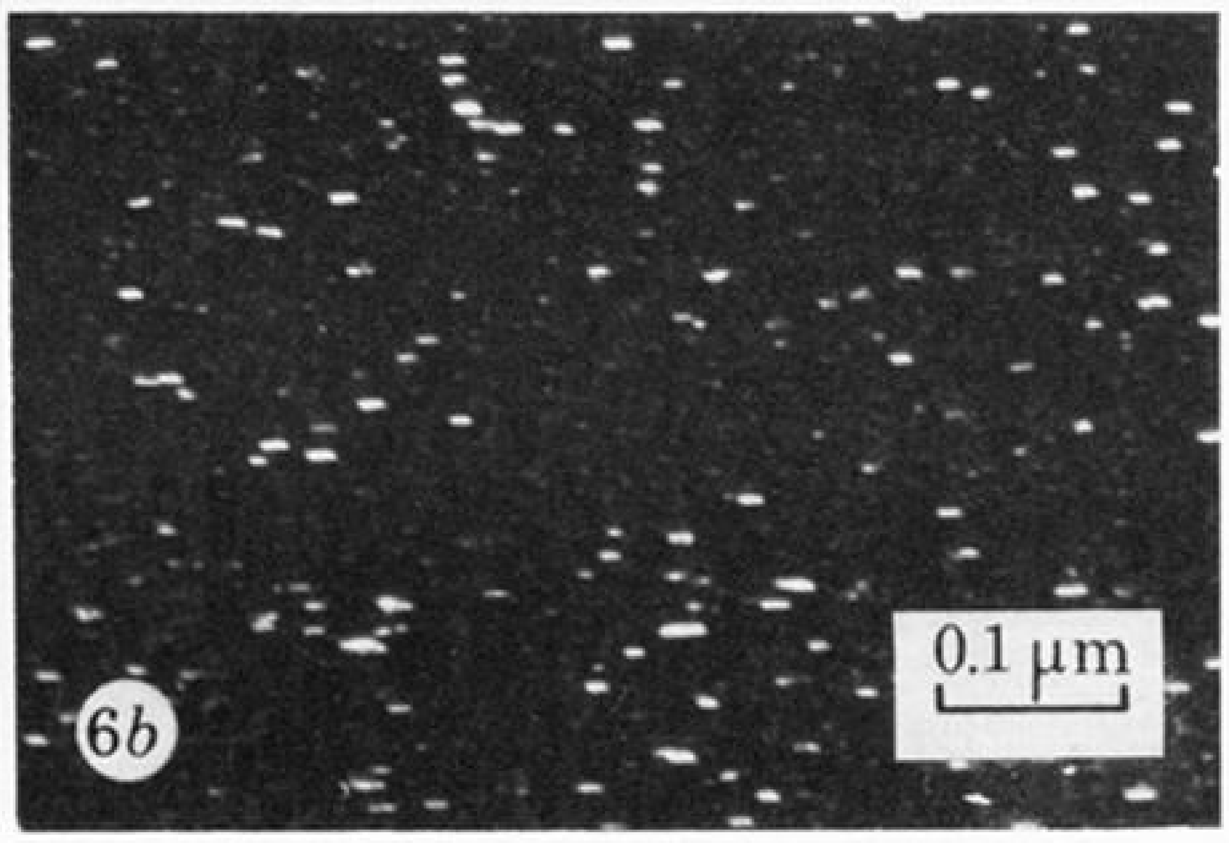


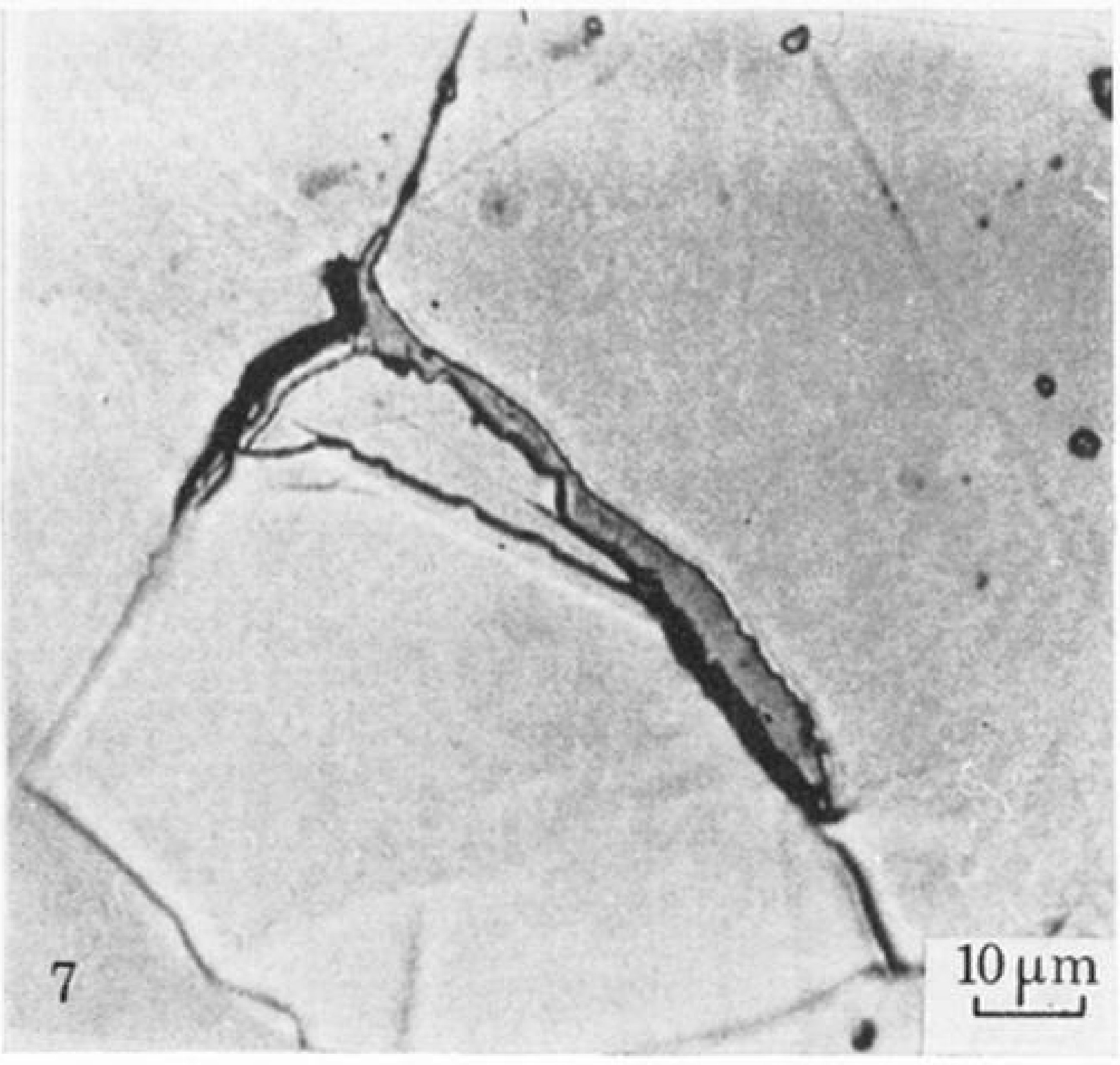


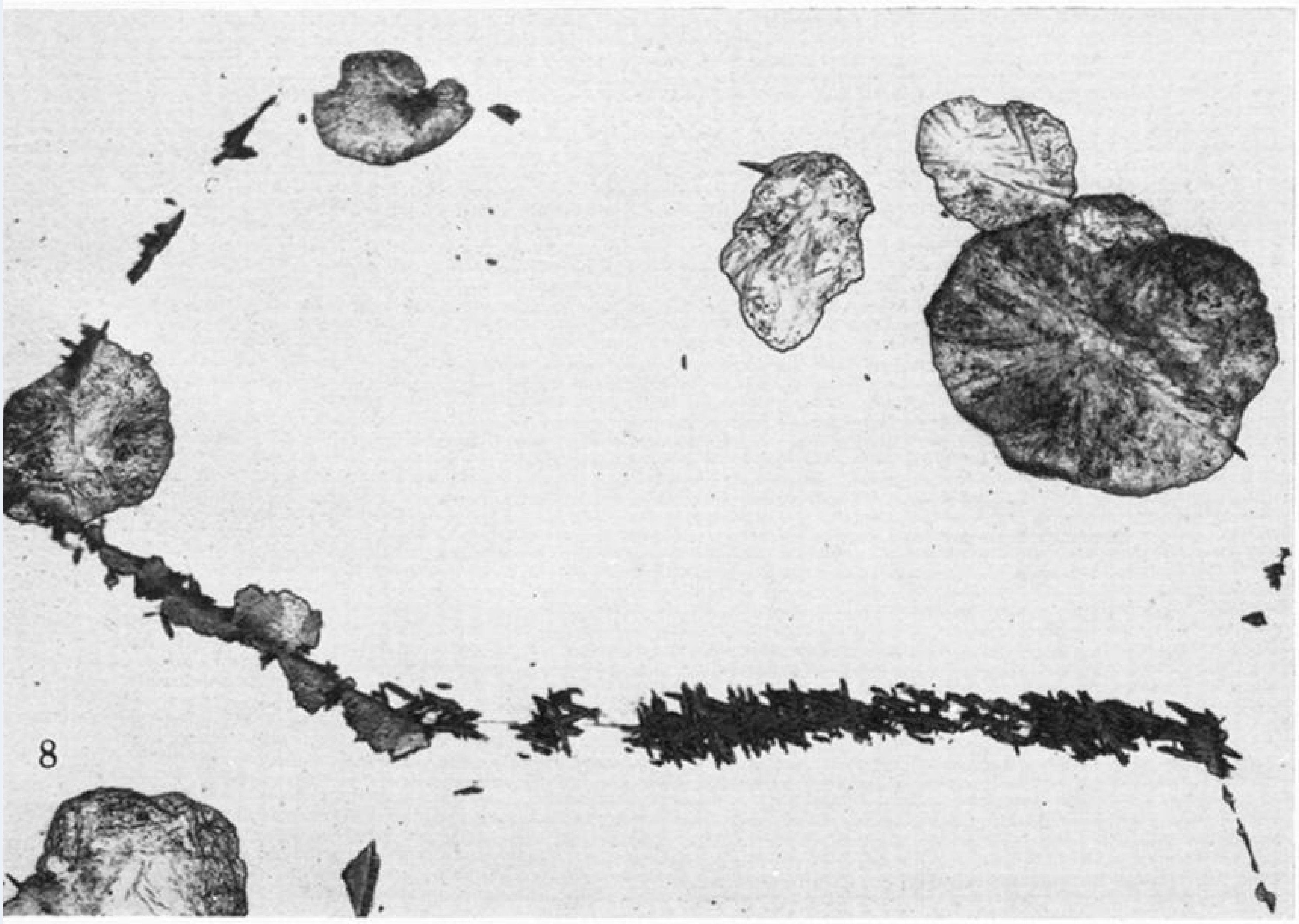


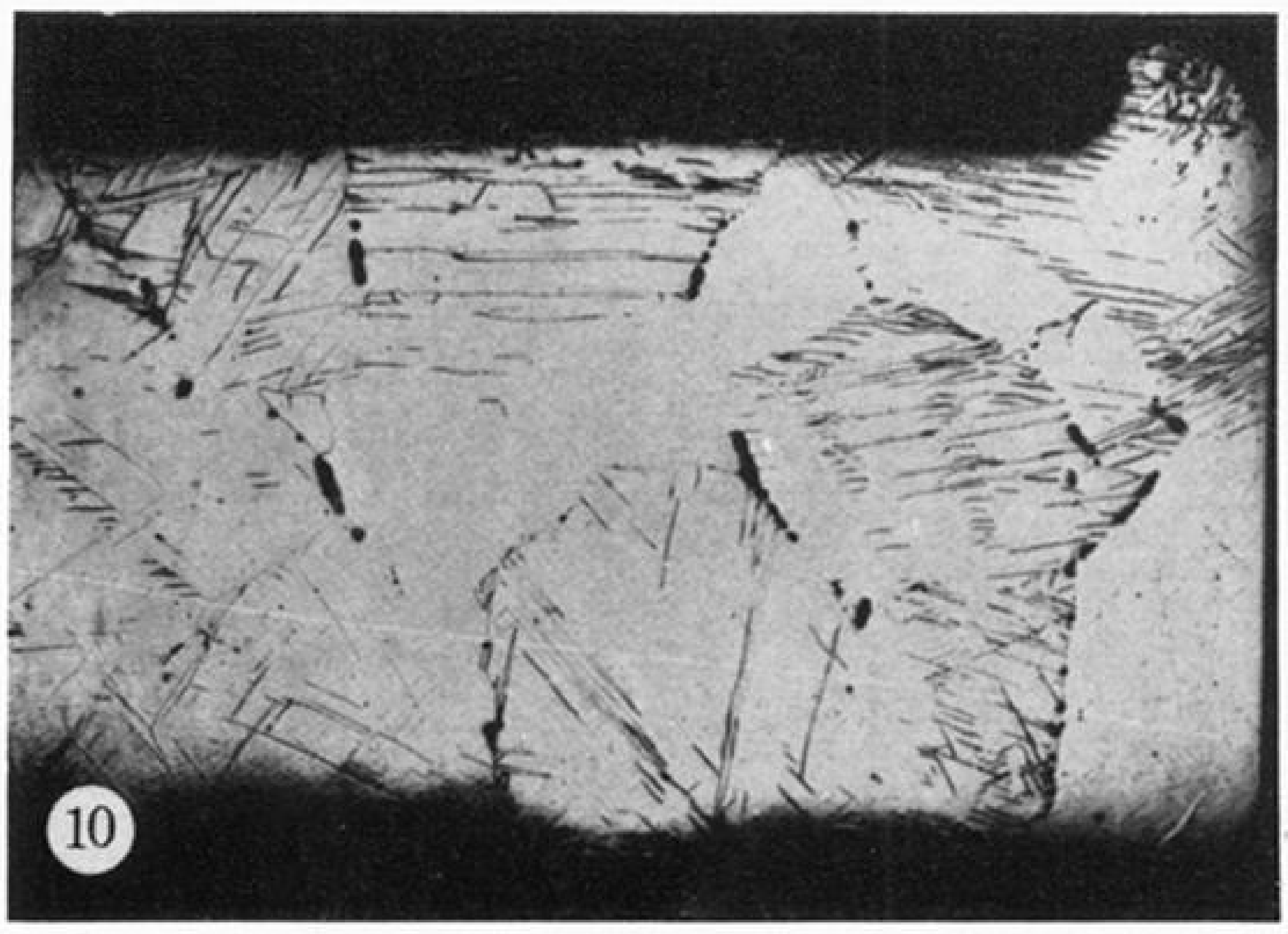












FIGURES 1, 5*a*–*d*, 6*a*, *b*, 7, 8 and 10. For description see opposite.