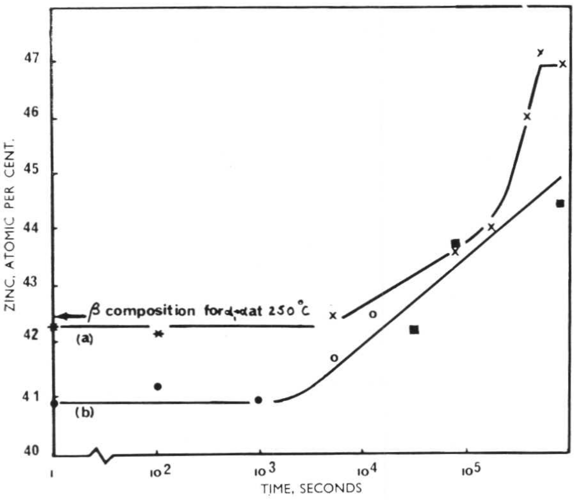

Fig. 2 *Results of electron-probe microanalysis indicating the variation of Zn content in the* β *matrix with reaction time at* 250° *C for:* (a) 42·3% *Zn alloy. The table below Fig.* 2 *gives specific values for* α_1 *and* α *in different forms, Phases observed:* ✱ β, X $\alpha_1 + \alpha + \beta$. (b) 40·9% *Zn alloy.*[4] *The* $\alpha_1 \rightarrow \alpha$ *transition temperature* (B_s) *is indicated. Phases observed:* ● β; O $\alpha_1 + \beta$; ■ $\alpha_1 + \alpha + \beta$. *Each point represents the mean of nine counts.*

48 h at 250° C	Product	Copper, %	Zinc, %
Combined $\alpha_1 + \alpha$	α_1	65·4	36·8
	α	66·0	35·0
	β	55·5	44·5
Independently nucleated α	α	66·0	35·0
	β	55·5	45·0
Equilibrium α	α	65·5	34·5
	β	52·7	47·3

when $(011)_\beta \parallel (111)_\alpha$, $[\bar{1}\bar{1}1] \parallel [\bar{1}01]$, then both the unfaulted regions of the α_1 and the preferentially nucleated α have a Kurdjumov–Sachs orientation relationship with the matrix. The α contains no specific substructure, only a random dislocation configuration.

Electron-probe microanalysis was carried out to follow the variation of β matrix composition with increasing reaction time when $\alpha_1 + \alpha$ forms. The table below Fig. 2 gives the concentrations of Cu and Zn associated with α that has grown from pre-existing α_1, as in Fig. 1(*a*) at X, the specific matrix composition of independently nucleated α, and equilibrium values. The variation of Zn concentration in the matrix with increasing reaction time is shown by curve (*a*) for a 42·3% Zn alloy at 250° C but this is too close to the $\alpha_1 \rightarrow \alpha$ transition temperature (B_s)[4] to quantitatively assess the onset of α precipitation. Such an assessment is possible for a 40·9% Zn alloy reacted at 250° C (curve (*b*)).

Specimens partially transformed to α_1 and subsequently reacted at a higher temperature where α only forms (Fig. 3), produce structures similar to those encountered after direct isothermal treatment just below the B_s temperature.

Rods of near-equilibrium composition nucleate at and grow from two distinct sites when formed from metastable β that contains some α_1: at the leading edges of the original α_1 growing along $\langle 111 \rangle_\beta$ habit directions (Figs. 1 and 3) and subsequently in the β adjacent to the α_1. The present results show this to be independent of the manner in which the reaction is carried out. Investigations concerning the nature and mode of formation of assemblages of products that have different shapes are limited mainly to Widmanstätten structures formed during the decomposition of austenite in steels[8,9] and this has led to the term "sympathetic nucleation". Since the supersaturation of the matrix in the vicinity of the first-formed precipitate should be quite small and nucleation rate decreases exponentially as supersaturation decreases, preferential nucleation at such a boundary should not be favoured. Heterogeneous-nucleation theory[9] has been used to indicate possible reasons for pre-existing crystals acting as preferred nucleation sites.

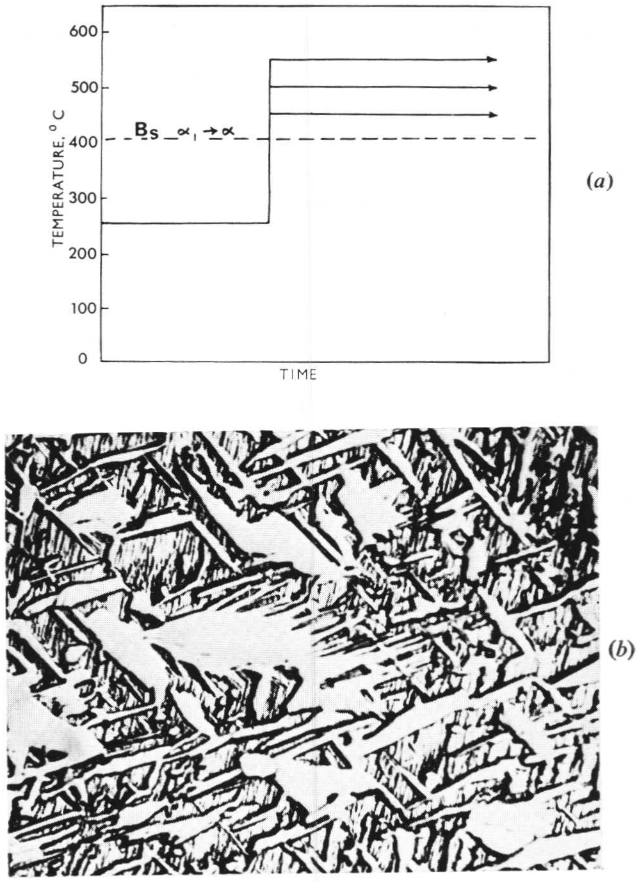

Fig. 3(a) *Schematic representation of the interrupted heat-treatment cycle. The micrograph* (b) *shows the growth of* α *rods from pre-existing* α_1 *plates for a* 40·9% *Zn alloy reacted at* 250° *C for* 100 *min and then at* 500° *C for* 10 *min. The original* α_1 *plate pair has been sectioned across the angle profile* $\{110\}_\beta$. *Etched with alcohol ferric chloride.* × 600.

Classical nucleation theory considers volume (ΔF_v), strain (ΔF_E), and surface (ΔF_s) free energies, i.e.

$$\Delta F = \Delta F_v + \Delta F_E + \Delta F_s$$

where ΔF_v is negative, and ΔF_E and ΔF_s are positive if the matrix is metastable with respect to the precipitate. A grain boundary is a favoured site since ΔF_s and ΔF_E are reduced, thereby decreasing ΔF. Similar arguments apply for second-phase crystal boundaries but in view of the present experimental evidence we wish to discuss nucleation at an α_1/β interface in terms of the crystallography and composition changes involved.

Original plates once nucleated grow rapidly in the lengthwise direction by a bainitic mechanism[1–5] with an attendant redistribution of solute atoms (Fig. 2). Growth of these faulted f.c.c. plates continues until either the solute concentration in the matrix ahead of the plate increases sufficiently for the $\alpha_1 \rightarrow \alpha$ transition temperature (B_s), which decreases with increasing Zn content,[4] to be exceeded, or the temperature is raised to a value in excess of B_s. The cessation of α_1 growth and the formation of α on upquenching confirms a limiting temperature for α_1 formation[4,5] and the importance of the α_1 as pre-existing sites for nucleation and growth. The microprobe value for the $\alpha_1 \rightarrow \alpha$ transition of 42·7% Zn for the 40·9% Zn alloy (Fig. 2), compares favourably with the critical value of 42·5% Zn at 250° C obtained from the earlier data.[4] Under these conditions the free energy of the system can be further reduced only by transformation to α. Increasing reaction time or temperature causes stacking faults within the original α_1 to annihilate non-uniformly leaving regions as much as 1 μm wide of almost perfect f.c.c. lattice (Fig. 1(*b*)). Considering the edge of the α_1, when the critical concentration is attained, the Zn content of the β further away will be slightly less than that adjacent to the α_1, giving a smaller chemical driving force for precipitation near the α. Only if nucleation rate has a greater dependence on interfacial energy than on supersaturation would the α_1/β interface favour nucleation. The specific interfacial free energy of a parent/product boundary and between a nucleus and precipitate against which it nucleates is orientation-dependent.[9] Since the unfaulted regions in the α_1 are not only f.c.c. in structure, but also have a K–S orientation relationship with the matrix, such regions provide ideal nucleation sites for α which grows with an inherited orientation and a near-equilibrium composition. From the table below Fig. 2, the measurements show that the α_1 from which the α grows has a higher Zn content which may constitute evidence of segregation of Zn atoms to the remaining stacking faults.[3,4] Rods develop two planar facets parallel with $\{110\}_\beta$,[4] (Fig. 1) along which the stacking faults lie and such low-energy interfaces[2] also favour growth.

The $\alpha_1 \rightarrow \alpha$ transition in the Cu–Zn system indicates the importance of crystallographic factors coupled with necessary composition requirements arising from the growth model[1–5] when a pre-existing precipitate acts as a nucleation site for a second precipitate.

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Research Note

The Nucleation of Graphite at an Austenite/Cementite Interface

N. Swindells and J. Burke

The decomposition of metastable cementite to graphite in white cast irons is a process of nucleation and growth.[1] The graphite nucleates mainly at the interface between the primary austenite and the eutectic cementite. The nucleation is obviously heterogeneous and will be strongly influenced by conditions at the interface. Tu and Turnbull[2] have described the importance of the relationships between the new phase and the matrix so that a semi-coherent interface develops with a corresponding reduction in the interfacial energy. Speich[3] showed that such a relationship is observed when the surface of supersaturated austenite was graphitized. The graphite formed most often with its basal plane parallel to the $\{111\}$ planes of the austenite. The mismatch here is $\sim 4\%$.

The present authors have estimated elsewhere[4] the energy required to form a graphite nucleus on the assumption that the nucleus was in the form of a disc oriented with the basal plane parallel to the interface. The metallographic evidence for this orientation was obtained by Hultgren and Östberg.[5] The authors used an equation for ΔG similar in form to equation (2) of the paper by Tu and Turnbull,[2] and the corresponding critical value for ΔG was then

$$\Delta G^* = \frac{4\pi\gamma_p^2\Sigma\gamma_{ij}}{\Delta G_v^2}$$

where γ_p is the specific interfacial energy for the interface between austenite and a prismatic plane of graphite and the γ_{ij} are the specific energies for the other interfaces present. When values of γ were estimated on the basis that all the interfaces were coherent, an activation energy for nucleation could be calculated which was satisfyingly close to the experimental values of $\sim$ 60 kcal/mole. The prediction was therefore that basal graphite planes were parallel to $\{111\}$ austenite planes at the interface.

The predicted relationship has now been checked on an optical metallographic scale by using a back-reflection Kossel microdiffraction technique to determine the orientation of the austenite phase forming part of the nucleating interface. The pole of the interface was then related to this orientation by a sectioning technique. The theory and experimental methods have been described by Bevis and Swindells.[6,7] The

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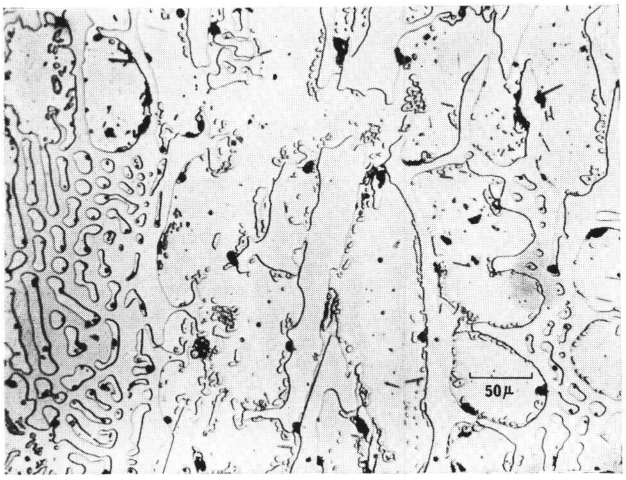

Fig. 1 *Fe–C–Si–Mn alloy graphitized at* 900° *C for* 2½ *h.*

alloy was basically Fe–3·4% C–1·8% Si with the austenite phase stabilized at room temperature by the addition of 10% Mn. Large phases with " smooth " boundaries were obtained by superheating the melt in an argon atmosphere and cooling very slowly. Graphitization to the extent shown in Fig. 1 was achieved in 2½ h at 900° C.

The results from measurements made on 25 sites from 4 areas containing a total of 70 sites are shown in Fig. 2. An X^2 test showed that the distribution is not random but neither is it grouped about {111} poles of the austenite crystals. Instead, for 75% of the cases, the pole of the interface is within 10° of the {110} poles of the austenite. The selection of these 25 sites was determined by the need to obtain as clear an indication of the interface trace as possible. The precipitates were either single or multiple nodules but there appeared to be no distinction between them in the crystallographic results.

The scale of these observations is important. It is on a far greater scale than the actual nucleation event and there is no indication of the shape of the original interface at the precipitate site. If the experimentally determined poles do describe the interface at the nucleation site, however, then the predominant result does not indicate any reasonable relationship between the austenite and the graphite, assuming that the basal plane of graphite is parallel to the interface. In this situation the assumption that all the interfaces are incoherent leads to an activation energy of a thousand times the experimental value.

The crystallographic results require an explanation based on concepts that fit the scale of the observations. A possible explanation could therefore be based on the coincident-site model for interfaces developed by Brandon[8] and confirmed experimentally by Morgan and Ralph.[9] Morgan and Ralph observed that a macroscopically curved boundary will show good fit on a microscopic scale if it exists on a series of the more densely packed planes of a coincident lattice. If the boundaries between austenite and cementite do show regions of good fit, these will be of low energy and there will not be very much segregation of carbon atoms to these areas. Rather, the carbon atoms will segregate to the regions of bad fit. Thus, nucleation is presumed to occur at a particular site on an austenite/cementite interface because of the greater probability of carbon atoms being present there and not because of a relationship between the precipitate and the original phases.

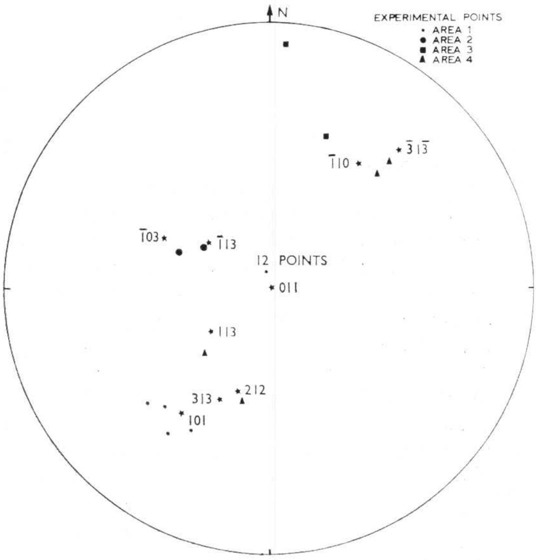

Fig. 2 *Interface poles on* 011 *standard projection.*

This explanation requires proof in the form of the orientation relationship between the austenite and the cementite at the nucleation site. This is more difficult to measure than the austenite case, but is now being done. Meanwhile, there are a few observations that provide some encouragement for these concepts. Sleeswyk[10] has shown that the austenite and cementite lattices can be related to each other and hence a coincidence-site lattice may exist. However, it would be easier to check any experimental relationships on this basis rather than to derive it theoretically. If the concept of segregation to areas of bad fit is a valid one, then there should be relatively clean areas of boundary which might show greater mobility, and such regions are observed. Further, metallographic and electron-probe microanalysis studies[7] suggest that the boundary in the vicinity of a graphite nodule is relatively immobile.

Acknowledgement

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Discussion

Dr. H. I. Aaronson (Ford Motor Co., Dearborn, U.S.A.): If the crystal structure of the precipitate is different from that of the matrix, perhaps the equations in the paper by Lorimer and Nicholson ought to be slightly rewritten. The G.P. zone then will not really be a nucleus, because it is the wrong crystal structure, but it will be a region of different solute concentration and therefore supplying a higher volume free-energy change.

Also, because of differences in the surface energy there will be a chemical interfacial free-energy change at the interface. Then the nucleus of critical size will have to form within this environment, i.e., the particular size of the G.P. zone. It will not be a critical nucleus size in the sense of normal nucleation theory, but it will simply reflect the amount of assistance that is provided to the nucleation process.

Professor J. W. Cahn (Massachusetts Institute of Technology, Cambridge, U.S.A.): I would like to disagree with my distinguished colleague. A prior precipitation process will always *lower* the volume free-energy change for the formation of a subsequent precipitate, if the composition changes from the matrix are in the same direction for both precipitates. This is readily shown by means of the free-energy/composition curves in Fig. D.II.1. PR is the free-energy change per mole to form a small amount of β from α at concentration C_0. After the G.P. zone has formed this is reduced to QR. Remember that the G.P. zones formed because they reduced the free energy of the system.

Of course new mechanisms become available for the formation of β from the G.P. zones. For instance, a diffusionless transformation is allowed in the case depicted by Fig. D.II.1 and we have an interface and strain field that did not exist before.

There are, however, some interesting cases in which a prior reaction increases the free-energy change for a subsequent reaction. This occurs, for example, when the composition of the prior precipitate is on the opposite side from the second precipitate. Another instance can occur when the matrix reacts martensitically or massively to form a phase with a lower free energy but whose free-energy tangent slopes upward.

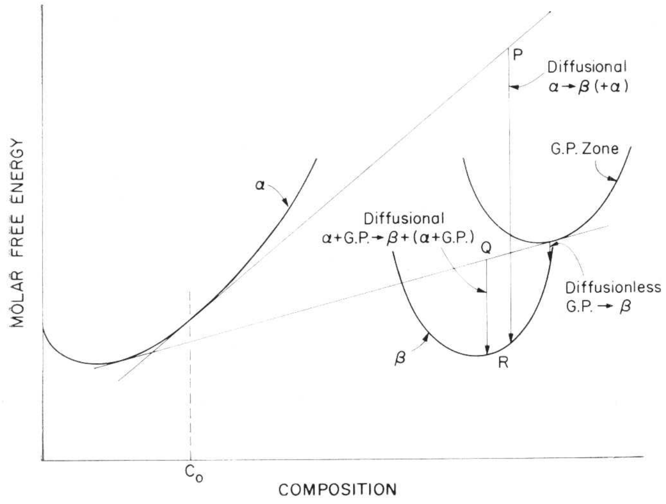

Fig. D.II.1 Schematic free-energy diagrams to illustrate that in an alloy of composition C_0 *the volume free-energy decrease on forming a small amount of* β *by diffusion is reduced from PR to QR by the formation of a G.P. zone. For the diffusionless formation of* β *from the zone it is even less than QR.* (Cahn.)

Professor J. W. Christian (University of Oxford): I agree with what Professor Cahn has just said, but I am very worried about the application of equation (4) of Lorimer and Nicholson's paper to what amounts to a set of subsystems that are supposed to be G.P. zones, each of which is of the order of the critical nucleus size for the subsequent formation of the β phase.

Equation (4) is based on the assumption that one sets up something like a quasi-steady-state distribution of potential β nuclei of various sizes, and this must break down if the whole system that is being considered is only of the order of the critical nucleus size.

Professor R. B. Nicholson (University of Manchester): I agree that equation (4) is probably very far from rigorous, and I also agree that it may not be possible to do what we have tried to do; that is, to try and apply classical nucleation theory to a very non-classical system. Taking your point and also the one that Dr. Aaronson raised earlier, I think it might be better for us to analyse the situation in terms of heterogeneous nucleation of the β phase at the G.P. zone/matrix interface.

Dr. F. G. Wilson (British Steel Corporation, Rotherham): Referring to Figs. 3 and 6 of the paper by Lorimer and Nicholson, it is indicated that the maximum frequency of nucleation occurs at the temperature $T_{G.P.}$. Would you not anticipate any change in nucleation rate at the spinodal temperature?

Dr. G. W. Lorimer (University of Manchester): In all the work we have done we have analysed the results on the basis of nucleation and growth. The spinodal may be there, but things behave as if it is simply nucleation and growth.

Professor Nicholson: Following the discussion in Session I, it is very likely that in these systems the G.P. zone solvus, i.e. the coherent solvus, and the spinodal are very close together, and we have not in effect distinguished between them. As our paper states, it is not really vital to the model whether G.P. zone formation occurs by very easy nucleation and growth or whether it occurs by spinodal decomposition.

Professor H. Kimura (Tohoku University, Japan): Do the quenched-in vacancies act as nucleating sites?

Dr. Lorimer: All the results referred to in our paper can be explained by invoking the effect of excess vacancies on the kinetics of growth of the G.P. zones only. It is possible that the vacancies play a thermodynamic role as well, e.g., by being an integral part of the zones. I should like to ask Mr. Jacobs a question. In his paper the temperature T_c is identified as " the temperature above which homogeneous self-nucleation of clusters does not occur ". Does he not think that it is very remarkable that this critical temperature just happens to coincide with or be slightly below a metastable solvus line in all the systems where it has been established?

Mr. M. H. Jacobs (Tube Investments Research Laboratories, Cambridge): The answer to this question depends upon the interpretation of experiments designed to determine the metastable solvus line. As discussed in our paper, the measurements of the critical temperature require step-quenching directly to the ageing temperature, whereas the so-called " metastable solvus line " has been identified in many systems with the reversion curve. As I have tried to point out, we feel that in the case of Al–Mg–Si (and also Al–Zn) there is a significant temperature difference between the critical temperature T_c (or T_c', which is equivalent to the G.P. zone solvus temperature) and the reversion temperature. Also, we find that in Al–Zn the minimum reversion temperature observed experimentally is dependent upon the thermal history of the sample.

Dr. LORIMER: But this effect can be explained simply in terms of undercooling. T_c may be 10, 20, or 30 degC below the metastable G.P. zone solvus. Could there not be sufficient undercooling to account for that?

Mr. JACOBS: The important difference between the two types of experiment (the direct-quench experiment and the two-step ageing treatment) is that we are dealing with a nucleation problem in the case of direct quenching, whereas in the case of the two-step ageing treatment one has overcome the nucleation problem by actually nucleating G.P. zones at the lower temperature. Therefore, in trying to understand their dissolution, we feel that you have now to take into account the remaining solute concentration in the matrix and its effect on the stability of these zones already nucleated. So in one case you are dealing with a nucleation problem and in the other case with a stability problem.

Dr. WILSON: I am not really clear about the difference between the thermodynamic and kinetic models. If I may quote from the second paragraph of the paper by Jacobs and Pashley: " According to the thermodynamic model, G.P. zones fail to nucleate above a certain temperature, which is determined directly by the metastable G.P. zone solvus. According to the kinetic model, self-nucleation of precipitates does not occur above a certain critical temperature T_c because of inadequate solute supersaturation. " Surely the G.P. zone solvus temperature is also determined by the solute supersaturation? Are you not saying the same thing here in two different ways?

Mr. JACOBS: What we are trying to do is to emphasize the role played by vacancies in the nucleation process.

Dr. WILSON: I do not think anyone would disagree that the nucleation temperature of the zones is affected by the vacancy concentration.

Mr. JACOBS: We are happy if you accept this.

Dr. WILSON: I think everybody will.

Professor KIMURA: I should like to ask Dr. Sen if the binding energy between a silver atom and a vacancy is really greater than between the other atoms and a vacancy?

Dr. N. SEN (Imperial College, London): No, this is an important point; the binding energy of Ag with vacancies is lower than for Mg or Cu. Hence it appears that in the silver-bearing alloy a cluster of solute atoms and vacancies forms.

Professor KIMURA: My comment is that the binding energy between vacancies and a solute atom comes partly from elastic distortion, but there is also an electronic contribution. So when copper and magnesium combine, the elastic energy may be released but the vacancy is not necessarily freed.

Dr. SEN: The concentration of vacancies precipitated in quenched and slightly aged Al–Cu–Mg has been estimated as $\sim 10^{-4}$ (volume fraction) which agrees reasonably with that for pure aluminium. This is consistent with vacancies being largely retained; although there is no direct evidence of subsequent vacancy release.

Mr. R. N. WILSON (Royal Aircraft Establishment, Farnborough): Have you found any treatment, e.g. direct quenching, that would give loops in the silver-bearing alloy similar to those in the silver-free alloy?

Dr. SEN: We have not carried out any direct-quenching treatment.

Professor CHRISTIAN: I am a little bit bothered about the suggestion both in the paper by Lorimer and Nicholson and that by Jacobs and Pashley, that what happens in a two-stage ageing treatment is that G.P. zones are formed at the lower temperature and transform into precipitates at the higher temperature. I wonder what evidence exists that the thing that transforms into a precipitate visible at the higher temperature is not already a precipitate, formed at the lower temperature. The reason I wonder about this is the statement by Lorimer and Nicholson that the rate of formation of the precipitate at the lower temperature will be slow essentially because of the effect of the parameter Q_m' in equation (4), whereas at a higher temperature it will be more rapid.

If you look at equations (3) and (4), Q_m and Q_m' are about the same, and I think you would agree that K_2 is about the same as K_3. Equation (4) may be wrong, but let us not make that assumption for the moment! Then there is not much difference between the nucleation rates of G.P. zones and of β. So if we nucleate G.P. zones in a reasonable time, we can nucleate β in a reasonable time.

Mr. JACOBS: In our model we do not necessarily require that the G.P. zones should change their structure when the alloy is up-quenched. We are more concerned with the stability of the zones. We do not directly consider whether the zones change their structure or not; normally we assume that they do not.

Dr. D. W. PASHLEY (Tube Investments Research Laboratories, Cambridge) (*written discussion*): Some of the comments made on our model by Lorimer and Nicholson in their paper have already been dealt with in our own contribution. Thus, we have stated exactly the same relationship between T_c, T_c', and $T_{\mathrm{G.P.}}$, and we have also noted that both models involve a combination of thermodynamic and kinetic factors. Their explanation of the effect of quenching rate on the determination of $T_{\mathrm{G.P.}}$, involving consideration of the role of undercooling in leading to an observed value $T_{\mathrm{G.P.}}'$, is completely equivalent to the explanation given earlier by us (see Ref. 4 of our paper). The difference is really no more than one of terminology, when the agreed equivalence between T_c and $T_{\mathrm{G.P.}}'$ and between T_c' and $T_{\mathrm{G.P.}}$ is taken into account. In both cases, the effect is a purely kinetic one involving the influence of vacancies on the rate at which solute atoms can arrive at a sub-critical nucleus.

It is not valid to argue that the Lorimer and Nicholson model is to be preferred because the critical temperature for nucleation of G.P. zones, for direct quenching to the ageing temperature, agrees closely with the known values of $T_{\mathrm{G.P.}}$. As pointed out in our paper, the value of $T_{\mathrm{G.P.}}$ is normally determined from observations on reversion, or from the direct-quenching experiments themselves. The values of $T_{\mathrm{G.P.}}$ so obtained depend upon the acceptance of the Lorimer and Nicholson model. We are, in effect, putting forward an alternative model for interpreting the measurements of $T_{\mathrm{G.P.}}$, and the fact that $T_{\mathrm{G.P.}}$ and T_c are nearly equal is certainly no unexpected coincidence. It is important to note that, in terms both of our model and the Lorimer and Nicholson model, it is necessary to take more care in interpreting the meaning of reversion experiments.

G.P. zones formed at T_1 do not necessarily start dissolving when the temperature is raised to $T_{G.P.}$. Because of the low number of excess vacancies, the more appropriate temperature is $T_{G.P.}'$, but additionally it is necessary to consider the effect of seeding, which allows the zones to be stable even though the temperature is raised above $T_{G.P.}$, as mentioned in our paper.

Dr. LORIMER and Professor NICHOLSON (*written reply*): We agree with Dr. Pashley that, since a phase equilibrium can equally well be regarded as a balance of the free energies of two phases or as a balance of the rates of forward and backward migration of an interface between the two phases, our two theories are essentially equivalent ways of looking at the same process. Unfortunately, however, we have developed different terminologies. We would suggest that since T_c (or $T_{G.P.}'$) is essentially a nucleation temperature—dependent on thermal history and, to a certain extent, on technique—T_c is the most appropriate terminology (a similar parameter is often used in the solidification literature). The temperature $T_{G.P.}$ (or T_c') is a point on Cahn's coherent solvus* and is thus a fundamental temperature in the system, like the solidus or equilibrium solvus temperature, but relating to the coherent phase G.P. zones. $T_{G.P.}$ is therefore the most appropriate term.

T_c is measured by nucleation experiments, whereas $T_{G.P.}$ is best measured by dissolution experiments while bearing in mind the precautions detailed above by Dr. Pashley.

Dr. P. WILKES (University of Manchester): I would like to make one additional point concerning the paper by Lorimer and Nicholson and that is that a similar effect is found in Al–Si, and yet in this alloy Rosenbaum and Turnbull† looked for zones and failed to find them. This was not just by electron microscopy but also by resistivity measurements, which should pick up any zones that form at a very early stage. It is a little disturbing to have to assume that the zones are there to cause the nucleation when there is no independent evidence for zones.

Dr. LORIMER (*written discussion*): In reply to Dr. Wilkes's remark I will refer to the paper by Rosenbaum and Turnbull.† They pointed out that if one Si atom in 10^3 was in a G.P. zone then there would be $\sim 10^{15}$ G.P. zones/cm^3, each containing 10^3 atoms. It is possible that Si-rich G.P. zones containing $< 10^3$ atoms are of sufficient size to act as precipitate nuclei, and that these G.P. zones have not been detected, even by electrical-resistivity measurements.

Professor J. NUTTING (University of Leeds): I wonder if we could resolve some of these arguments by asking Professor Nicholson to comment on how he sees this transition from G.P. zones to a precipitate. Say that we take the case of Al–Cu with G.P. zones transforming to θ''. The manner in which we imagine this taking place must surely influence all the arguments here. Professor Nicholson previously outlined two possibilities, but I think we must try to be specific on this issue.

Dr. LORIMER: Can I make one comment first in answer to Professor Christian's question as to what is the evidence that we have only zones and not the precipitate itself at the lower temperature? This is based not on our work but on previous work by X-ray diffraction. Even after much longer periods than we are dealing with, the X-ray diffraction results give no evidence of anything but zones being present.

Professor NICHOLSON: Dealing with Professor Christian's point first, on the kinetics of the process, I think the important figures are actually hidden in the parameters K_2 and K_3, which are not in fact constant. When the material is immediately quenched and G.P. zone formation is taking place, we know that we have a large excess of vacancies and K_2 is large. Therefore, there is a very rapid rate of zone formation. The excess vacancies are present only for a relatively short time, and one takes advantage of this in forming the G.P. zones in the manner predicted by equation (3). There is no such advantage built into K_3 to aid the transformation process. I think this is well illustrated by the two-stage ageing treatment. One generally finds a very much larger effect with variations over short times at the low temperatures than one does over long times, i.e., the effect saturates after a relatively short time at low temperatures. Thus, one takes advantage of the excess vacancies for zone formation but not for transformation, although I suppose if you had a very rapid quench and a very rapid up-quench then one might do so.

Professor CHRISTIAN: This must require that the vacancy lifetime is about the time of nucleation of the G.P. zones and not about twice this time. It seems to me a bit of a coincidence. I am talking about nucleating β entirely at the lower temperature.

Professor NICHOLSON: I do not think that is quite true because, in the model which we use, one has not only to nucleate zones but grow them to a certain size before one can use equation (4).

On the point that Professor Nutting raised, I shall try to transfer this question to Professor Turnbull. I think it is very difficult to understand quite how this transformation takes place, but I find it equally difficult to understand in classical nucleation theory how a transient with the new crystal structure is formed. The embryo of the new crystal structure is formed in the matrix crystal and I do not really understand how classical nucleation theory sees this. I think if I understood that, I might be able to suggest how the G.P. zone → β transformation takes place, because all we are really saying in our model is that we have got the G.P. zone and that this then transforms to the β precipitate in the same way as it does for classical nucleation, except that you do not first have to get together the solute atoms because this has already been done by the G.P. zone formation.

Professor NUTTING: I think the paper by Cook and myself provides an answer to this point. I will accept Professor Nicholson's comment that it is difficult to see how it is done, and essentially on the classical picture you cannot get an answer, or at least I do not believe you can. But if you start introducing some idea of a defect, then there may be an answer to the problem. If you say that there is a problem similar to nucleation on a dislocation and if you move away from the idea that the next stage is really homogeneous, in the sense that the zone formation is homogeneous, then I think you can begin to develop some ideas about it.

Professor CHRISTIAN: It seems to me that a lot of the trouble lies in what Professor Cahn pointed out earlier and what Hardy and Heal‡ pointed out a long time ago. If you imagine the process as taking place in two stages, then the total driving force is divided between these two stages. If you write down the rate equations, the final rate depends on the total driving force, which is independent of the path of the reaction. The individual stages may determine the path by

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* J. W. Cahn, *Acta Met.*, 1962, **10**, 907.

† H. S. Rosenbaum and D. Turnbull, *ibid.*, 1958, **6**, 653.

‡ H. K. Hardy and T. J. Heal, *Progress Metal Physics*, 1954, **5**, 143.

which the reaction occurs, but not the rate at which it occurs. The diagram shown by Cahn was drawn by Hardy and Heal* years ago. They considered the various possible paths of a reaction and came to the conclusion that the overall rate would be the same in each case.

Professor NICHOLSON: This is certainly true if the reaction all takes place at one temperature but the reason for saying that the rate is different is that in classical nucleation theory when you are creating an embryo or nucleus at the precipitation temperature it is possible that it will dissolve, whereas in our case it cannot, because it is being created below the temperature where such a cluster is stable. Subsequently, there is a limited but finite time at the precipitation temperature above $T_{\text{G.P.}}$ where the reaction rate is much faster owing to the presence of these pre-formed nuclei.

Dr. AARONSON: I quite agree with Professor Christian that the driving force is reduced. However, to say that the nucleation rates are the same is forgetting the key point that Professor Turnbull makes in his paper in equation (1), namely, that the logarithm of the rate of nucleation is dependent on the cube of the surface energy but only on the square of the free-energy change. By introducing a G.P. zone you introduce a supply of interfacial energy, and even a little change there can completely outweigh the loss of a fraction of the driving force. So I think that may be the key to it, just introducing a high concentration of compositional imperfections throughout the matrix.

Mr. G. B. BROOK (Fulmer Research Institute, Stoke Poges): I would like to ask Lorimer and Nicholson if they consider that their theory applies to the Al–Cu–Mg system. Here you have a very stable zone structure and, in the end, *S* phase is always heterogeneously nucleated; there is no transformation from a zone structure to the final precipitate.

Dr. LORIMER (*written discussion*): The principles of our theory do apply. The *S* phase is only heterogeneously nucleated because the G.P. zone → *S* transformation does not readily occur; G.P. zones and *S* coexist, as do G.P. zones and γ' in Al–Ag. However, if Si is added to the ternary alloy the G.P. zone → *S* transformation takes place readily and a homogeneous distribution of the *S*-phase precipitate is formed.

Mr. BROOK (*written reply*): Dr. Lorimer implies that Si aids the transformation of ternary G.P. zones to homogeneous *S*. This is contrary to evidence† that Si delays G.P. zone formation and promotes finer and more homogeneously nucleated S'; nor is there any evidence of direct transformation of G.P. zones to S'. Since it is now known that Mg and Si associate in solid solution and can cause homogeneous nucleation of θ' in Al–Cu alloys, it is possible that S' might nucleate directly by a similar mechanism in Al–Cu–Mg alloys containing Si. The slow growth of both S' and θ' in the presence of Mg + Si indicates the close association of these atoms with the matrix/precipitate interface.

Professor M. HILLERT (Royal Institute of Technology, Stockholm, Sweden): I would like to disagree slightly with my distinguished colleague from M.I.T. Professor Cahn has pointed out that to help nucleation of the β phase you should form another new phase that is more solvent-rich than the matrix. This is not the whole truth. We all know that if you want to help the nucleation of carbide from austenite, a very effective method would be to transform the austenite to ferrite. This may be the most effective way you can tilt the balance to get the high driving force for the β phase.

What we are actually talking about, if I understand the paper by Lorimer and Nicholson, is that the formation of G.P. zones can help the nucleation of an interface if you raise the temperature so that the G.P. zones would dissolve. Then I suppose Professor Cahn would agree that the presence of G.P. zones which would like to dissolve means that you have a higher driving free energy for the formation of β than you would have had for a homogeneous solution.

I would like to suggest that what is really most important is that during the dissolution of the G.P. zones there may be something left—some kind of imperfection—which in some way provides a high local supply of driving free energy. So this means that we may have a heterogeneous aid for the nucleation step.

Dr. AARONSON: In a recent paper‡ we estimated that the interfacial energy of the broad faces of θ' plates in Al–Cu is ~ 40 ergs cm^{-3}, and at the edge ~ 80 ergs cm^{-3}, a trifle less than the result obtained by Cook and Nutting! Perhaps part of the discrepancy can be explained as follows. In a study of the thickening kinetics of θ' plates, Laird and I§ found that the thickening rate is significantly less than that allowed by volume-diffusion control, and we have to explain that on the basis of a ledge mechanism. Let us assume for the purposes of discussion that coarsening also takes place by this type of mechanism. This means that the average concentration at the α/θ' boundary would be appreciably higher than the equilibrium figure given by the θ' solvus. So if the concentration is increased by an appreciable factor this would increase γ_F toward Cook and Nutting's value.

As a second point, they might find it better to use the diffusivity data of Murphy,‡ whose results are pretty reliable. I think that these two points might allow them to get somewhat better agreement with reasonable estimates of the interfacial energy.

Dr. J. D. COOK (U.K.A.E.A., Harwell): I was only trying to obtain an order of magnitude: one can only get an order of magnitude with four points!

Dr. F. G. WILSON: In Fig. 1 of the paper by Cook and Nutting there is a drop in strength between the solution-treated condition and the first-determined point. What causes this? Is there a corresponding drop in hardness?

Dr. COOK: Yes. One gets some recovery.

Dr. AARONSON: There is a proposal that I should like to make to those investigators who are concerned with the effect of trace elements upon the kinetics of θ' growth in Al–Cu. Both the lengthening and thickening of θ' plates, which I mentioned earlier, have been investigated in high-purity Al–Cu; equations have been set up for these rates and calculations made which were compared with the interdiffusion coefficient for thickening at the edge of a ledge, and at the edge of the plate using short-circuit diffusion.|| Whether or not you accept the particular interpretations placed upon these growth rates, this seems a logical jumping-off place for a more fundamental investigation of trace-element effects. By comparing growth kinetics in Al–Cu and Al–Cu–X (taking care to make sure that your precipitates are suf-

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* H. K. Hardy and T. J. Heal, *loc. cit.*

† R. N. Wilson, D. M. Moore, and P. J. E. Forsyth, *J. Inst. Metals*, 1967, **95**, 177.

‡ J. B. Murphy, *Acta Met.*, 1961, **9**, 563.

§ H. I. Aaronson and C. Laird, *Trans. Met. Soc. A.I.M.E.*, 1968 **242**, 1437.

|| H. I. Aaronson, J. B. Clark, and C. Laird, *Metal Sci. J.*, 1968, **2**, 155.

ficiently far apart that their diffusion fields do not overlap—otherwise the mathematics becomes horrible) one can then back-calculate interdiffusion coefficients and also look at the question of inter-ledge spacing, &c. The one ancillary measurement needed here is the chemical interdiffusion coefficient in the presence of these trace elements. I would suggest that the interdiffusion coefficient will not be much changed, since the work of Balluffi indicates that the binding energies are quite small. At least with such an approach one would have a chance of isolating in quantitative form the unit processes in operation.

Dr. LORIMER: I would like to make a point on the nucleation of θ'. I have studied θ' nucleation above the θ'' solvus, which is 200° C in Al–4% Cu. θ' is initially nucleated on dislocations. As the ageing time is increased the areas of dislocation-nucleated θ' expand into the matrix, and it appears that one θ' particle sympathetically nucleates another. These areas of θ' growing from the original dislocation-nucleated θ' gradually fill in the whole volume of the material. The same thing happens in Al–4% Cu + cadmium as a trace addition at temperatures above 200° C. In Al–4% Cu, θ' is also sympathetically nucleated below the θ'' solvus. Thus, even when θ'' is present, the θ' is initially nucleated on dislocations and fills the volume of the material by sympathetic nucleation. (*Written discussion*): The nucleation of θ' proceeds in a manner similar to that observed in the autocatalytic nucleation of successive martensite plates.* I suggest that for consistency, the nucleation of θ' which I have described be known as autocatalytic nucleation rather than sympathetic nucleation, as I first proposed.†

Mr. BROOK: This is certainly not true in the Al–Cu–Mg–Ge system, where nucleation occurs more rapidly in the matrix than on dislocations. In fact you do see some dislocation-nucleated θ' in that system but it is very rare. If you cold work 5% before ageing, which would eliminate any effect due to In or Cd, the Al–Cu–Mg–Ge alloy is not affected because nucleation is so rapid in this system. (*Written discussion*): Above 200° C, precipitation of indium is very rapid and specific nucleation of θ' would be limited. We have little information on precipitation of Cd-nucleated θ' in *high-purity* Al–Cu alloys as we found it impossible to prevent volatilization of cadmium during solution-treatment in sections $\frac{1}{2}$ in. thick. I would accept that trace-element nucleation had occurred only if *P* diffractions were detected in X-ray or electron-diffraction patterns. I should be surprised if the diffraction pattern from dislocation-nucleated θ' in Al–Cu–Cd showed any evidence of *P* diffractions.

Dr. LORIMER (*written discussion*): The Al–Cu–Cd alloy to which I referred contained 4·05% Cu and 0·11% Cd after heat-treatment and after the surface layers had been electropolished away. This was nominally the same composition as before heat-treatment.

It is possible that in some ternary systems one must go through the sequence: G.P. zone nucleating θ'', θ'' nucleating θ', whereas in Al–Cu and Al–Cu–Cd the θ'' does not nucleate the θ'.

Mr. BROOK: We do not see any evidence of G.P. zones or θ'' in the Al–Cu–Mg–Ge system.

Professor NUTTING: I think one must visualize some kind of mechanism like the one Dr. Lorimer is suggesting. You have the situation in which the θ' looks as though it is homogeneously nucleated throughout the whole of the grain, i.e., a general Widmanstätten distribution of the θ'. When one says "sympathetic nucleation", what is meant surely is that where some θ' growth centre exists this is throwing off dislocations and it is these dislocations that are acting as the growth mechanism rather than the strain-induced sympathetic type of nucleation.

Dr. LORIMER: I have seen no proof of such a mechanism. I have tried to investigate the nucleation event by hot-stage microscopy, but I have not been successful. There is no evidence of any dislocations being thrown off from the growth centres. The point is that every plate, if you look at it carefully, is connected or immediately adjacent to one other. It is possible that they were a very short distance apart and have coalesced, that they have been nucleated by strain energy, that they have been nucleated at the periphery of the plate, or that dislocations have been thrown out.

Dr. V. A. PHILLIPS (General Electric Research Laboratories, Schenectady, U.S.A.): I would like to make a suggestion. The effect of solutes in forming atmospheres at dislocations is well established, and it would seem to me that there ought to be an analogous effect when you have a G.P. zone with a strain field. It should be possible for segregation of other atoms into the field to occur to relieve the strain. Does Mr. Brook have any comments on this? It is an effect I have looked for but have not so far been able to establish. It would seem likely to be an important one, because it could be envisaged as exerting a considerable influence on the growth of zones.

Mr. BROOK: We have not seen any evidence of this.

Professor NICHOLSON: I would like to ask Mr. Brook a question. I am still bothered by the fact that in all these trace-element studies two effects seem to be observed most of the time. One of these is the slowing down of the G.P. zone reaction and the other is faster nucleation of the θ'. This is strong evidence that the two are related in some way and yet it does not seem to me that any of the mechanisms proposed for the faster nucleation of θ' take the G.P. zone effect into account. Mr. Brook suggested a mechanism whereby the growth rate should change because of a change in diffusivity, but why is the nucleation of the θ' also affected?

Mr. BROOK: In Al–Cu–Mg–Ge alloys, we think that the trace additions associate with a complex assembly of vacancies (which is aided by the relatively high solute concentration, i.e. 0·2% compared to the 0·01% of indium or tin, that would be in solution). Thus, few vacancies are available for copper transport to form G.P. zones. During ageing at elevated temperatures, the Mg + Ge atoms diffuse rapidly to form the embryo structure that nucleates θ' and in so doing release their associated vacancies which then allows rapid transport of Cu to the growing nuclei.

In the case of Al–Cu–Mg–Si alloys, the Mg + Si complexes interact weakly with vacancies so that the normal binary Al–Cu sequence of precipitates is obtained, i.e. G.P. zones followed by θ''. However, the Mg + Si complexes diffuse slowly to form the structure that nucleates θ'. Because of the low available vacancy concentration this takes place more slowly in alloys with Mg + Si, e.g. 16 h compared with 2 h at 165° C with Mg + Ge. Thus, the rate-controlling factor is the diffusion of trace elements to form the nucleating structure.

Professor K. K. RAO (University of Nebraska, U.S.A.): With reference to Professor Nicholson's comment, in the case of Cd as a trace element, its addition to Al–4% Cu

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* J. W. Christian, "The Theory of Transformations in Metals and Alloys", p. 824. **1965:** Oxford, &c. (Pergamon Press).

† G. W. Lorimer, paper presented at "Fourth European Regional Conference on Electron Microscopy" (Rome, 1968).

increases the dislocation-loop density and their distribution is more uniform. Cd has a stabilizing effect on the as-quenched structure and it has been suggested that the increasing rate of θ′ precipitation may be due to both a lowering of interfacial energy and the availability of vacancies for a longer period of time. The reduction in G.P. zone formation on the other hand is considered as due to the trapping of vacancies by Cd, thus reducing the number of vacancies available for the G.P. zone formation.

Dr. D. H. WARRINGTON (University of Sheffield): Does Mr. Brook have any real evidence that the process speeds up at a later stage in the transformation? Very often we use a log time scale, but if we were to use a linear scale then we might get a curve that showed a continuously decreasing rate of transformation.

Mr. BROOK: This is a problem of which one has to be aware. In some cases you get very little change up to 20 or 30 days but then you do get a rapid increase.

Miss J. M. SILCOCK (Central Electricity Research Laboratories, Leatherhead): In the Al–Cu–Cd system θ′ formation is accelerated and the θ′ is modified, i.e. the X-ray *P* reflections are present, whether the alloy is aged at 110° C to give prior G.P. zone formation or aged at 165 and 190° C where no G.P. zones are detected. The size of the copper segregate therefore does not appear to affect the nucleation. If the trace elements are associated with G.P. zones, a different distribution of dislocation loops might be expected when zones are formed. However, it seems that the G.P. zones have no subsequent influence on the effect of cadmium in nucleating θ′. Is this true for Mg + Ge additions?

Mr. BROOK: This is true in all these cases. It appears, although one cannot prove it, that the θ′ is nucleated homogeneously throughout the lattice and the other structures are at this stage redissolved.

Dr. T. R. RAMACHANDRAN and Professor J. BURKE (University of Swansea) (*written discussion*): From the contributions to the Conference (particularly that by Brook and Hatt) and previously published information it appears that trace elements in Al–Cu alloys may be roughly divided into two groups:

(I) Elements such as Ag and Mg, which exert a moderate retarding influence on the rate of G.P. zone formation and have little effect on the formation of θ′.

(II) Elements such as In, Cd, Sn, which markedly retard zone formation and increase the rate of formation of θ′.

The influence of trace elements on the kinetics of zone formation is usually explained on the basis of vacancy trapping and the distinction between Class I and Class II is drawn as between low solute/vacancy binding (Class I) and strong binding (Class II). No completely satisfactory explanation of the dual effect of In, Cd, and Sn in retarding zone formation while accelerating θ′ formation is available. We have recently carried out a detailed investigation of the effects of trace additions of In on vacancy-loop formation and annealing in pure aluminium and the results may throw some light on this problem since θ′ is nucleated on dislocations. Our results may be summarized as follows:

(1) Small amounts of In appreciably retard loop formation compared with pure Al. For example, in an alloy containing 375 ppm In, loops form only after annealing in the range 50–100° C compared with 0–50° C in pure Al.

(2) The loops eventually formed in Al–In alloys are all prismatic in type. In pure Al quenched under identical conditions > 90% of the loops are faulted.

(3) The loops in the alloy are much smaller but have a substantially higher density than in pure Al.

These results are consistent with a high indium/vacancy binding energy* and indicate that vacancies are effectively trapped by indium atoms but that, once they are released from these traps, the rate of nucleation of loops is greatly increased, possibly owing to heterogeneous nucleation by indium atoms.

Prismatic loops are effective nucleation sites for θ′ in Al–Cu. Also the copper/vacancy binding energy is very small and thus we expect that the vacancy behaviour in Al–Cu will resemble that in pure Al. Thus, Class II behaviour may be rationalized on the basis of strong vacancy trapping retarding Cu diffusion (and hence zone formation) and increased nucleation of prismatic loops accelerating θ′ formation.

In the case of Class I the available evidence suggests that the solute/vacancy binding energies are smaller than those for Class II and also that these solutes have little effect on vacancy recovery or on loop formation and annealing.

Mr. BROOK (*written reply*): The contribution by Dr. Ramachandran and Professor Burke is most relevant to the problem of nucleation by trace elements. We have found that there is always an incubation time for nucleation of θ′ which is dependent on the apparent strength of the interaction of the trace element with vacancies (based on the reduction in the rate of G.P. zone formation at low temperatures). This incubation time depends solely on the trace elements and not on the diffusion rate of Cu, as other Cu-containing structures may form independently. This incubation time could be the time required for the formation of loops, though we have failed to find evidence of such defects before nucleation. In one system only, Al–Cu–Mg–Ge, have we found needle-like structures with an X-ray and electron-diffraction pattern similar to zones in Al–Mg–Ge which are immediately followed by a dense distribution of θ′ with *P* diffractions. Any mechanism would also have to account for the detection of the *P* diffractions corresponding to a trace-element substructure at the matrix/precipitate interface which appear slightly before or simultaneously with θ′. On the loop hypothesis, presumably the trace element(s) would precipitate in the dislocation bounding the loop, thus preventing lateral growth of the precipitate, but this would give the wrong orientation relationship for the precipitate.

Mr. A. F. ROWCLIFFE (University of Manchester): If Frank partial precipitation is inhibited by a high vacancy supersaturation, would you not expect Frank partial precipitates to form preferentially near grain boundaries, which is the region that has the lowest vacancy supersaturation after quenching?

Miss SILCOCK: Frank partial precipitation does not start until the dislocation has climbed into the correct orientation, so that at least 3% of the precipitation has occurred before Frank partial precipitation starts. What we are trying to say is that this initial precipitation reduces the excess-vacancy concentration, so that the situation is reversed in that the grain boundary becomes a vacancy source.

Dr. WARRINGTON: I would like to refer to some work of Froes† which seems to be slightly at variance with some of Miss Silcock's observations on matrix dot precipitation. He found that he could, by prior ageing at lower temperatures,

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* F. C. Duckworth and J. Burke, *Phil. Mag.*, 1966, **14**, 473; *Brit. J. Appl. Physics*, 1967, **18**, 1071.

† F. H. Froes, Ph.D. Thesis, Univ. Sheffield, **1967**.

increase the amount of matrix dot precipitation and decrease the precipitate free-zone width by ageing at successively lower temperatures. This may be because there were different metal : carbon ratios in his alloys.

Miss SILCOCK: Yes, we found it rather difficult to age without forming the carbide, and if you have actually formed the carbide at the lower temperature then you do get a difference.

Mr. B. LYNCH (University of Aston in Birmingham): My question to Miss Silcock is concerned with her observation of precipitate-enhanced regions adjacent to grain boundaries. The explanation given in the paper is that the grain boundary acts as a vacancy source during ageing. I should like to ask if she has studied the formation of this zone, and its possible variation in width, with heat-treatment cycles designed to eliminate the excess-vacancy concentration rapidly?

Miss SILCOCK: We have not done very much work on these enhanced zones but in fact we expect the precipitation of carbide to affect the vacancy concentration very quickly in any case. The fact of the grain boundary behaving as a source is important only when there is a precipitate that will remove the excess vacancies.

Dr. F. G. WILSON: Concerning Darbyshire and Barford's dilatometric measurements for the study of alloy carbide precipitation, have they precipitated the cementite first?

Mr. J. M. DARBYSHIRE (Central Electricity Research Laboratories, Leatherhead): Yes.

Dr. WILSON: Presumably this is picked up as a length change. How can you separate this from the alloy carbide precipitation?

Mr. DARBYSHIRE: Both factors are involved in the process. To enable VC to precipitate, the pre-existing cementite must dissolve to provide the necessary carbon.

Dr. WILSON: But your length changes will, in fact, be a composite effect?

Mr. DARBYSHIRE: Yes, indeed. This is illustrated by the good correlation between the composite length change calculated for the transformation:

$$\alpha\text{-Fe(V)} + Fe_3C \rightarrow \alpha\text{-Fe} + VC$$

and the experimentally observed length change corresponding to complete precipitation of VC.

Dr. WARRINGTON: May I ask Mr. Ryan whether his calculations were made for an infinite interface?

Mr. N. E. RYAN (University of Oxford): Yes, for what can be considered a plane-stress condition, i.e., the precipitate is considered to be infinitely thin. In point of fact this is virtually true; the particles are only a couple of atom layers thick, and 2000–5000 Å in dia., so there is a thickness/diameter ratio of the order of 500 : 1.

Dr. AARONSON: Is not interfacial energy as well as volume strain energy of importance?

Mr. RYAN: In establishing coherency across these interfaces and minimal mismatch relationships, we do in fact simultaneously reduce the interfacial energy.

Dr. AARONSON: I do not know if they would be entirely equivalent. I consider that an independent interfacial-energy calculation would be desirable.

Mr. RYAN: I think, if we attempted it, there would be a very low interfacial energy for these particular habit-plane relationships.

Dr. PHILLIPS: I would like to ask Mr. Ryan if he observes much hardening in the molybdenum systems and, if so, whether there is any correlation with strain energy?

Mr. RYAN: These systems show classical precipitation-hardening behaviour, with the usual effect that coherency is maintained up to peak hardness. The only odd thing that we had to rationalize was the differences in habit plane established between apparently similar precipitate phases.

Professor CHRISTIAN: Is it not possible, Dr. Flewitt, that your rods are in fact growth instabilities of the Mullins type on the diffusion-controlled face?

Dr. P. E. J. FLEWITT (University of Sheffield): At low temperatures, when only plates are present, you get fault annihilation and boundaries bowing out. This is a different mechanism, occurring along the plane of interface and not at the leading edge. I think this bowing mechanism is distinct from the nucleation of the rods.

Professor CHRISTIAN: I am suggesting that the rods are not nucleated at all; they are a growth phenomenon.

Dr. AARONSON: Professor Christian raised the point that the rods emanating from the plates might be Mullins-type growth instabilities. I should like to propose the opposite. What Dr. Flewitt has described sounds just like sympathetic nucleation which I reported some years ago* for the austenite → proeutectoid ferrite reaction but with rather less complete experimental evidence. This was an f.c.c. → b.c.c. transformation.

Dr. K. EASTERLING (Imperial College, London): With reference to Dr. Aaronson's remark there is another transformation similar to this: when precipitates of austenite grow by nucleation and growth into rods of ferrite, you get a very large number of dislocations at the interface. In the picture shown by Dr. Flewitt the interface appeared to be dislocation-free. I could not quite follow his point about this; he apparently thinks the rods are simply nucleated from faults in the plate.

Dr. FLEWITT: I agree that you cannot see the stacking faults within the plates very clearly, but previous investigations† have shown that one has a high density of faults within these plates (the α_1 product). With increasing reaction time or increase in temperature, you get annihilation of these stacking faults and large regions that are fault-free. It is these sites that provide the f.c.c. product at a correct orientation for the nucleation of the α rods.

Professor NUTTING: I should like to make some comments on the paper by Murphy, Whiteman, and Woodhead. I am particularly interested in the comment that the early carbide might have a formula of $Fe_{4\cdot6}C$. I think this is a very happy suggestion, because in some of the early work on the tempering of steel using rather primitive techniques,‡ the argument was always that the techniques must be wrong because the volume fraction of the carbide was very much greater than one would estimate using a formula of Fe_3C or $Fe_{2\cdot7}C$. I wonder in fact whether the authors have any other evidence that might suggest this composition. I also do not understand why they use the stoichiometric formula of $Fe_{4\cdot6}C$. Is it in fact a question of actually forming a carbide with a crystal structure that would have a stoichiometric composition of $Fe_{4\cdot6}C$ or is it a case of forming another carbide that is carbon-deficient?

Dr. S. MURPHY (University of Sheffield): We obtained the formula $Fe_{4\cdot6}C$ from the magnetic results. Admittedly there is some doubt about this, as stated in our paper. In the 0·16% C steel, at low tempering temperatures, one

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* H. I. Aaronson and C. Wells, *Trans. Amer. Inst. Min. Met. Eng.*, 1956, **206**, 1216.

† P. E. J. Flewitt and J. M. Towner, *Acta Met.*, 1966, **14**, 1013.

‡ E. D. Hyam and J. Nutting, *J. Iron Steel Inst.*, 1956, **184**, 149.

observes a small increase in magnetic moment that cannot be explained by, say, considering it to be due to retained austenite. If retained austenite were responsible, it would require that in this steel, with an M_f of 300° C one had ~ 1% of retained austenite, which seems unlikely. Furthermore, one finds this same effect not only in the carbon steel but also in Fe–W–C and Fe–Mo–C. Lupton* has tried quenching a series of W steels with and without supercooling in liquid nitrogen, and there was no significant change in this respect. We therefore explain the effect as being due to the decomposition of a carbon-deficient carbide, say $Fe_{(3+x)}C \rightarrow Fe_3C + x\ Fe$. In other words, the excess iron has been thrown out of solution. If one says that at 300° C the cementite has a composition of Fe_3C (which we don't believe anyway) then the ratio of iron to carbon at the start of the tempering process is 4·6. It is emphasized that, if this explanation is correct, this is a minimum value and could well be much higher.

Dr. P. J. GAVIN (University of Cardiff) (*written discussion*): In the literature on tempering considerable confusion exists with regard to the formation of carbides and an attempt has been made to review and clarify this situation.† Two detailed reports have recently been devoted to the transition carbides by well-known authorities,‡ and the structure of χ-carbide has been established.§ All the transition carbides appear to be stabilized by silicon.|| In the magnetic investigation Dunner and Muller claim to distinguish the χ carbide from the strained cementite.¶ The designations, structures, and Curie points of the carbides may be summarized as follows:

Epsilon,	ε (Hofer),	hexagonal,	" Fe_2C ", 380° C
Percarbide,	χ (Hägg),	monoclinic,	Fe_5C_2, 250° C
Cementite,	θ	orthorhombic,	Fe_3C, 210° C

and the temperature ranges of stability for short tempering times† is given as

ε	$T < 200°$ C
χ	$200 < T < 300°$ C
θ	$T < 300°$ C

Thus ε-carbide would not be stable under the present conditions in steels not containing silicon. The interpretation of the 250° C Curie point by Murphy, Whiteman, and Woodhead does not agree with that of Dunner and Muller.¶

Mr. S. MURPHY (*written reply*): As reported in the paper, a first-stage tempering reaction in the high-carbon steel is evident from the magnetic data. This is commonly attributed to the precipitation of ε-carbide. At this stage, electron microscopy showed some evidence for ε-carbide but much more evidence for the existence of cementite. It was concluded that the principal product of the first stage of tempering is cementite (probably modified) rather than ε-carbide.

At the higher temperatures associated with the third stage of tempering, Dunner and Muller claim from their magnetic measurements that χ-carbide exists in substantial quantities. This is simply not confirmed by our electron microscopy, despite a diligent search.

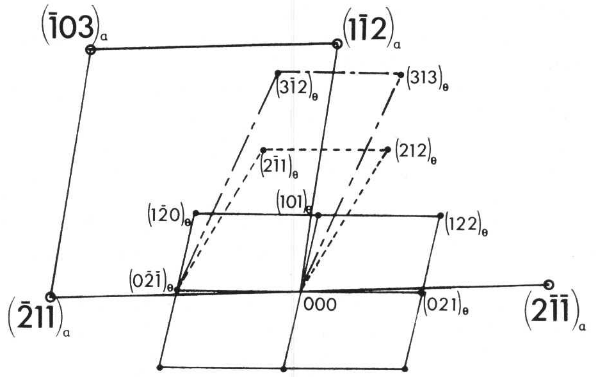

*Fig. D.*II.2 *Proposed modification of indexing of Fig.* 5 *in the paper by Murphy, Whiteman, and Woodhead.* (Kelly.)

Dr. P. M. KELLY (University of Leeds) (*written discussion*): Murphy, Whiteman, and Woodhead discuss two possible modifications of the normal cementite structure in tempered steels. Type-I modification is little different from normal cementite. However, on the basis of only *one* diffraction pattern (Fig. 5) they propose a more dramatic modification of cementite in low-carbon steels. They term this modification Type II and devote some discussion to the possibility of forming this peculiar structure. Unfortunately, their interpretation of the vital diffraction pattern in Fig. 5 is far from convincing. This pattern can in fact be indexed as belonging to a perfectly normal cementite structure, the only complexity being that more than one cementite zone is present. The pattern consists of three cementite zones $[\bar{2}\bar{1}2]_\theta$, $[\bar{5}\bar{3}6]_\theta$, and $[\bar{3}\bar{2}4]_\theta$ (see Fig. D.II.2). Since these zones are between 2 and 7° apart and the spots are somewhat streaked it is quite reasonable for three such zones to appear on the same pattern. The proposed correct indices for Fig. 5 are shown in Fig. D.II.2 and a comparison of the *d* values (as measured from Fig. 5) with those of *normal* cementite is given in Table D.II.1. The agreement between the measured *d* values and those of normal cementite under the proposed correct indexing scheme is well within the usual accuracy of electron diffraction from such a " blurred " pattern (see columns 3, 4, and 5, Table D.II.1), while a comparison of columns 2 and 3 in this table shows how much the normal cementite structure must be " modified " to agree with the Murphy, Whiteman, and Woodhead indexing of Fig. 5. The pattern also fits the Bagaryatsky ferrite/cementite orientation

TABLE D.II.1

M–W–W Indices	*d* Values, Å, for M–W–W Indices (Normal Fe_3C)	Measured *D* Values, Å	Proposed Correct Indices	*d* Values, Å, for Proposed Correct Indices (Normal Fe_3C)
$(020)_\theta$	2·544	2·38	$(021)_\theta$	2·380
$(101)_\theta$	3·757	3·80	$(101)_\theta$	3·757
$(121)_\theta$	2·107	1·89	$(122)_\theta$	1·853
$(1\bar{2}1)_\theta$	2·107	2·20	$(1\bar{2}0)_\theta$	2·218
$(212)_\theta$	1·762	1·76	$(212)_\theta$	1·762
$(2\bar{1}2)_\theta$	1·762	1·92	$(2\bar{1}1)_\theta$	1·976
$(313)_\theta$	1·213	1·22	$(313)_\theta$	1·216
$(313)_\theta$	1·213	1·31	$(3\bar{1}2)_\theta$	1·329

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[*] J. B. Lupton, Ph.D. Thesis, Univ. Sheffield, **1967.**

[†] P. J. Gavin, Ph.D. Thesis, Univ. Liverpool, **1967**: *BISRA Rep.* **(MG/A/202),** 1968.

[‡] L. F. E. Hofer, " The Nature of the Carbides of Iron ", *U.S. Bur. Mines Bull.* **(631),** 1966. E. Schenck *et al.*, " Uber die Existenz Berichte der Eisen Karbide ", *Forsch. Ber. Landes Nordheim-Westfalen* **(1589),** 1966.

[§] K. M. Jack and S. Wild, *Nature,* 1966, **212,** 248.

[||] J. Pomey, *Mém. Sci. Rev. Mét.*, 1958, **55,** 627, 638, 725; 1966, **63,** 509.

[¶] P. M. Dunner and S. Muller, *Acta Met.*, 1965, **13,** 25.

relationship within 1–2°, further confirming that the pattern in Fig. 5 is almost certainly of *normal* cementite and is *not* a seriously modified form of cementite as proposed by Murphy, Whiteman, and Woodhead.

Mr. S. MURPHY (*written reply*): We have re-examined the diffraction pattern of Fig. 5 in the light of Dr. Kelly's written contribution and agree that his indexing is correct. Our suggested structure for the Type-II carbide is thus untenable. The Type-I modifications are of course still valid, but we must acknowledge complete ignorance as to the nature of the intragranular carbide in the untwinned regions of the low-carbon steel.

Dr. T. BROOM (Central Electricity Research Laboratories, Leatherhead): Professor Cahn said earlier that it was very difficult to devise experimental tests for spinodal decomposition. I would very much like to know whether there are any rigorous tests for true homogeneous nucleation. It seems to me that Miss Silcock had difficulty in postulating whether VC precipitation was true homogeneous nucleation or whether it was nucleated by loops. I think Mr. Brook was in some difficulty in persuading us that by adding pinches of this and pinches of that to Al–4% Cu he was getting true homogeneous nucleation. I wonder whether we are *ever* in the classical situation referred to by Professor Turnbull, because we always have to consider the influence of quenched-in vacancies. Hence we have a ternary system and the possibility of quenched-in vacancies producing loops or associating with minor impurities to give something that is not readily amenable to classical nucleation theory.

Professor R. W. K. HONEYCOMBE (University of Cambridge): There seems to be fairly good evidence that matrix precipitation in steels is associated with vacancies, or at least vacancy/solute-atom groupings. The mere fact that if you quench directly to the ageing temperature you get no matrix precipitation, is an indication of this.

Professor CHRISTIAN: It seems to me that one can never eliminate a small cluster of vacancies as a nucleating agent, because, if you carry out the arithmetic, the number of such possible clusters is always larger than the highest nucleation density that has been observed. But, with this single exception, I think one can claim homogeneous nucleation in some cases because as you go up the scale to the next most likely nucleation site, which is a small dislocation loop, it has been shown that the number of precipitates is larger than the number of loops could ever be.

Dr. A. BAR-OR (Israel Atomic Energy Commission, Negev, Israel): I think there is a clear criterion for homogeneous nucleation—it is the pre-exponential term. According to the theory of homogeneous nucleation its value should be 10^{31}. If nucleation is heterogeneous the value would be much lower.

Professor D. TURNBULL (Harvard University, Cambridge, U.S.A.): There is a fair amount of flexibility in that pre-exponential term. One could also be misled by getting a higher value if the phase that nucleated referred to a different solvus temperature from that of the equilibrium precipitate. I think the principal evidence would be copious nucleation on a scale much higher than expected for heterogeneous nucleation. In such cases you could carefully measure the nucleation frequency and I think the time-dependence could give some indication.

Professor CAHN: In Cu–Co you get 10^{18}–10^{19} precipitate particles per cubic centimetre which I think exceeds the vacancy concentration at the ageing temperature.

Professor CHRISTIAN: Is this in slowly cooled specimens?

Professor CAHN: This is in a ¼-in.-dia. rod plunged into molten lead. I would also like to say something about the definition of heterogeneous nucleation in this regard. When vacancies are present and are active in catalysing nucleation, they should really be treated as part of the homogeneous phase. I would like to reserve heterogeneous nucleation for something that is not present as part of a phase but is pre-existing, e.g. a dislocation or a grain boundary—a definite pre-existing heterogeneity. The vacancies could be considered as a component that comes and goes and appears anywhere.

Professor HONEYCOMBE: What about a group of vacancies that could condense to a dislocation loop?

Professor CAHN: I would consider that to be part of a two-stage nucleation process. The first step is the homogeneous nucleation of the loop and the second is heterogeneous nucleation of the precipitate on this loop. It depends on how detailed you want to be. I think if we understand it in that way it does not matter if you cannot distinguish the two steps.

Particle Coarsening

G. W. Greenwood

Particle coarsening results from the higher solubility of small particles, which may tend to dissolve and cause the growth of larger particles. The driving force is provided by the reduction of total interfacial energy. Theoretical analyses of this process are reviewed in the cases where diffusion of the solute between particles is the rate-limiting process and where the rate-determining step is the transfer of material across the particle/matrix interface. Experimental studies mainly support the first case and indicate that, although some parameters may be altered numerically, major changes in the form of analysis are not required even when the particles cause substantial strain in the matrix. The theory further describes the particle-size distribution curve after a long period of growth and predicts a maximum particle radius of one and a half times the mean radius. Experimental results agree only approximately with this and suggest that the maximum particle size may be somewhat greater. The theory has also been developed for the growth of particles on grain boundaries where diffusion takes place only in the boundaries and corresponds to the situation at temperatures well below the melting point. When the particles contain two or more components that are different from the matrix, complications arise in the theory and much further theoretical and experimental work is required in this area. There is experimental indication that particle coarsening can be greatly affected when the matrix is undergoing deformation, recrystallization, or recovery but these situations have not yet been analysed.

Where dispersed particles have some solubility in the matrix in which they are contained, there is a tendency for the smaller particles to dissolve and for the material in them to precipitate on larger particles. The driving force is derived from the consequent reduction in total interfacial energy and ultimately only a single large particle would exist. The problem of deriving a function that describes the rate of change of size of any particle must take into account the relationship between particle solubility and size, the rate-controlling step of material transfer, whether movement across the particle/matrix interface or diffusion through the matrix is involved, and the particle-size distribution in the system. These aspects and the extent to which theoretical approaches can be substantiated by experimental results are reviewed.

Particle Size, Shape, and Solubility

The simplest relationship of particle size and solubility is for a spherical particle of radius r, non-coherent with the matrix, where the interfacial energy γ is independent of orientation. This relationship is often termed the Gibbs–Thomson or Thomson–Freundlich equation and is written

$$\ln (S_r/S) = 2\gamma\Omega/kTr \qquad \ldots (1)$$

where S is the solubility of a particle of infinite radius, S_r is the solubility of a particle of radius r containing atoms of atomic volume Ω, k is Boltzmann's constant, and T is the absolute temperature.[1] Since in practice, $2\gamma\Omega \ll kTr$, it is sufficiently accurate to write $S_r = S[1 + (2\gamma\Omega/kTr)]$ and this form of the equation is used in subsequent analyses.

Equation (1) is readily extended to the case of non-spherical particles, provided they are close to an equilibrium shape. If the latter condition does not hold, the tendency to approach this shape will occur simultaneously with the coarsening process.[2] At the equilibrium shape, the right-hand side of equation (1) becomes $(\Omega/kT)\ \partial(\Sigma A_i\gamma_i)/\partial V$, where V is the precipitate volume and A_i is the area of a face of the precipitate which has interfacial energy γ_i. Evaluation of this expression is simplified by using the Wulff equation γ_i/x_i = a constant, where x_i is the distance of the i^{th} face from the centre of the precipitate[3] and equation (1) thus becomes

$$\ln (S_x/S) = 2\gamma_i\Omega/kTx_i \qquad \ldots (2)$$

Experimental evidence supporting the validity of equations (1) and (2) has been available for a long time[4] and has been obtained principally on salt solutions. Some of the limitations of these equations have also been noted and it is relevant to enquire how far they influence subsequent analyses. The principal assumptions are that the solution is ideal and that the interfacial tension and particle density are independent of particle size. It has been demonstrated that interfacial tension may vary with radius of curvature but the effect is usually insignificant when particles are greater than one micron in radius.[5] Further, since the solutions to be considered are generally dilute, they can be considered ideal to a first approximation.

Estimates of Growth Rate

The driving force for particle growth is derived from the concentration gradients that exist in a system containing particles of different size. The solute concentration round any particle is known from equation (1) or (2). Immediately, however, we need to ask whether atoms can transfer sufficiently quickly across the interface between the particle and matrix for these concentration gradients to be maintained.

Manuscript received 24 April 1968. Professor G. W. Greenwood, B.Sc., Ph.D., D.Met., F.Inst.P., is in the Department of Metallurgy, University of Sheffield.

When diffusion through the matrix is the rate-controlling process, the particle growth is then said to be " diffusion-controlled ". Conversely, when the most difficult step is for an atom to enter solution, the growth is then termed " interface-controlled ". It is next important to decide whether the diffusion gradients change significantly with time or whether they may be regarded as almost time-independent. The latter is generally found to be a reasonable approximation and so Fick's first law is usually considered adequate to describe the diffusion gradients. An additional common assumption is that the solute diffusion coefficient is independent of solute concentration. Since we usually consider dilute solutions, this assumption again would appear adequate.

The behaviour of any individual particle in the system under the condition that solute diffusion through the matrix is the rate-limiting factor is first analysed. This particle may be growing or dissolving, depending on the solute concentration gradient near its surface, and the rate of change of particle radius is derived[6] from the equation

$$4\pi r^2 dr/dt = D 4\pi R^2 dS/dR \qquad \ldots (3)$$

where dS/dR is the concentration gradient across an annulus at a distance R from the particle centre. Rewriting the equation after integration we obtain

$$dr/dt = -D(S_r - S_a)/r \qquad \ldots (4)$$

where S_a is the average solute concentration a long distance from the particle and D is the solute diffusion coefficient. If the rate-controlling step is the passage of material across the particle/matrix interface, then the rate of growth is given instead by the equation

$$dr/dt = -C(S_r - S_a) \qquad \ldots (5)$$

where C is a constant and equation (5) replaces equation (4) when D is very much greater than the product Cr. When D is of the same order of magnitude as Cr, allowance can be made[8] for the simultaneous importance of both time-dependent processes, such that equations (4) and (5) are limiting cases, and the full equation then becomes

$$dr/dt = -CD(S_r - S_a)/(Cr + D) \qquad \ldots (6)$$

We now take into account further conditions which the system may approximately satisfy. When the particle solubility is small, the total number of atoms contained in the particles is constant, independent of particle-size distribution. This may be expressed as

$$\Sigma 4\pi r^2 dr/dt = 0 \qquad \ldots (7)$$

Undue difficulties are not introduced if the particle solubility is not small and the particles not widely spaced.[7] We can now make a substitution for dr/dt from equations (4), (5) or (6) into equation (7). Dealing first with the diffusion-controlled case, equation (4), we obtain

$$\Sigma - 4\pi r_i D(S_{r_i} - S_a) = 0 \qquad \ldots (8)$$

Taking into account equation (1) we now make further substitution for S_{r_i} and obtain the equation

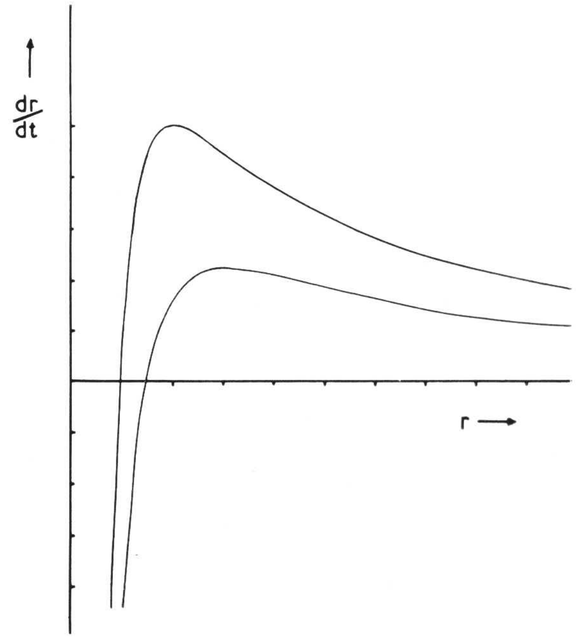

Fig. 1 *The variation of growth rate* dr/dt *with particle radius* r *for diffusion-controlled growth, plotted from equation* (10) *for two values of* r. *The value of* r *for the lower curve is* 1·5 *times that for the upper curve. Particles of radius equal to the mean radius of all particles in the system at any instant are neither growing nor dissolving. Particles of twice this radius are growing at the fastest rate. The smallest particles are dissolving at a rate approximately proportional to* r^{-2}.

$$\Sigma 4\pi r_i D[S_a - S(1 + 2\gamma\Omega/kTr_i)] = 0$$

On rearranging this equation, we can write

$$(S_a - S)\Sigma r_i = \Sigma 2\gamma\Omega S/kT = 2n\gamma\Omega S/kT$$

where n is the total number of particles in the system at any instant and it is noted that the value of $\Sigma r_i/n = \bar{r}$, the arithmetic mean radius of the particles in the system. With this substitution and again using equation (1), it follows that

$$S_a - S_r = (2\gamma\Omega S/kT)\left(\frac{1}{\bar{r}} - \frac{1}{r}\right) \qquad \ldots (9)$$

Combining equations (9) and (4) we derive the increase in radius of any particle, which is thus given by the following equation

$$dr/dt = (2DS\gamma\Omega/kTr)\left(\frac{1}{\bar{r}} - \frac{1}{r}\right) \qquad \ldots (10)$$

The variation of particle growth rate with radius is shown in Fig. 1. Particles of radius equal to the mean radius of the system are instantaneously neither growing nor dissolving. Particles of radius $< \bar{r}$ are dissolving at increasing rates with decreasing values of r. All particles of radius $> \bar{r}$ are growing but the graph shows a maximum value for the growth rate that corresponds to the particle which is twice the mean radius. Over a period of time the number of particles decreases discontinuously when particles dissolve and disappear. It is a consequence of this that the system would ultimately tend to form one large particle. Long before reaching this state, however, the mean particle radius $\bar{r}$ increases as the number of particles decreases and thus the growth rate of the whole system slows down.

Fig. 1 has other interesting features. It is apparent that if all the particles were initially of the same radius there would be no growth in the system. Any slight deviation from this situation, however, leads to instability, since if any particle becomes even slightly greater than its neighbours that particle will continue to grow at their expense. Thus, a particle-size distribution of limited range will become wider in its spread for increasing times. Even from the elementary analysis above, however, it is clear that the spread of particle sizes will be limited. This conclusion is reached because of the sharp maximum in Fig. 1. Although any particle of radius greater than twice the mean value continues to grow, it does so at a rate slower than that for particles which are somewhat smaller. It follows that particles which have a radius much more than twice the mean radius of the system cannot exist in the system. It is thus apparent that there must be some relatively sharp cut-off in the particle-size distribution curve. The above analysis indicates a cut-off at about twice the mean radius. More detailed analyses,[8,9] reviewed later, confirm this general confinement of particle-size distribution though they indicate that particles which are more than 1·5 times the mean particle radius in size cannot continue to exist. The fuller analyses further indicate that the distribution reaches a pseudo-static form.

We next turn to the case where the growth kinetics is determined by interface control and begin by combining equations (5) and (7), from which it is deduced that

$$\Sigma - 4\pi r_i^2 C(S_{r_i} - S_a) = 0 \qquad \ldots (11)$$

Using equation (1) and making further rearrangements

$$(S_a - S)\Sigma r_i^2 = \Sigma(2\gamma\Omega S/kT)r_i$$

so that $S_a - S_r = (2\gamma\Omega S/kT)[(\Sigma r_i/\Sigma r_i^2) - (1/r)]$ and by substituting from equation (5) we obtain:

$$dr/dt = (2C\gamma\Omega S/kT)[(\Sigma r_i/\Sigma r_i^2) - (1/r)] \quad \ldots (12)$$

Equation (12) describes the growth rate of any particle when the kinetics depends on interface control and is analogous to equation (10), which describes the diffusion-controlled case.

The elementary analyses given above describe completely the physical parameters involved in a solution of the problem but they tell us nothing of the effect of spread of particle sizes or of the detailed change of particle distribution with time.

Particle-Size Distributions

A particle-size distribution coefficient, $f(r, t)$, can be defined that corresponds to the number of particles of a given radius r at time t. The total number of particles in the system at any instant is thus given by

$$z = \int_0^\infty f(r,t)dr \qquad \ldots (13)$$

When the particle-size distribution is initially narrow, z is constant. As the size distribution broadens, an increasing number of particles approach zero radius and disappear; thus z decreases with time. Using the following equation[8]

$$\partial f/\partial t = -\partial(f\dot{r})/\partial r \qquad \ldots (14)$$

we can deduce that the rate of change of the total number of particles in the system is given by

$$dz/dt = -d/dt\left[\int_0^\infty f(r,t)dr\right] = \lim_{r \to 0}(f\dot{r}) \qquad \ldots (15)$$

We can further describe the rate of decrease in average solubility as the particle size increases by the equation

$$\frac{dS}{dt} = \int_0^\infty (4\pi r^2/\Omega)(dr/dt)f(r,t)dr \qquad \ldots (16)$$

When particles have low solubility the rate of change of solubility must be small and as a first approximation equation (16) may be equated to zero. On making this approximation, we can derive a value for the average concentration in the system in terms of the solute concentration in contact with a particle of infinite radius. Combining equations (16) and (6), which gives the growth rate for the general case of either interface- or diffusion-controlled growth, we obtain the rate of growth of any particle in the system.

$$\frac{dr}{dt} = \frac{-2\gamma\Omega S}{kTr}\frac{CD}{(Cr + D)}\left[1 - r\left(\frac{\int_0^\infty f(r,t)rdr/(Cr + D)}{\int_0^\infty f(r,t)r^2dr/(Cr + D)}\right)\right] \qquad \ldots (17)$$

Equation (17) gives results that are closely analogous to equation (10) when $Cr \gg D$ and to equation (12) when $Cr \ll D$.

The form of curve derived from equation (17) is not dissimilar from Fig. 1. It leads, only in the diffusion-controlled case and not in the general case, to the simple prediction that the fastest-growing particle is that which has twice the mean radius of the particles in the system. It does indicate, however, that a narrow particle-size distribution will initially spread and that spreading will be restricted since very large particles in the system grow less rapidly than particles that are somewhat smaller. Equation (17) can be used to deduce the rate of change of the particle-size distribution with time and to estimate the time required for the size-distribution profile to reach a pseudo-static value. Further analysis derives from equations (14) and (17) in the form

$$\frac{\partial f(r,t)}{\partial t} = \frac{-2\gamma\Omega S}{kTr^*}\frac{\partial}{\partial r}\left[\frac{CD}{(Cr + D)}(r - r^*)\frac{f(r,t)}{r}\right] \qquad \ldots (18)$$

where r^* is the radius of a particle that is neither growing nor dissolving. To appreciate the implications of equation (18) we can either take an arbitrary initial particle-size distribution function or, more generally, manipulate the equation to show that a quasi-static distribution profile in terms of r/r^* will ultimately be achieved which is independent of time.

Time-Dependence of Particle-Size Distribution

Wagner[8] showed how relatively simple expressions could be obtained from an initial particle-distribution function assumed to take the form of a narrow Gaussian curve:

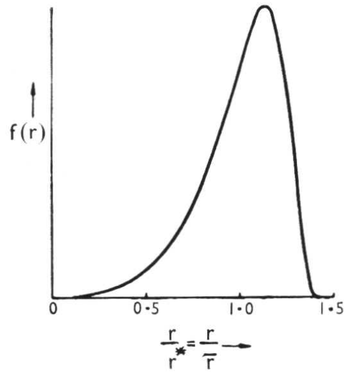

Fig. 2 The form of particle-size distribution f(r) *predicted after long periods of time*[8,9] *under conditions of diffusion-controlled growth, plotted from equation* (21). *The abscissa* r/r* *in this case is identical with* r/r̄.

$$f(r,t=0) = S\exp[-(r-\bar{r}_0)^2/2\varepsilon_0^2\bar{r}_0^2] \quad \ldots (19)$$

where $\bar{r}_0$ is the mean particle radius, $\varepsilon_0\bar{r}_0$ is the standard deviation and, since the distribution is narrow, $\varepsilon_0 \ll 1$. Substituting this value of $f(r, t)$ in the growth equation (18) we obtain

$$\frac{d\varepsilon}{dt} = \frac{2\gamma\Omega S}{\bar{r}_0^2 kT}\,\frac{CD}{(C\bar{r}_0 + D)}\,\varepsilon$$

which has a solution for the value of $\varepsilon(t)$ at any time t given by

$$\varepsilon(t) = \varepsilon_0 \exp(t/\tau)$$

where τ is an effective time constant for the rate of spread of the distribution and is expressed as

$$\tau = \frac{\bar{r}_0^2 kT}{2\gamma\Omega S}\,\frac{(C\bar{r}_0 + D)}{CD} \quad \ldots (20)$$

The distribution is effectively stable unless the time allowed for growth is at least of the same order of magnitude as τ. For diffusion-controlled growth where $C\bar{r}_0 \gg D$, we note that $\tau \propto \bar{r}_0^3$, and for interface-controlled growth where $C\bar{r}_0 \ll D$, then $\tau \propto \bar{r}_0^2$.

There is clearly a limit to the extent of spreading of the distribution in the above form when some particles begin to dissolve. We first consider the case when diffusion transfer is rate-controlling. From equation (10) we deduce that $dr/dt \propto r^{-2}$ for $r \ll \bar{r}$ and it follows that $f(r, t) \propto r^2$ for values of r near zero. Using this latter proportionality, it is convenient to write $f(r, t)$ as the product of a time function $g(t)$ and a particle-radius function $\rho^2 h_1(\rho)$ where $\rho = r/r^*$, so that for $\rho \simeq 0$, $h_1(\rho) = 1$. Now in diffusion-controlled growth from equation (17), r^* equals the mean radius $\bar{r}$ since

$$r^* = \bar{r} = \frac{\int_0^\infty rf(r,t)dr}{\int_0^\infty f(r,t)dr}$$

and so the function $h_1(\rho)$ must satisfy the condition

$$\int_0^\infty \rho^2 h_1(\rho)d\rho = \int_0^\infty \rho^3 h_1(\rho)d\rho$$

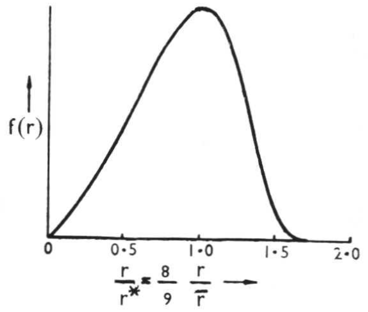

Fig. 3 The form of particle-size distribution f(r) *predicted*[8,9] *after a long period of interface-controlled growth, plotted from equation* (23). *In this case, the abscissa* r/r* *is equal to* 8r/9r̄.

Wagner[8] has shown how this equation can be satisfactorily solved and confirmed the finding of Lifshitz and Slyozov[9] that the solution corresponds to a quasi-stationary form of particle-size distribution, i.e a distribution that retains the same profile when the abscissa is $= r/r^*(t)$. Thus $f(r,t) \propto \rho^2 h_1(\rho)$ and it can be shown that

$$f(r,t) \propto \rho^2[3/(3+\rho)]^{7/3}[1{\cdot}5/(1{\cdot}5-\rho)]^{11/3}\exp[-\rho/(1{\cdot}5-\rho)] \quad \ldots (21)$$

for $\rho \leqslant 1{\cdot}5$ and $f(r, t) = 0$ for $\rho > 1{\cdot}5$. This implies a sharp cut-off in the distribution such that no particles exist at long times that have a radius $> 1{\cdot}5$ times the mean radius of the distribution. The distribution has a maximum at $\rho = 1{\cdot}135$ and the form of the distribution is shown in Fig. 2.

For times that are long compared with τ, an expression is derived for the approximate variation of mean particle radius with time

$$\bar{r}^3 = (8DS\gamma\Omega t/9kT) \quad \ldots (22)$$

for growth under diffusion-controlled conditions. We note that equation (22) is almost identical with the result of integrating equation (10) in the elementary theory and assuming that the mean radius is increasing at half the rate of that of the fastest-growing particles.

The more detailed theory allows further predictions. Since the total volume fraction occupied by the dispersed precipitates is constant, the rate of change of the number of particles with time dz/dt can be calculated. We arrive at an expression $z(t) = z_0/(1 + \alpha t/\tau)$, where α is a constant $\simeq 4/9$. This equation is also similar to the rate of change of the number of particles by colliding,[10] but the latter process is unlikely to be of importance in solid matrices except perhaps when the precipitates are gas bubbles.[11]

The case for interface control can be treated in a way closely analogous to the above. The principal difference arises from the deduction from equation (12) that now $dr/dt \propto 1/r$ for $r \ll \bar{r}$ and so in this case we consider the most useful particle-distribution function to take the form $\rho h_2(\rho)$. Since the particle radius r^* which is now neither growing nor dissolving is given from equation (17) by

$$r^* = \frac{\int_0^\infty r^2 f(r,t)dr}{\int_0^\infty rf(r,t)dr}$$

we again arrive at an equation for $h_2(\rho)$ similar to that derived for $h_1(\rho)$. Further requirements, however, which must be satisfied on the basis of equation (12) lead to the function $h_2(\rho)$ not being identical with $h_1(\rho)$ and a detailed analysis is again necessary. It is found that

$$\rho h_2(\rho) \propto f(r,t) \propto \rho[2/(2-\rho)]^5 \exp[-3\rho/(2-\rho)] \qquad \ldots (23)$$

for $\rho \leqslant 2$ and $f(r,t) = 0$ for $\rho > 2$.

Again we have a cut-off in the particle-size distribution, which now occurs at a particle radius equal to twice that of the particle which is neither growing nor dissolving at that instant. The latter radius r^* can be shown[8] to be equal to $9\,\bar{r}/8$ and the shape of the curve is shown in Fig. 3.

At long times, $t \gg \tau$, the approximate relationship between mean particle radius and time for growth under interface-controlled conditions can be shown to be

$$\bar{r}^2 = (64CS\gamma\Omega t/81kT) \qquad \ldots (24)$$

Thus we have equations that enable growth rates of systems to be assessed when the growth is predominantly by diffusion-control (equation (22)) or by interface control (equation (24)). The expressions relate growth rates to important physical parameters that can often be determined independently. Before turning to a comparison with experimental results in this field we consider the special case where diffusion processes do not take place isotropically through the matrix volume but are confined to grain boundaries.

Growth of Particles Situated on Grain Boundaries

Grain boundaries may play an important role in particle growth, since particles may tend to concentrate on grain boundaries by finding it easier to nucleate there. They may further pin the boundaries to restrict their movement because of the particle/grain boundary binding energy.[12] Especially at relatively low temperatures ($< \sim 0{\cdot}6\ T_m$) and when the mean particle size is small, the grain boundaries are the principal paths for transport between particles. A treatment of this problem has been given for the diffusion-controlled case.[13] It is unlikely that the interface-controlled case would be important in practice, since the majority of solute atoms would be expected to leave the precipitates at areas away from the grain boundary.

It is first necessary to analyse the way in which the grain boundary influences the equilibrium particle shape. Full analysis of this for particles with crystallographic faces, where equation (2) would normally apply, is complicated.[14] The analysis is much simpler for particles that would normally be spherical in shape. When situated on a grain boundary and with the boundary tensions in equilibrium, such a particle takes a form bounded by two symmetrical spherical caps as in Fig. 4, the angle 2θ to their tangents at any point on the line of intersection being given by $\gamma_g = 2\gamma \cos\theta$, where γ_g is the grain-boundary energy per unit area. Developing a similar but somewhat more detailed argument than that behind equation (1), we find that

$$\ln(S_r/S) = (2\gamma - \gamma_g)\Omega/kTy$$

where $2y$ is the thickness as defined in Fig. 4. We note that for $2\gamma < \gamma_g$ the equation does not hold, since the particle then spreads along the boundary and no longer has a discrete form. From the geometry of Fig. 4 we readily deduce that $(2\gamma - \gamma_g)/y = 2\gamma(1 - \cos\theta)/y = 2\gamma/r$, where r is the radius of the spherical caps. Hence we obtain a precisely analogous equation and there is no ambiguity in notation, since r can be taken either as the radius of a cap for a grain-boundary particle or of an entire sphere when the particle is not on a boundary.

The next step in the analysis is to determine the rate of change of particle volume in terms of the simplest geometrical parameters and this can be shown to be

$$\begin{aligned}\frac{dV}{dt} &= \left[\frac{2}{3} - \cos\theta + \frac{1}{3}\cos{}^{3}\theta\right] 6\pi r^2 dr/dt \\ &= \left[\frac{2}{3} - \left(\frac{\gamma_g}{2\gamma}\right) + \frac{1}{3}\left(\frac{\gamma_g}{2\gamma}\right)^3\right] 6\pi r^2 dr/dt \\ &= 6\pi A r^2 dr/dt \qquad \ldots (25)\end{aligned}$$

where A is a constant defined as above for a given system.

Following the earlier treatment for diffusion-controlled particle growth, but now writing the steady-state equation for diffusion entirely confined to the plane of the boundary, we have

$$6\pi A r^2 \frac{dr}{dt} = D_g 2\pi x w dS/dx \qquad \ldots (26)$$

where D_g is the solute diffusion coefficient in the grain boundary, w is the grain-boundary width, and dS/dx the solute concentration gradient at a distance x from the particle centre. Integrating equation (26) we find

$$\frac{dr}{dt} = \frac{D_g w\,(S_{gL} - S_{gr})}{3\,Ar^2 \ln\left(\frac{L}{r}\right)} \qquad \ldots (27)$$

where S_{gr} is the solute concentration in the grain boundary adjacent to the particle surface and S_{gL} the concentration at a distance L away. Since the total volume of all particles is again constant $\Sigma r^2\, dr/dt = 0$ and using this in conjunction with equation (27), then

$$\sum \frac{D_g w}{3A \ln\left(\frac{L}{r_i}\right)} \left[S_{gL} - S_g - \frac{2\gamma\Omega S_g}{kTr_i}\right] = 0 \qquad \ldots (28)$$

where S_g is the solute concentration in the grain boundary near an infinitely large particle. Since usually $L \gg r_i$, $\ln(L/r_i)$ is approximately constant and can be written as B. Its value can be most simply estimated from the relation $B \simeq (\frac{1}{2}) \ln(1/f)$, where f is the fractional area of grain boundary occupied by the particles. Continuing the analysis along the line developed earlier, the rate of growth of a particle of radius r_i is given by

$$\frac{dr_i}{dt} = \frac{2D_g S_g w\gamma\Omega}{3ABkTr_i^2} \left[\frac{\Sigma(1/r_i)}{n} - \frac{1}{r_i}\right] \qquad \ldots (29)$$

Thus, any particle greater than the harmonic mean radius r_m at any instant is growing and particles smaller than this are dissolving. Particles of radius $r = 3r_m/2$ are growing at the fastest rate and the maximum growth of particles over

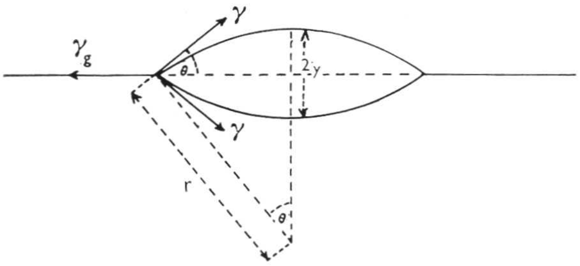

Fig. 4 *The simplest equilibrium shape of precipitate situated on a grain boundary consists of two spherical caps, symmetrically placed, each of radius* r. γ *is the particle/matrix interfacial energy per unit area and* γ_g *is the energy of unit area of grain boundary.*

a period of time t is for those whose radii remain close to this value throughout their growth. A full statistical analysis for the case of growth of particles on a grain boundary has not yet been developed, but one can observe by integration of equation (29) that their growth will follow a law of the form

$$r_f^4 - r_0^4 = \frac{4\,D_g S_g \gamma \Omega w t}{3\,ABkT} \qquad \ldots (30)$$

from initial radius r_0 to final radius r_f of the fastest growing particles. On average the particles will grow at a rate somewhat slower than predicted by equation (30) but generally particle growth is expected to follow an equation of this form and the fourth power of the average particle radius is thus expected to increase approximately linearly with time. This contrasts with the growth of precipitates by diffusion control where the diffusion flux takes place in three dimensions through the matrix. In the latter case the third power of the radius increases linearly with time.

This difference in the time-dependence of the change in average radius is not the only feature that in theory distinguishes the growth of precipitates on grain boundaries from the growth of precipitates within the grain. A major difference is that we are now dealing with grain-boundary diffusion, which is characterized by an activation energy much less than that for diffusion within the matrix. There is consequently a less-strong dependence on temperature for the growth of grain-boundary precipitates and for this reason their preferential growth is likely to be predominant only at relatively low temperatures.

So far we have considered the growth of precipitates in the matrix and that of precipitates on the grain boundaries as being entirely separate processes. This is a convenient separation for theoretical analyses of the respective growth mechanisms, but it may well be less relevant to the modes of growth that can occur in practice. At some intermediate temperatures there is likely to be competition between particles on the grain boundaries and those within the grains. In particular, the shapes of the particles on the grain boundary (Fig. 4) are such that their effective size is governed by the radius of the spherical caps (equation (25)). Thus, a particle of given volume on a grain boundary has a larger driving force for growth when compared with a particle of the same volume within the matrix. Further, there may be a change with time in the relative importance of grain-boundary and matrix-growth processes. Initially, we may expect particles on grain boundaries to grow at a relatively fast rate. Their growth rapidly decreases, however, as the average particle size increases (equation (29)) and at some stage grain-boundary particles will tend to grow primarily at the expense of neighbouring particles situated within the matrix. This situation is likely to be a complicated one to analyse in detail and will depend on the particle sizes, concentration, and grain size. It is conceivable that some systematic fluctuation in neighbouring particle sizes may be developed for particles within the grain. For example, those matrix particles adjacent to grain boundaries may dissolve in favour of the growth of the grain-boundary particles, but the particles in the matrix that are in the second row would initially tend to grow because of the depletion of the particles between them and the grain boundary. Thus, there would be some tendency for alternate rows of particles to grow and dissolve on average, though the amplitude of these fluctuations would be expected to decrease rather rapidly with distance away from the grain boundary. The importance of the processes outlined above has not yet been investigated experimentally. Possibly they are of no great importance because, at temperatures well below the melting point, the particle-growth process is rather slow except when particles are very small and it may be that the average growth rate could generally be too slow to be of real significance except, perhaps, at relatively short times.

It is mentioned again that no case has been worked out for interface-controlled particle growth of grain-boundary particles. The reason for this is not difficult to find, since interface-controlled growth requires a given probability of atoms leaving any area of the particle surface. If atoms leave a particle not along the grain boundary, some diffusion through the lattice to the grain boundary is necessary. This implies that interface-controlled growth is unlikely to have a clearly defined relevance to the growth kinetics of particles on grain boundaries.

Experimental Studies of Particle Growth

The theoretical analyses previously outlined have not all received reliable experimental confirmation and at present firm support seems to have been provided only for the diffusion-controlled growth of particles within the matrix. The first measurements of growth rates followed the conditions specified in the earlier growth theories, namely, that the particles existed in a strain-free medium which was usually a liquid phase. Such experiments had the further advantage that diffusion in the liquid was rather faster and experiments could be done in somewhat shorter periods of time and for particle sizes that were relatively easy to observe.[6]

More recently, attention has been devoted to the coarsening of particles entirely in solid matrices and many such studies have been reported that cover both experimental and theoretical aspects.[15–29] Some measurements have been made of particles contained entirely within thin foils and examined by transmission electron microscopy.[26,27] Such measurements can then be made with considerable precision and it is especially interesting to know whether the theories are adequate to explain growth in the cases where one must also take into account the possible influence of strain fields introduced by the particles and the further possibility that interfacial energies vary with particle size. Recently it has also been shown feasible to obtain accurate quantitative measurements of particles too great to be accommodated entirely within thin foils yet too small to be observed by optical microscopy.[30,31]

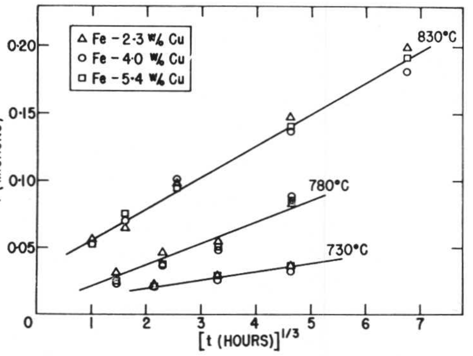

Fig. 5 *The linear variation of* r̄ *and* $t^{1/3}$ *suggests diffusion-controlled growth of copper particles in an iron matrix.*[21] *The growth rate is strongly temperature-dependent and substantially independent of copper content.*

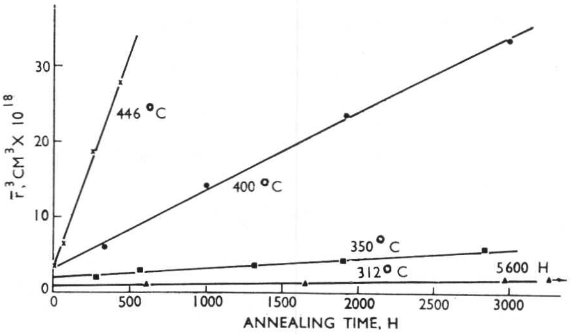

Fig. 6 *The linear variation of* $\bar{r}^3$ *and* t *indicates diffusion-controlled growth of manganese precipitates in a magnesium matrix.*[28] *This form of plotting experimental results is generally most convenient, since it reveals linear relationships independently of the initial mean particle radius when an appropriate power law is chosen.*

Increasing attention has been placed on the method of plotting experimental results. It is only in the cases where the initial average radius of the particles is very small that it is appropriate to present results as a logarithmic plot of the variation of mean particle radius with time. In the more general case, where the mean initial radius of the particles of the system is not negligible, it is simpler to assume a law of particle growth and, for example, plot the cube of the mean particle radius vs. time. Any departure from linearity in such a plot indicates that a wrong exponent of particle radius has been chosen or that an alternative relationship is required.

The first studies of particle coarsening in entirely solid systems[15] were on a system involving cobalt particles dispersed in a copper matrix and used magnetic methods for average particle-size measurement. The studies were aimed principally at the determination of a critical particle size for precipitation-hardening. The variation of mean particle radius with time, however, was also determined and showed quite clearly that r^3 was proportional to t. This work thus formed the basis of the first published account of experimental results supporting the theory of diffusion-controlled particle growth in a solid system. Of particular interest was the known coherency of small particles and the matrix in this system. The lattice misfit between copper and cobalt is relatively large ($\sim 2\%$), but despite the strain fields resulting from coherency the growth/time relationship appears unaffected. A re-assessment of the experimental results[27] has shown that there is a significant but not substantial change necessary in the value of some parameters of the growth equation (22) to obtain quantitative agreement between theory and experiment.

A considerable amount of further attention has recently been given to the influence on particle growth of strain due to coherency.[32–34] It has been convincingly argued that a coherent precipitate, because of its associated strain energy, must always have a higher solubility than a non-coherent precipitate of the same phase. Although some alteration to the magnitudes of growth parameters is anticipated, serious modification to the general form of the growth analysis is not expected to be required.[9]

The theory of particle coarsening by diffusion control has also been applied to the case where particles have a markedly non-spherical shape. Studies of copper precipitates in an α-iron matrix[21] indicate that there is a large anisotropy in the particle/matrix interfacial free energy. Despite this, the cube of the effective particle radius was again linearly proportional to time (Fig. 5). In this system, however, a number of complicating features may be envisaged in a quantitative analysis of the situation. In particular, since some coherency strains are likely, the particle shape would be modified from the true equilibrium form determined purely by interfacial-energy considerations. It is not surprising then that equation (22) does not predict growth rates precisely when the values of unmodified parameters are used in the theoretical calculation.

The most detailed information is on the Ni–Al system[26,27] where much work has been done on the coarsening of Ni_3Al (γ') particles. These studies have generally confirmed the relationship that the cube of the mean particle radius varies linearly with time and, in addition, since the size distribution of particles has been measured, valuable statistical information has been obtained. The experimental results establish that there is a quasi-stationary particle-size distribution and a marked cut-off in the distribution curve. This point of cut-off, however, tends to be at a value rather higher than 1·5 times the mean particle radius but the form of curve is roughly similar to that predicted theoretically by Lifshitz and Slyozov[9] and Wagner.[8] On this point it is worth noting that, though the analysis of particle-size distributions is sound mathematically, the approximations implicit in the theory appear to result in some numerical discrepancies. From equation (10), and as illustrated in Fig. 1, the fastest-growing particles are those of twice the mean radius of the system and it would thus be expected that there would be a cut-off in the particle-size distribution curve at a radius approximately equal to twice the mean radius. According to the statistical analysis of particle-size distributions from equation (21), which is also based on equation (10), particles that are greater than 1·5 times the mean radius do not exist. The precise origin of this difference remains to be resolved.

In the nickel–aluminium system there is excellent agreement between experimental results and the predictions of equation (22) and no alterations to any parameters are required, despite evidence of elastic interaction between particles arising from the difference between the elastic moduli of precipitate and matrix. These interaction effects are thus at most of only second-order importance in altering the kinetics of the growth process and either do not significantly change the solubility and solute diffusion coefficient or do so in a way such that their product remains essentially constant. One feature assisting the close agreement between theory and experiment in this system may be the isotropy of the particles which are in the form of cubes so that an effective particle radius can be readily defined. The agreement also persists when particles are close together and this may be accounted for by the dominating effect of solute concentration gradients near the particle surfaces.[6]

Although the agreement between theory and experiment is generally less precise than in the case of the Ni–Al system, the usefulness of the theory is becoming evident in assessing the behaviour of an increasing number of other systems. An example is the growth of manganese precipitates in a magnesium–manganese alloy which has been studied in some detail[28] and has involved observations of sufficient numbers of particles to obtain size-distribution curves. The cube of the mean particle radius was shown to vary linearly with time (Fig. 6), suggesting diffusion-controlled growth, although the measured rate did not agree closely with the predictions of equation (22) when reasonable values were inserted for the parameters. It must be noted, however, that calculations from equation (22) often require a more precise knowledge than is available of the magnitudes of the parameters involved. In the particle-size distribution curves it was again noted that the cut-off point was at a particle radius $> 1{\cdot}5$ times the mean radius of the system. The prediction of particles, existing at long times, of radius $\sim$ twice the mean radius of the system which emerges as a consequence of equation (10) may be relevant in this connection, since it does not depend on subsequent approximations which are required in statistical development of the theory.

Some of the most interesting experimental cases involve precipitates that consist of two or more components, but a full analysis of the growth process in such instances is likely to be much more complicated.[25] The rate-limiting cases must be considered and very often insufficient data are available to obtain quantitative information on the value of parameters which are required by theory. That unpredicted effects can be quite large is already clear from experimental work.[35] Particularly interesting cases concern those where one of the species may diffuse interstitially.[24] A rather special case involves the growth of iron-carbide particles in an iron matrix. It is clear in the latter case that the coarsening rate of Fe_3C is too rapid for the diffusion of iron to be rate-controlling but too slow for the process to depend solely on carbon diffusion when unmodified parameters are used. The reduced coarsening rate of Fe_3C in alloys containing chromium has long been known and it is now well established that carbides with the general formulae M_3C, M_7C_3, and $M_{23}C_6$ coarsen at rates very much less than Fe_3C.[35] It has been suggested that the coarsening of the series of carbides is related to the rate-controlling step of chromium diffusion. A recent view is that, in general, growth is controlled by the slowest-moving species but the diffusion coefficients and solubility may be affected by the stress gradients that surround the particles. Further complications can arise when the matrix is unstable and recovery processes occur simultaneously with the particle coarsening. Relatively simple growth equations do not appear to fit these cases.

Conclusions

The theory of particle coarsening limited by the rate of diffusion of solute from particle to particle is well substantiated by experiments on a variety of systems. There does not yet appear to be firm experimental support for particle growth limited by interface control in entirely solid systems, although this condition may arise when particles with contaminated surfaces grow in a liquid phase through which solute diffusion is rapid.[36]

Particle-size distribution curves have been found to assume a form which is independent of time, in agreement with theory. There is some discrepancy, however, in the shape of the predicted curves and those measured experimentally. In particular, it appears from experimental results that particles which have a radius somewhat greater than 1·5 times the mean particle radius can continue to exist.

The theory of diffusion-controlled growth is not greatly modified when the precipitates produce strain in the matrix, though the parameters describing diffusion and solubility may be altered numerically.

The situation is more complicated when the particles consist of two or more components, both of which are different from the matrix. Growth may then be limited by the component that diffuses more slowly but stress gradients surrounding the particles may be built up and may influence growth.

At present there is no experimental evidence for the theory of particle growth for grain-boundary particles at temperatures well below the melting point, but the theory appears to be soundly based.

When the matrix is unstable, for example undergoing recrystallization or recovery, particle-coarsening rates are affected in a way that has not yet been analysed.

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Experimental Confirmation of the Lifshitz–Wagner Theory of Particle Coarsening

A. J. Ardell

Various aspects of the Lifshitz–Wagner theory of particle coarsening are examined using data on the γ' precipitate in binary Ni-base alloys of Al, Ti, and Si. The kinetics of growth of the average particle, the experimental distributions of particle sizes, and the variation with time of the average solute concentration of the matrix are all demonstrated to be in excellent quantitative agreement with the predictions of the Lifshitz–Wagner theory. A small discrepancy between the experimental and theoretical values of the " cut-off " particle size (the largest particle size observed in the distribution) is briefly discussed. A kinetic equation for the variation of the volume fraction of γ' during coarsening is presented. Data on the Ni–Al system are used to illustrate the change in volume fraction that accompanies coarsening of the γ' precipitate.

Almost eight years have passed since Lifshitz and Slyozov[1] and Wagner[2] independently solved the complicated problem of diffusion-controlled coarsening, or Ostwald ripening. In its original form the Lifshitz–Wagner theory is applicable to spherical particles dispersed in a fluid matrix, but Li and Oriani[3] have shown that many of the factors that complicate the coarsening process for particles of arbitrary equilibrium shape in solid matrices[4] can, in principle, be accounted for quantitatively. Even though the Lifshitz–Wagner theory has been demonstrated to hold semiquantitatively for particle coarsening in several solid systems,[5–7] good quantitative agreement between theory and experiment is relatively scarce. A notable exception is provided by one family of systems, the γ' precipitate in Ni-base alloys. In this paper data on the coarsening of the γ' precipitate in three binary Ni-base alloys (Ni–Al, Ni–Ti, and Ni–Si) will be presented, partly to illustrate the basic validity of the Lifshitz–Wagner theory and partly to discuss the minor discrepancies that remain.

Theoretical Considerations

Growth of the Average Particle[1,2]

The theoretical kinetic equation for particle growth is

$$\bar{r}^3 - \bar{r}_0^3 = kt \qquad \ldots (1)$$

where $\bar{r}$ is the average particle radius at time t, and $\bar{r}_0$ is the average particle radius at the onset of coarsening. The rate constant k is given by

$$k = \frac{2\gamma D c_e V_m^2}{\rho_c{}^2 RT} \qquad \ldots (2)$$

where γ is the interfacial free energy of the particle/matrix interface, D is the coefficient of diffusion of the solute in the matrix, c_e is the concentration of solute in equilibrium with a particle of infinite size, V_m is the molar volume of the precipitate, ρ_c is a numerical constant related to the distribution of particle sizes (theoretically $\rho_c = 3/2$), and RT has its usual meaning.

Equations (1) and (2) are written for spherical particles coarsening in fluid matrices. Nevertheless, we will continue to use them with the understanding that they incorporate the modifications necessary for particles of arbitrary equilibrium shape in solid matrices.[3]

Theoretical Distribution of Particle Sizes[1,2]

The distribution of particle sizes evolves towards a " quasi-steady-state " distribution, $f(r,t)$, which is independent of the initial distribution $f(r,0)$. The distribution function is

$$f(r,t) = f'(t)\rho^2 h(\rho) \qquad \ldots (3)$$

where $f'(t)$ is a function of time only, $\rho = r/\bar{r}$, and $h(\rho)$ is given by

$$h(\rho) = \left(\frac{3}{3+\rho}\right)^{7/3} \left(\frac{3/2}{3/2-\rho}\right)^{11/3} \exp\left(\frac{-\rho}{3/2-\rho}\right) \qquad \ldots (4)$$

$$\rho < \rho_c = 3/2; \; h(\rho) = 0; \; \rho > \rho_c = 3/2.$$

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The size distribution is such that particles greater than $1{\cdot}5\ \bar{r}$ should not exist. The function $\rho^2 h(\rho)$ is time-invariant and has the property that

$$\int_0^\infty \rho^2 h(\rho)\, d\rho = \rho_c^2 \qquad \ldots (5)$$

The "cut-off" radius, $\rho_c = 3/2$, enters into the Wagner formulation[2] through equation (5), and is the only parameter associated with the theoretical distribution of particle sizes in the kinetic equations for coarsening.

The Average Concentration of Solute in the Matrix[1]

The supersaturation $\Delta = c - c_e$ asymptotically obeys the relationship

$$\Delta = c - c_e = (\varkappa t)^{-1/3} \qquad \ldots (6)$$

where c is the average concentration of solute in the matrix, and $\varkappa$ is given by

$$\varkappa = \frac{D(RT)^2}{4\gamma^2 \rho_c^2 c_e^2 V_m} \qquad \ldots (7)$$

It is possible to obtain an expression for $\Delta(t)$ valid for all ageing times,[8] but the general expression is neither as useful nor as easy to test as equation (6) because c_e is usually not known with sufficient accuracy. Note, however, that values of c_e can be obtained by extrapolation, to $t^{-1/3} = 0$, of data plotted according to equation (6).

The Time-Dependence of the Volume Fraction of Precipitate

It is generally taken for granted that the volume fraction of precipitate remains constant during coarsening, although it is recognized that the volume fraction must increase slightly as coarsening proceeds. An increase in the volume fraction of precipitate must accompany the decrease in solute concentration because these quantities are related by the lever rule. If φ represents the volume fraction of precipitate, w_i the total wt. fraction of solute in the alloy and $w_{\gamma'}$ the wt. fraction of solute in the γ' phase, we have

$$\varphi = \frac{w_i - w}{w_{\gamma'} - w} \qquad \ldots (8)$$

Equation (8) is written under the assumption that the mass density of γ' is equal to that of the matrix. With the solute concentration in units of wt. fraction, rather than moles/cm^3, substitution of equation (6) into equation (8) yields

$$\varphi = \frac{w_i - w_e - (\varkappa t)^{-1/3}}{w_{\gamma'} - w_e - (\varkappa t)^{-1/3}} \qquad \ldots (9)$$

which is valid at long ageing times. By expanding the denominator of equation (9) and discarding all terms of higher order than $(\varkappa t)^{-1/3}$, we arrive at the expression

$$\varphi = \varphi_e - (\varkappa^* t)^{-1/3} \qquad \ldots (10)$$

where φ_e is given by equation (8) with $w = w_e$, and

$$\varkappa^* = \left(\frac{w_{\gamma'} - w_e}{1 - \varphi_e}\right)^3 \varkappa \qquad \ldots (11)$$

Experimental Results

The γ' precipitate has the following characteristics: *(a)* the particles have the composition Ni_3X and possess the Cu_3Au ($L1_2$) crystal structure;[9] *(b)* they are usually perfectly coherent with the matrix; *(c)* the particle shape is a function of the fractional misfit, δ, between the unstrained lattices of the precipitate and matrix.[10] In Ni–Al ($\delta = +0{\cdot}5\%$) and Ni–Ti ($\delta = +0{\cdot}85\%$) the γ' particles are cuboidal with interfaces parallel to $\{100\}$. In Ni–Si alloys ($\delta = -0{\cdot}25\%$), the γ' particle shape is more nearly spherical in the early stages of ageing but becomes clearly cube-shaped as ageing proceeds.

The particle sizes referred to herein were all determined by transmission electron microscopy. The matrix concentrations of the various solutes during coarsening were determined by a magnetic technique which takes advantage of the fact that the ferromagnetic Curie temperature for the three binary alloys is a very strong function of the solute content.[11] The reader is referred to the original papers for further experimental details.

γ' in Ni–Al

The coarsening behaviour of γ' in this system has been studied extensively.[12–14] Particle-growth data[12,13] for alloys containing 6·35 and 6·71 wt.-% Al, plotted as half the average length of the cube edge ($\bar{a}/2$) vs. $t^{1/3}$, are shown in Fig. 1. The representation of the data in Fig. 1 is consistent with equation (1) as long as $\bar{a}_o \simeq 0$, which it is for γ' in Ni–Al. Values of k, obtained from the slopes of curves of $(\bar{a}/2)^3$ vs. t, are summarized in Table I. The temperature dependence of k, compensated for the factor T/c_e in equation (2), has been shown to be of the Arrhenius type[13] with an activation energy of approximately 64·4 kcal/mole. This value is very close to the activation energy for the diffusion of Al in very dilute Ni–Al alloys (64 kcal/mole) determined by Swalin and Martin.[15]

The particle-size distributions[13] are reproduced in Fig. 2. The overall agreement between the experimental histograms and the theoretical distribution of particle sizes is very good. The most notable discrepancy concerns the experimental cut-off sizes, which generally lie in the range $1{\cdot}6 < \rho_c < 1{\cdot}8$ as opposed to the theoretical value $\rho_c = 1{\cdot}5$. The steady-state size distribution is evidently established early in the ageing process and there is no systematic variation of ρ_c with the testing variables.

The predictions of equation (6) are exemplified by the data[14] in Fig. 3. Although the data for the 6·35% Al alloy are scattered, the data for the 6·50% Al alloy show excellent linearity. The values of w_e and $\varkappa$, obtained from the intercepts and slopes of the curves in Fig. 3, are also summarized in Table I. The values of w_e are ~ 10% higher than the

TABLE I

Values of the Coarsening Parameters for γ' in Ni–Al Alloys

Temp.,°C	k, cm^3.sec^{-1}	$\varkappa$.sec^{-1}	w_e (wt. fraction)
625	$2{\cdot}07 \times 10^{-24}$*	$1{\cdot}10 \times 10^4$	$5{\cdot}605 \times 10^{-2}$
715	$7{\cdot}01 \times 10^{-23}$*	$3{\cdot}61 \times 10^6$	$6{\cdot}048 \times 10^{-2}$
750	$1{\cdot}60 \times 10^{-22}$	—	—
775	$3{\cdot}61 \times 10^{-22}$	—	—

*Average values for the 6·35 and 6·71 wt.-% Al alloys.

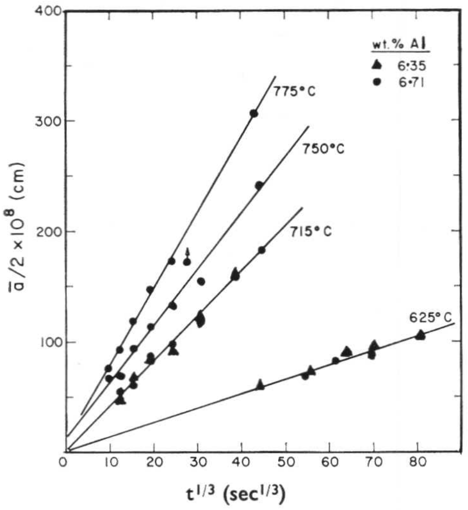


Fig. 1 *Variation of the average particle size* ($\bar{a}/2$) *as a function of* (*time*)$^{1/3}$ *for* γ' *in Ni–Al alloys.*[12,13]

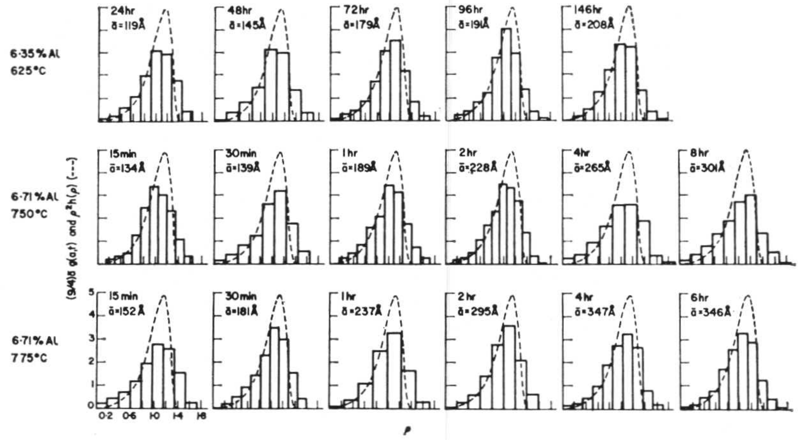


Fig. 2 *Comparison of the experimental histograms*, (9/4) $\bar{a}g$ (a, t), *for* γ' *in Ni–Al alloys,*[13] *with the theoretical distribution function* $\rho^2 h(\rho)$.

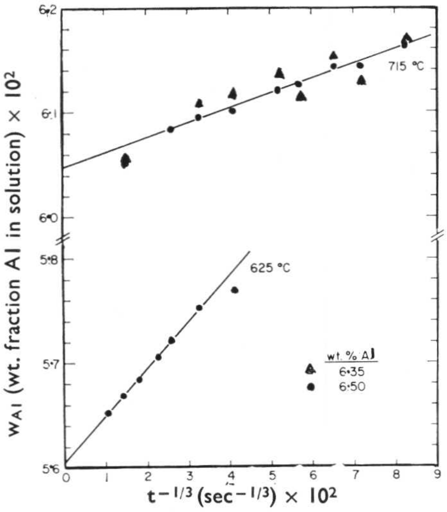


Fig. 3 *Variation of the average Al content of the Ni-rich matrix* (w_{Al}) *as a function of* (*time*)$^{-1/3}$ *during coarsening of the* γ' *precipitate.*[14]

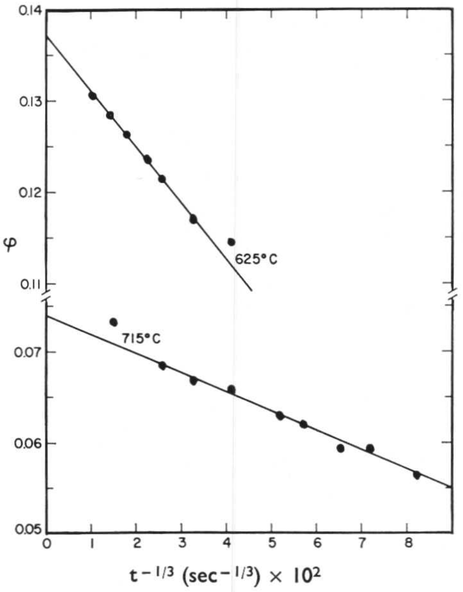
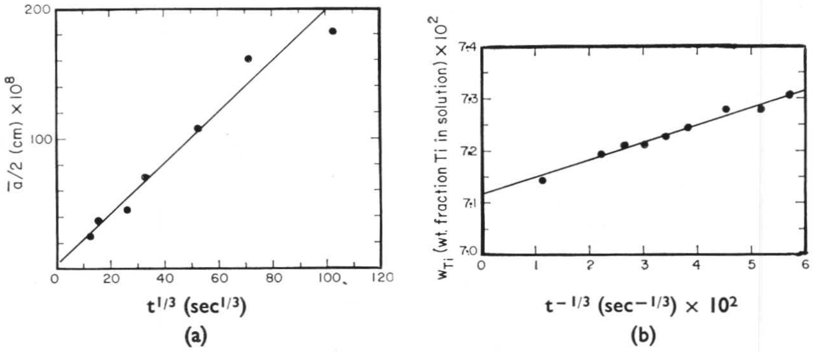


Fig. 4 *Variation of the volume fraction* (φ) *of the* γ' *precipitate in the Ni-6·50 wt.-% Al alloy as a function of* (*time*)$^{-1/3}$ *during coarsening. These data have been converted from the values of* w_{Al} *in Fig.* 3 *according to equation* (8).



(a)

(b)

Fig. 5 *Data on the coarsening of the* γ' *precipitate in Ni–Ti alloys:* (a) *Ni–9·08 wt.-% Ti, variation of the average particle size* ($\bar{a}/2$) *as a function of* (*time*)$^{1/3}$ *at* 700° *C;*[23] (b) *Ni–8·40 wt.-% Ti, variation of the average Ti content of the Ni-rich matrix* (w_{Ti}) *as a function of* (*time*)$^{-1/3}$ *at* 700° *C.*[24]

reported solubilities[16,17] of Al in equilibrium with γ'. The values of w_e in Table I most likely represent the solubilities of the coherent γ' precipitate, which must be greater than the corresponding incoherent solubilities.[18]

The time variation of the volume fraction of γ', calculated from the values of w_{Al} in Fig. 3 according to equation (8), is shown in Fig. 4. It should be emphasized that the curves in Fig. 4 do not provide a test of the validity of equation (10), i.e. the linear relation of φ to $t^{-1/3}$, because of the demonstrated linearity between w_{Al} and $t^{-1/3}$ (Fig. 3). However, the curves in Fig. 4 do illustrate the extent to which φ varies during coarsening of the γ' precipitate in the 6·50% Al alloy. It is clear from these curves that the assumption of constant volume fraction is not necessarily a good one. It follows that constancy of volume fraction cannot necessarily be used as a criterion for the process of precipitate coarsening.

γ' in Ni–Ti

The γ' precipitate in Ni–Ti alloys is metastable with respect to the stable hexagonal η phase.[9] Nevertheless it persists for long ageing times and its properties have been studied fairly thoroughly.[19,20] The majority of evidence[20] suggests that γ' in Ni–Ti behaves in a similar manner to γ' in Ni–Al, although there remains some controversy regarding the later stages of γ' growth in Ni–Ti alloys.[21,22]

The data for 700° C are presented in Fig. 5. The particle-size measurements of Sass and Cohen,[23] from an alloy containing ~ 9·08 wt.-% (10·9 at.-%) Ti, are shown in Fig. 5(*a*). Fig. 5(*b*) shows the variation of Ti content during the ageing of a Ni–8·40 wt.-% (10·1 at.-%) Ti alloy, taken from the data of Ben Israel and Fine.[24] The values of k, $\varkappa$, and w_e are shown in Table II.

Additional data for the variation of Ti content are available for lower temperatures.[24] These data also obey the functional form of equation (6)[8] and yield physically acceptable values of w_e, i.e. they are greater than the reported solubilities of η, as is the value for 700° C in Table II. However, the temperature-dependence of $\varkappa$ does not obey an Arrhenius relationship. The reason for this is not readily apparent. The data of Ben Israel and Fine were not taken with a specific emphasis on the coarsening behaviour of the γ' precipitate and it is probable that the later stages of the growth of γ' in this alloy should be re-examined.

Particle-size distributions for γ' in Ni–Ti have not been reported.

γ' in Ni–Si

There is some evidence that the γ' precipitates in Ni–S alloys lose coherency with the matrix as the particle size increases.[25] Current research in the author's laboratory confirms that this may be the case (there is no evidence that γ' precipitates in Ni–Al and Ni–Ti alloys ever lose coherency) and the results that follow refer only to the coherent γ' precipitate.

The available data for coarsening of the coherent γ' precipitate are limited to measurements of the Si content of the Ni-rich matrix. Some of the recent data of Rastogi[26] are shown in Fig. 6. Once again the functional form of equation (6) is supported. The values of $\varkappa$ extracted from Fig. 6 are reported in Table III. The temperature-dependence of $\varkappa$, compensated for the factor w_e^2/T^2, is shown in Fig. 7. The activation energy of ~ 62 kcal/mole, determined from Fig. 7,

TABLE II

Values of the Coarsening Parameters at 700° C for γ' in Ni–Ti Alloys

k, cm^3.sec^{-1}	$\varkappa$.sec^{-1}	w_e (wt. fraction)
$7{\cdot}46 \times 10^{-24}$	$3{\cdot}08 \times 10^{4}$	$7{\cdot}122 \times 10^{-2}$

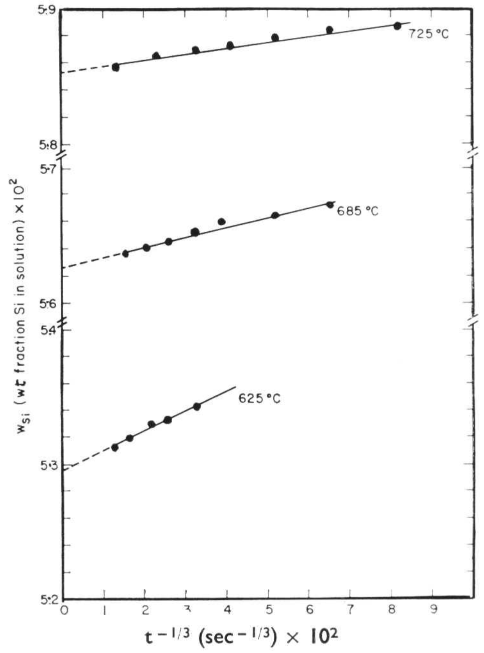


Fig. 6 *Variation of the average Si content of the Ni-rich matrix* (w_{Si}) *as a function of* (*time*)$^{-1/3}$ *during coarsening of the* γ' *precipitate in a Ni–6·50 wt.-% Si alloy.*[26]

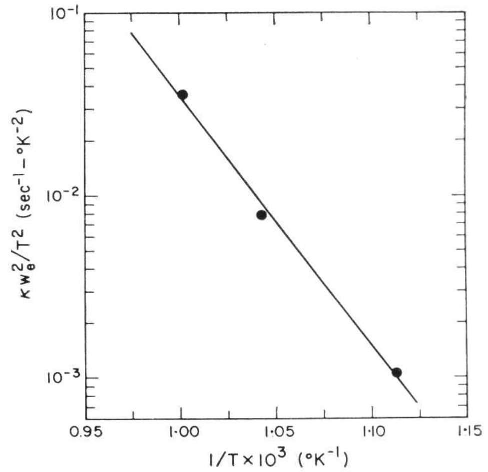


Fig. 7 *Arrhenius plot of the rate constants* $\varkappa$, *in Table III, compensated for the temperature-dependent factor* w_e^2/T^2 *in a Ni–6·50 wt.-% Si alloy. The activation energy determined from this curve is ~ 62 kcal/mole.*

TABLE III

Values of the Coarsening Parameters for γ' in Ni–Si Alloys

Temp., °C	$\varkappa$.sec^{-1}	w_e (wt. fraction)
625	$2{\cdot}99 \times 10^5$	$5{\cdot}296 \times 10^{-2}$
685	$2{\cdot}28 \times 10^6$	$5{\cdot}626 \times 10^{-2}$
725	$1{\cdot}05 \times 10^7$	$5{\cdot}854 \times 10^{-2}$

TABLE IV

The Interfacial Free Energies, γ, and the Solute-Diffusion Coefficients, D, Evaluated from the Coarsening Experiments*

Temp., °C	System	γ, ergs cm^{-2}	D, cm^2 sec^{-1}	D, cm^2 sec^{-1}†
625	Ni–Al	14·4	$9{\cdot}20 \times 10^{-16}$	$4{\cdot}81 \times 10^{-16}$
715	Ni–Al	14·2	$2{\cdot}79 \times 10^{-14}$	$1{\cdot}27 \times 10^{-14}$
700	Ni–Ti	13·0	$5{\cdot}26 \times 10^{-15}$	$1{\cdot}33 \times 10^{-14}$

* The experimental values of γ and D were calculated from equations (12) and (13) with $\varkappa$ in units of mole^3 cm^{-9} sec^{-1} and c_e in units of mole/cm^3.

† Extrapolated from the high-temperature diffusion data of Swalin and Martin.[15]

is almost identical to the activation energy for diffusion of Si in dilute Ni–Si alloys (61·7 kcal/mole) determined by Swalin *et al.*[27]

The values of w_e, also shown in Table III, are definitely coherent solubilities. This conclusion has been confirmed by other experiments in the author's laboratory.[26]

Quantitative Considerations

In order to assess the theory in a quantitative manner we must compare the experimental rate constants k and $\varkappa$ with the predictions of equations (2) and (7). Fortunately, the only parameters in equations (2) and (7) that are not known with reasonable precision are D and γ, which can be eliminated successively from these equations to yield two further equations

$$\alpha = (k/\varkappa)^{1/3} = \frac{2\gamma c_e V_m}{RT} \qquad \ldots (12)$$

and

$$\beta = (k^2\varkappa)^{1/3} = \frac{D V_m}{\rho_c^2} \qquad \ldots (13)$$

Since α and β can be determined from the experimental values of k and $\varkappa$ in Tables I and II, we can solve for γ and D separately from equations (12) and (13). This procedure, applied to the data for γ' in both Ni–Al and Ni–Ti alloys (unfortunately, values of k are not yet available for Ni–Si), results in the values of γ and D presented in Table IV. For the application of equations (12) and (13), the values of w_e in Tables I and II were converted to molar concentrations (mole/cm^3), and V_m was taken as 27·16 cm^3/mole for Ni_3Al and 27·2 cm^3/mole for Ni_3Ti. The values of D in Table IV were calculated from equation (13) using the theoretical value $\rho_c^2 = 9/4$. The solute diffusivities, extrapolated from the results of the elevated-temperature diffusion experiments of Swalin and Martin,[15] are also shown in Table IV for comparison.

Discussion

The data for the coarsening of γ' in Ni–Al, Ni–Ti, and Ni–Si are clearly consistent with the semiquantitative predictions of the Lifshitz–Wagner theory: (*a*) the various kinetic equations are obeyed; (*b*) the activation energies are consistent with a solute-diffusion-controlled process (with the exception of γ' in Ni–Ti); (*c*) the equilibrium solubilities of the three solutes are all reasonable and physically acceptable; (*d*) the distributions of γ' particle sizes in Ni–Al alloys are evidently steady-state distributions established early in the ageing process.

We now assess the values of the parameters in Table IV. Unfortunately, independent experimentally determined values of γ are not available. However, we know from theoretical considerations that the {100} interface between pure nickel and stoichiometric γ' has approximately zero interfacial free energy.[13] Allowing for deviations from stoichiometry in γ' and for the concentrations of solute in the Ni-rich matrix, the low values of γ (13–14 ergs/cm^2) in Table IV must be considered satisfactory.

It is also seen in Table IV that the application of equation (13) to the coarsening data yields values of D that are within a factor of ~ 2 of the diffusivities of Al and Ti in the dilute alloys. If we allow for the fact that the solute contents involved in the coarsening experiments are much greater than those used in the diffusion experiments,[15] and that fairly large extrapolations of the high-temperature data must be made for the solute diffusivities in Table IV, the observed discrepancy is very small. Incidentally, this discrepancy cannot be accounted for by the complicating effect of volume-constrained diffusion, which is predicted to be small.[14]

It is interesting to recalculate the values of D in Table IV in recognition of the fact that the experimental values of ρ_c are somewhat greater than 3/2, at least for γ' in Ni–Al. It is clear that if the actual distribution differs from the theoretical distribution of particle sizes, the coarsening rates must be affected. To see this we need only consider the extreme case of a monodisperse assembly of particles, which will remain indefinitely in unstable equilibrium unless it is disturbed. To estimate the effect of the observed discrepancy on the coarsening rates, we assume that the experimental value of ρ_c for γ' in Ni–Al can be used as an additional disposable parameter in equations (2), (7), or (13), even though there is no real justification for this procedure. Taking the value of $\rho_c = 1{\cdot}7$ as representative of γ' in both Ni–Al and Ni–Ti, the values of D, calculated from equation (13), are increased by a factor of ~ 1·28 over the previously calculated values. Even with this correction, the predictions of the Lifshitz–Wagner theory are in excellent quantitative agreement with experiment.

Perhaps the most significant observation regarding the discrepancy between the theoretical and experimental values of ρ_c is that the observed ρ_c appears to be characteristic of the system (γ' in Ni–Al), and not the various testing variables, either imposed or implicit. There is no obvious way to account for such a discrepancy within the framework of the Lifshitz–Wagner theory, as other theoretical work by Lifshitz and Slyozov[28] has shown. We will probably have an answer to this problem only when the Lifshitz–Wagner theory is reformulated to incorporate some of the factors peculiar to solid systems which have not been dealt with. Among these are: (*a*) the effect of elastic energy on the equilibrium particle shape and the related effect on the Gibbs–Thomson equation; (*b*) the effect of elastic interactions among precipitates,[12] which introduces space-dependent factors (and hence, presumably, volume-fraction effects) into the problem. It is only fair to point out, however, that ρ_c has been observed to be $> 3/2$ in other systems, both fluid[29] and solid,[7] which have little in common (structurally) with γ' in binary nickel alloys.

Summary and Conclusions

The Lifshitz–Wagner theory of diffusion-controlled coarsening is in very good agreement with all aspects of the later stages of ageing in binary Ni-base alloys of Al, Ti, and Si. A small discrepancy remains between the experimental and theoretical distribution of particle sizes. However, it is felt that this discrepancy may be peculiar to solid systems containing elastically interacting coherent precipitates, and therefore cannot be accounted for by the theory. It is thus concluded that the Lifshitz–Wagner theory, in its original form, is confirmed by the data presented herein. It is also shown that the volume fraction of γ' in Ni–Al alloys cannot necessarily be considered constant during coarsening.

Acknowledgement

Support for this work was provided by the U.S. Atomic Energy Commission.

NOTE ADDED IN PROOF: After submission of this manuscript, the author became aware of recently published particle-size measurements on γ' in a N–i11·46 at.-% Si alloy (E. Hornbogen and M. Roth, *Z. Metallkunde*, 1967, **58**, 842). Hornbogen and Roth determined the average γ' particle sizes as functions of time at 600 and 750° C. From the values of $2k^{1/3}$, obtained directly from their published curves of particle dia., d, vs. $t^{1/3}$, and values of $\varkappa$, obtained by interpolation of the data of Rastogi[26], γ and D have been estimated from equations (12) and (13). The estimated values of γ are 13·0 ergs/cm^2 (600° C) and 10·5 ergs/cm^2 (750° C), which are comparable to those in the Ni–Al and Ni–Ti systems. However, the estimated values of D are about a factor of 10 greater than the extrapolated high-temperature diffusivities of Swalin *et al.*[27] There is no apparent reason for this comparatively large discrepancy.

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Research Note

Measurement of Diffusion Fields around Precipitate Particles by Electron-Probe Microanalysis

M. G. Hall and C. W. Haworth

The work outlined in this note has been concerned with the direct measurement of concentration gradients around dissolving precipitate particles. There are two distinct possibilities for the rate-controlling mechanism governing precipitate growth and dissolution—diffusion in the matrix or reaction at the matrix/particle interface.

Although kinetic measurements on the growth of precipitates may give some indication of the process involved, there have been no direct measurements of the concentration gradients around the particles at intervals during the heat-treatment. In the present work such measurements have been made using electron-probe microanalysis. If the concentration C_s in the matrix at the matrix/particle interface remains constant at the value given by the equilibrium diagram for the temperature of the heat-treatment C_E, and the diffusion profile is described in terms of the classical diffusion coefficient for the system at the concentration and temperature involved, then the process is shown to be diffusion-controlled. An interface-controlled reaction is indicated by $C_s \neq C_E$.

An Al–4·8 wt.-% Cu alloy was prepared by melting 99·999% Al and 99·9% Cu in an alumina crucible under vacuum and casting a 1-in.-dia. ingot, which was hot swaged to $\frac{5}{8}$ in. dia. and then homogenized by annealing at 540° C for 1 week. Large (50–200 μm) Widmanstätten plates and needles of θ phase were formed by slowly cooling a section of this ingot from 540 to 464° C at 3 degC/day and annealing at 464° C for 1 week to give an equilibrium structure of matrix composition C_0. The alloy was quenched into water.

Specimens from this alloy were then reheated for times of up to 1 h at 541° C to redissolve partially the θ particles, the enveloping diffusion field extending up to 60 μm into the matrix around each particle.

A section through each specimen was polished and lightly etched to delineate the extent of the diffusion field. Isolated extensive Widmanstätten plates were selected (Fig. 1), and further metallography[1] gave the angle that individual plates made with the specimen surface. Suitable particles were marked by microhardness indentations and the etch removed by a light polish.

The Cu concentration was then measured by electron-probe microanalysis along a line across the centre of each plate and perpendicular to the trace of the plate. The intensity of CuK_α radiation from the specimen was referred to that from a pure-copper standard specimen and the intensity ratio calculated after allowing for counter dead-time losses and background count-rate. The beam voltage was 25 kV. The correction to weight concentration was established from measurements of a homogeneous alloy of chemical composition 4·94% Cu for which the intensity ratio obtained was 4·33%. Application of the various theoretical correction procedures[2] showed that no absorption correction was involved and that the measurements agreed closely with the procedure of Poole and Thomas.[3] The atomic-number correction of Duncumb and da Casa[4] gave a chemical analysis that was too high by ~ 5% of content. The accuracy of the analysis is relevant only to comparison with previous phase-diagram data and in the present work the important comparisons are made only between analyses obtained by electron-probe microanalysis. The precision of the analyses is estimated to be better than ± 0·1% Cu for the range of compositions measured; repeated measurements of the intensity ratios from the matrix gave a standard deviation of ± 0·05% Cu.

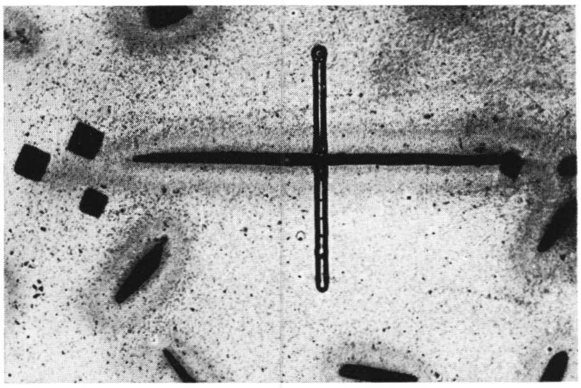

Fig. 1 Isolated Widmanstätten plate showing microprobe contamination trace, subsequently etched to show diffusion field. × 180.

The resolution of the electron probe was measured by traversing across plates in the equilibrium (464° C) alloy. This " blank " profile was then subtracted from the profiles measured on the diffused specimens (Fig. 2).

We make the approximation that the Widmanstätten plate is of infinite extent and that the dissolution of the precipitate is a one-dimensional diffusion problem. By integration under the measured concentration curve, it can be shown that the precipitate interface moves less than 1 μm during dissolution, while the diffusion profile is more extensive than this by at least an order of magnitude. Thus, the moving-boundary solution to the diffusion equation is closely approximated by the equation.

$$\frac{C - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left\{\frac{x}{2\sqrt{(Dt)}}\right\} \qquad \ldots (1)$$

where C_0 is the original concentration in the matrix, C is

Manuscript received 3 July 1968. M. G. Hall, B.Met., and C. W. Haworth, M.A., D.Phil., are in the Department of Metallurgy, University of Sheffield.

TABLE I

Dissolution Time, min	15		30		60				
Plate No.	1	2	1	2	1	2	3		
C_s, %Cu interface conc.	5·79	5·25	5·86	5·36	5·47	5·56	5·65	Av. C_S = 5·56%	C_E(541° C) = 5·51%
C_0. %Cu minimum matrix conc.	2·96	2·90	2·96	2·96	3·13	3·19	3·06		C_E(464° C) = 2·92%
$D(10^{-10}$ cm^2 sec$^{-1})$	10·6	9·42	10·3	12·5	9·78	8·03	11·6		

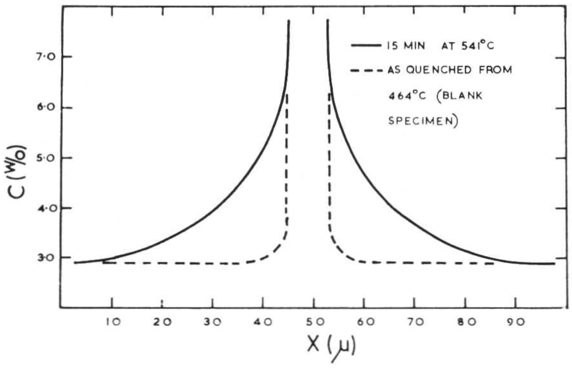

Fig. 2 *Diffusion profile across Widmanstätten plate of Fig.* 1 *and " blank " profile across similar plate equilibrated at* 464° *C*

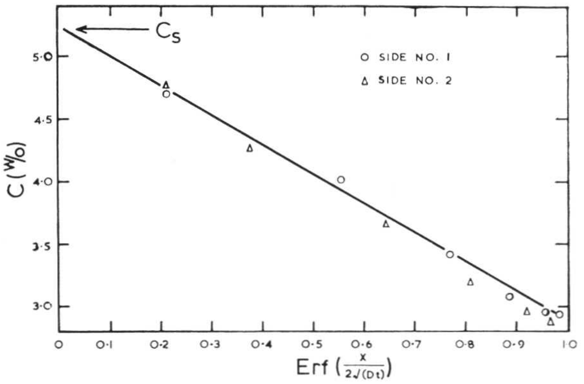

Fig. 3 C *vs. erf* {x/2√(Dt)}, *using approximate value of* D *for specimen annealed for* 15 *min.*

the Cu concentration in the matrix at distance x from the interface, C_s is the Cu concentration in the matrix at $x = 0$, t is the time of anneal, and D is the diffusion coefficient of Cu in the matrix, assumed to be independent of concentration.

In the experiment, C was measured as a function of x but direct measurement of C_s was not possible owing to the lack of spatial resolution of the analysis. The two unknown parameters in equation (1), C_s and D, were determined by fitting the measured profile to an error-function curve. Hence approximate values of C_s and D were found and the graph of Fig. 3 could be plotted. The process could be iterated with more accurate values of C_s obtained from the graph. The linear plot shows that the diffusion profile away from the flat surfaces of the precipitate can be described in terms of a constant value of D. This process was repeated for the profiles from each of the Widmanstätten plates measured. The values of C_s and D obtained from the graphs for different times of dissolution are given in Table I.

Although the values of C_s in Table I show some scatter, there is no obvious trend with time and the mean value of $C_s = 5{\cdot}56\%$ Cu is close to the equilibrium solubility C_E at the dissolution temperature of 541° C. The solubility limit by microprobe analysis of a 15% Cu alloy equilibrated for 14 days at 541° C gave a mean figure of 5·51 wt.-%Cu; Hansen[5] reports a solubility limit at this temperature of 5·46% Cu and this close agreement lends support to the microanalysis procedure.

For the composition range seen in this experiment values for the chemical diffusion coefficient of copper in aluminium have been given by Mehl *et al.*[6] At 540° C, $D = 1{\cdot}8 \times 10^{-9}$ cm^2 sec^{-1} for a 1% Cu alloy and $D = 5 \times 10^{-10}$ cm^2 sec^{-1} for a 5% Cu alloy; for the composition range in the present work $D \simeq 10^{-9}$ cm^2 sec^{-1} is expected. These data are not very satisfactory, and new measurements of the diffusion coefficient at 541° C are in progress, but there is good agreement between the conventional diffusion coefficients and those derived from measurements of the precipitate particles shown in Table I.

It is apparent that after dissolution for 1 h the measured value of C_0 shows some increase and this is because the diffusion fields from adjacent particles had started to impinge on the measured profile. The values of D obtained in this case will not be reliable because of the effect of change in C_0 during dissolution.

The results show that at 541° C the rate of dissolution of θ-phase Widmanstätten plates is controlled by the diffusion of solute in the matrix, away from the precipitate/matrix interface, and not by transport across the interface. If the interface reaction was the controlling process then a value of $C_s \neq C_E$ would be expected. In addition the value of D which describes the diffusion fields is very similar to that measured by a conventional experiment.

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JIST May 1969 p 674

Research Note

The Coarsening of Spherical Intermetallic Particles in a Ferritic Fe–Si–Ti Alloy

E. N. Bower and J. A. Whiteman

A study has been made of precipitate coarsening in a ferritic alloy containing 3·5% Si and 1·0% Ti. This alloy has been shown previously[1] to undergo pronounced precipitation-hardening when solution-treated and aged. The alloy was made from pure materials, by argon-arc melting, to form a 50-g ingot that was subsequently hot swaged at 1200° C to 0·187-in.-dia. bar. Sections ~ $\frac{1}{4}$ in. long were heat-treated in argon-filled silica capsules. Solution-treatment at 1200° C for 1 h was followed by water-quenching and subsequent ageing between 550 and 700° C. The hardness of the alloy increased from ~ 240 HV30 in the solution-treated state to ~ 500 HV30 after ageing for 1 h at 600° C. Carbon extraction replicas were examined in a A.E.I. EM6 electron microscope, the magnification being calibrated with " Latex " particles for each micrograph. Measurements of mean particle radius and size distribution were made from micrographs of the replicas, using a Zeiss particle-size analyser.

The extraction replicas showed a fine spherical precipitate in the overaged material that is presumed to be responsible for the observed hardening (Fig. 1). High-resolution electron diffraction suggested that the precipitate structure was probably the DO_3 ordered structure which is closely related to the b.c.c. matrix structure. The lattice parameter of the precipitate reached an " equilibrium " value of 5·72 Å. Thus, the precipitate has a lattice parameter very close to twice that of the parent ferrite and is probably based on Fe_3Si (which is known to have the DO_3 structure and a lattice parameter of 5·644 Å).

Measurements of particle size and size distribution were made after overaging at 600, 650, and 700° C. In each case between 600 and 1000 particles were measured. The observed values of mean particle size were corrected by the formula of Ashby and Ebeling[2] to give the mean of the volume distribution. Particle-size distributions were converted to volume distributions by dividing the number in each group by the mean size of the group. These calculations were necessary since (i) the replica extracts only a surface distribution of particles and (ii) the probability of a particle being intersected by a plane of sectioning, and hence by the replica, is proportional to its diameter.

The theoretical relationship between mean precipitate radius ($\bar{r}$) and the time of coarsening (t), has been shown by Lifshitz and Slyozov[3] and Wagner[4] to be of the form

$$\bar{r}^3 - \bar{r}_0{}^3 = Kt$$

where $\bar{r}_0$ is the mean precipitate radius at the beginning of coarsening and K is a constant.

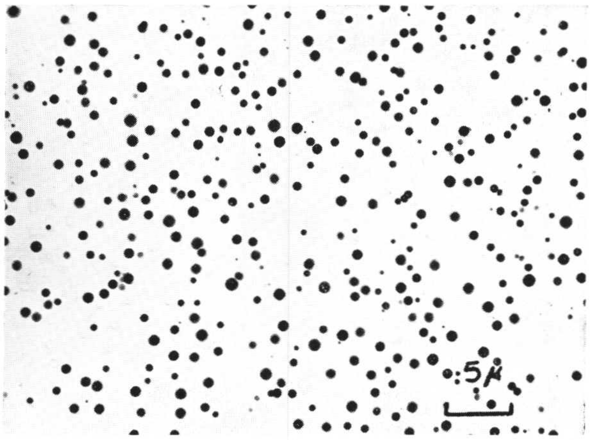

Fig. 1 A typical distribution of Fe_3Si-type precipitates in ferrite (carbon extraction replica).

To test the validity of this relationship, graphs of $\bar{r}^3$ vs. ageing time (t) were plotted and analysed by a least-squares method (e.g. Fig. 2(a)). In all cases the data resulted in a straight-line relationship with an intercept ($\bar{r}^3$) of zero within the significance of the experimental measurements. The agreement with this form of growth law indicates that the coarsening process involves the growth of large particles at the expense of small ones by a diffusion-controlled mechanism.

Particle-size distributions were determined for specimens covering a range of mean particle radii from 66 to 877 Å. Typical distribution curves are shown in Figs. 2(b), (c), and (d), which also include the theoretical distribution curve of Wagner. It is noticeable that for the smaller particle sizes the distribution is nearly normal, with a peak at $\rho = 1 \cdot 0$ (where $\rho = \dfrac{\text{mean radius of the group}}{\text{mean radius of the distribution}}$) and a cut-off at $\rho = 1 \cdot 65$. As ageing, and hence the coarsening process, progresses the distribution becomes broader, but in general the peak occurs at $\rho \simeq 1 \cdot 1$ in agreement with Wagner's theory. The cut-off point is clearly not in agreement with the theory, however, and gradually increases from $\rho = 1 \cdot 65$ to $\rho = 2 \cdot 05$ for the largest particle sizes. It also appears that the distribution may be tending towards log-normality at the longest ageing times.

In considering these results it must be remembered that there are inherent errors in measuring particle-size distributions from replicas. The first of these arises from the possibility of collecting particles that were loose on the specimen surface, having dropped on to the surface from the layer etched away. This effect was minimized by thorough washing after the primary etch; as has been shown by Stumpf[5]

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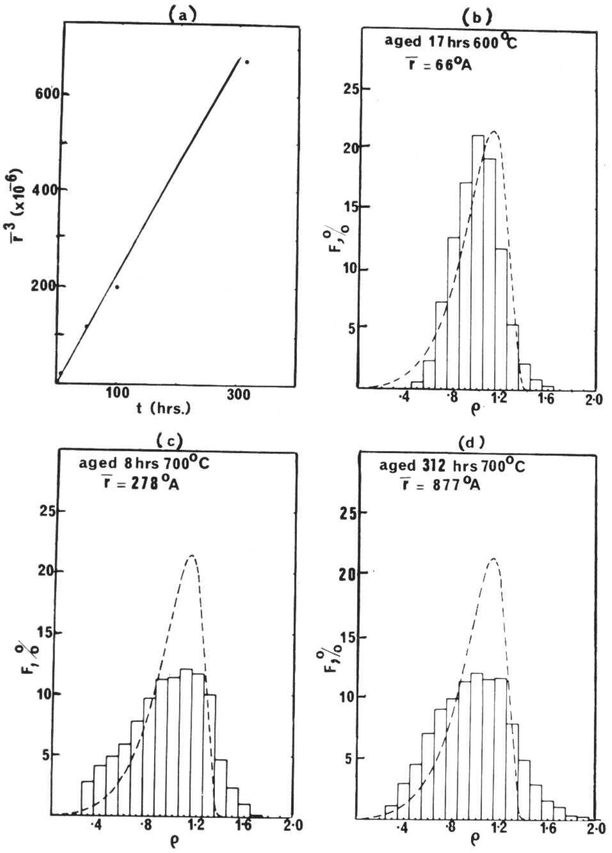

Fig. 2(a) *Precipitate-coarsening data for ageing at* 700° *C* (*r in* Å); (b), (c), *and* (d) *particle-size distributions in which the volume frequency* (F) *is expressed as a function of* ρ.

the error is then reduced to negligible proportions if sufficient care is taken. A second possibility is that not all the particles within a given area were extracted. However, this will not affect the distribution if the sample extracted is representative of the actual distribution. Examination of Au–Pd-shadowed replicas suggested that the extracted distribution was in fact representative of the surface distribution. Finally, the probability of intersecting a particle, and hence the probability of extracting it, is proportional to its diameter; there is therefore less probability of picking up the finer particles. Although an attempt has been made to correct for this in the determination of $\bar{r}$ by the use of Ashby and Ebeling's formula, the effect is still evident in the distribution curves as a lack of very fine particles.

This last source of error involves only the smallest particles, which represent a very low percentage of the total number of particles measured; the effect on the measured values of the mean particle radius ($\bar{r}$) will therefore be of little significance. The excellent agreement with the theoretical growth law also suggests that the measured values of $\bar{r}$ are accurate. It is possible, nevertheless, that the shape of the distribution curves could be slightly altered by errors inherent in the replication technique, though these have been minimized. The values of ρ at the cut-off must be considered to be accurate, however, since these are governed only by $\bar{r}$ and the size of the largest particles observed. Thus, it is established that the value of ρ at the cut-off increases as ageing progresses, reaching a value of $\nless 2$ upon prolonged ageing. This finding is contrary to the theory of Wagner, which predicts that the distribution reaches a pseudo-static form with a cut-off at $\rho = 1{\cdot}5$.

Precipitate coarsening in the system investigated probably comes nearer to the ideal than in any other so far studied since the particles remain spherical over a very wide range of particle sizes. This has allowed coarsening to be observed over a wider range of particle sizes than is usually possible.

Acknowledgements

The authors wish to thank Professor A. G. Quarrell for the provision of research facilities and a scholarship for one of them (E.N.B.). Useful discussions with other colleagues are also gratefully acknowledged.

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Research Note

Effect of Matrix Structure on Carbide Coarsening and Transformations

W. E. Stumpf and C. M. Sellars

In previous work[1] it was shown that at 700° C the coarsening rates of cementite and of the chromium carbides M_3C and M_7C_3 are significantly higher in as-tempered steels than in the same steels when the matrix has been recrystallized after cold work. The as-tempered steel has a very fine grain size and, at times of > 5 h, a well-recovered dislocation substructure linking practically all the particles (Fig. 1(*a*)), while the recrystallized steel has a much larger grain size with a very low dislocation density in the matrix (Fig. 1(*b*)). To isolate the respective contributions of the fine grain size and the substructure to the enhanced coarsening rate of cementite in the as-tempered steel, stable substructures were deliberately introduced into the recrystallized and the as-tempered steels by an 11% creep deformation at 700° C before further tempering. The resulting structure is shown in Fig. 2.

Manuscript received 3 July 1968. C. M. Sellars, B.Met., Ph.D., is in the Department of Metallurgy, University of Sheffield, where the work was carried out. W. E. Stumpf, B.Sc., Ing.Met., Ph.D., is now with the Atomic Energy Board, Pretoria, South Africa.

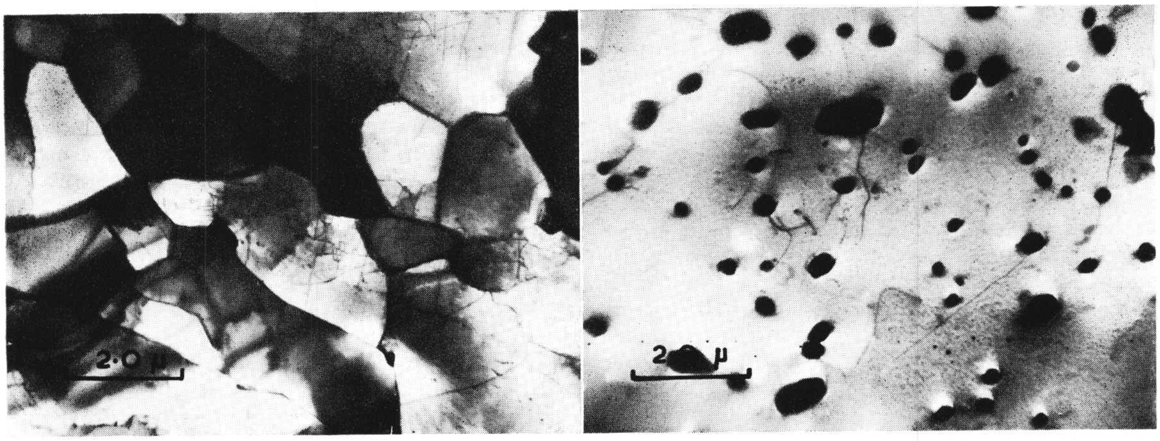

Fig. 1 *Thin-foil micrographs of a* 0·21% *plain carbon steel:* (a) *tempered,* 10 *h at* 700° *C;* (b) *tempered* 1 *h, then cold swaged* 27% *and tempered* 4 *h at* 700° *C to recrystallize the matrix.*

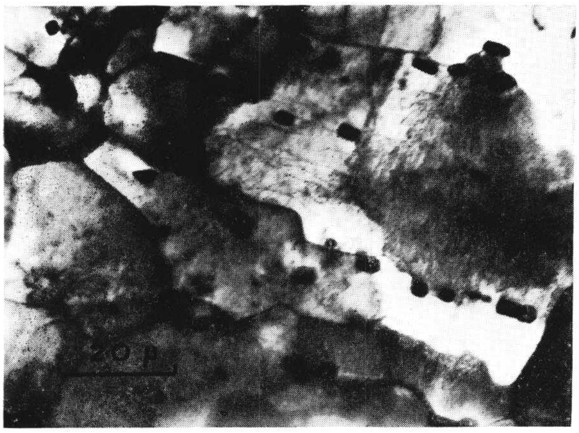

Fig. 2 *Thin-foil micrograph of* 0·21% *plain carbon steel recrystallized as in Fig.* 1(b), *then creep-deformed* 11% *at* 10,500 *lb/in*^{2} *and* 700° *C.*

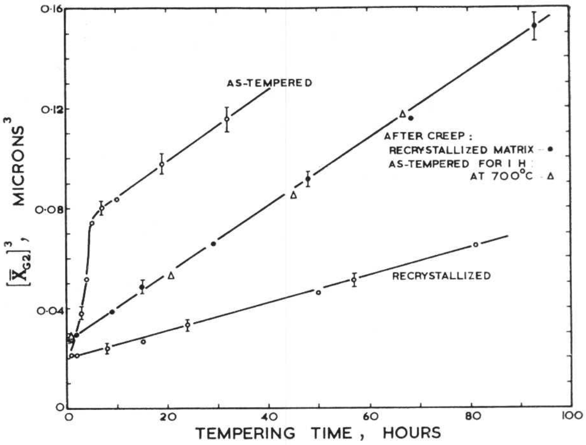

Fig. 3 *Relation between the cube of the geometric volume mean particle diameter and tempering time at* 700° *C for* 0·21% *plain carbon steel with different matrix structures.*

Fig. 3 shows the coarsening rate of cementite at 700° C in these different matrix structures. In the as-tempered steel, a transitional period of very rapid coarsening is found initially, which is followed by a much slower rate of coarsening after ~ 5 h. This slower rate is, nevertheless, still about 2·5 times faster than that in the recrystallized steel. The very rapid rate of coarsening during the early stages of tempering is associated with rapid recovery of the unstable dislocation structure inherited from the martensite to form a stable substructure. This stage is completely suppressed by creep deformation. The coarsening rate of cementite after creep deformation is independent of grain size and is similar to that in the later stages of coarsening of the as-tempered steel. This indicates that the enhanced coarsening in the as-tempered structure is due mainly to the presence of a recovered substructure linking all the particles.

Observations on a 1·2% Cr steel also show that the time for the start of transformation of M_3C to M_7C_3 at 700° C is retarded from 750 h during normal tempering to > 1500 h when the matrix is recrystallized. This was determined by electron diffraction from extracted carbides, but is also borne out by particle-size measurements as shown in Fig. 4. In the as-tempered steel, the coarsening of M_3C at times of < 750 h occurs very rapidly because of an unstable matrix

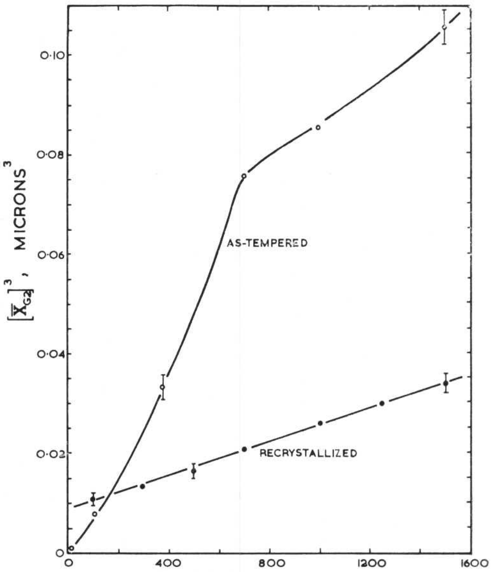

Fig. 4 *Relation between the cube of the geometric volume mean particle diameter and tempering time at* 700° *C for* 1·2% *Cr,* 0·2% *C steel.*

structure. At ~ 750 h, however, when the first M_7C_3 was detected, the measured coarsening rate slows down significantly. In the recrystallized matrix, no such reduction in coarsening rate was found and no M_7C_3 was detected even after 1500 h tempering at 700° C. The start of transformation in an as-tempered steel, therefore, depends significantly on the presence of an unstable dislocation structure.

By considering the effects of solute additions or concurrent creep on the recovery of the dislocation structure in as-tempered steels, this observation of the large effect of matrix structure on the start of transformation allows a consistent interpretation of some of the reported results.[2–5] If recovery of the initial complex dislocation structure is accelerated by creep (as was found to occur by creep deformation of the as-tempered plain carbon steel, Fig. 3) and is complete before the transformation starts, then the transformation could be retarded compared with that under static tempering conditions. If, on the other hand, the transformation starts during the initial accelerated recovery period, then the transformation could be accelerated. This suggests that the effect of creep would depend markedly on whether the transformation initiates during the primary or secondary stage of creep. Unfortunately, workers have not published creep curves that will allow this to be checked. However, Nileshwar and Quarrell[4] found that retardation of the $Cr_7C_3 \rightarrow Cr_{23}C_6$ transformation was a maximum at an intermediate creep rate and decreased progressively as the creep rate was increased or decreased from this value. This is consistent with the effects expected in the matrix: as stress increases from low values, the amount of recovery of the initial structure before the start of transformation should increase progressively, leading to increasing retardation. At higher stresses, the dislocation structure and continuing dynamic recovery introduced by creep become of greater significance, resulting in a progressive decrease in the retardation.

To separate the intrinsic effects of solutes or creep deformation from those of recovery of the initial dislocation structure, further work on recrystallized steels is required.

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Research Note

Influence of Concurrent Deformation on Coarsening of Carbides

T. Mukherjee and C. M. Sellars

It has been established that carbide particles in a recovered matrix coarsen more rapidly than in a recrystallized structure.[1] During rapid recovery in the early stage of tempering of a plain carbon steel at 700° C, the coarsening rate of Fe_3C is an order of magnitude more rapid than when a well-formed substructure is present, indicating an important dynamic enhancement effect. Similarly, during recrystallization after cold work, a significant increase in particle size occurs. This note reports results on the influence of concurrent deformation on carbide coarsening in as-tempered and recrystallized chromium steels.

Tests were conducted in tension and in torsion at 700° C in an inert atmosphere on 0·87%, 4·2%, and 6·1% Cr, 0·2% C steels which had been tempered at the same temperature. Tensile tests were carried out at a constant cross-head speed of 0·1 cm.min^{-1} (initial strain rate $1{\cdot}3 \times 10^{-3}$ sec^{-1}) and torsion tests at constant speeds of 0·25–300 rev/min (equivalent true strain rates $1{\cdot}9 \times 10^{-3}$–$2{\cdot}3$ sec^{-1}). Torque/revolutions curves were converted to true stress/true strain curves using established criteria.[2] All specimens were quenched immediately after testing and carbide sizes were determined as described previously[1] from extraction replicas taken from the gauge-lengths and heads of the specimens.

Typical stress/strain curves are shown in Figs. 1 and 2. The steels tempered for 10 or 100 h, which had a complex matrix structure inherited from the martensite, showed work-softening under both testing conditions. Optical micrographs revealed little change in matrix structure after deformation, but in steels tempered for 10 h the room-temperature proof stress was reduced by 1/3 by 10% prior strain at 700° C, indicating that accelerated recovery occurred during the work-softening. Necking in tension (broken portions of the curves) was observed only after extensive work-softening had already occurred. The 0·87% Cr steel after tempering for 1000 h had a structure that optically appeared to be recrystallized[1] and showed initial work-hardening similar to that in the recrystallized steel.

The coarsening rates for M_3C and M_7C_3 in the 0·87% and 6·1% Cr steels, respectively, are shown in Fig. 3. From the data it is not certain whether time or strain is the more significant parameter, but a linear relationship between the cube of the particle diameter and time has been assumed to allow comparison with the coarsening rates during static tempering. The calculated coarsening rates are summarized in Table I, from which it is evident that at normal tensile strains concurrent deformation enhances the coarsening rate by ~ 3 orders of magnitude. At the strain rates involved, the excess-vacancy concentration is too small to play a significant role in this enhancement. It is therefore concluded that dislocation movement is responsible, though

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Manuscript received 3 July 1968. C. M. Sellars, B.Met., Ph.D., is in the Department of Metallurgy, University of Sheffield, where the work was carried out. T. Mukherjee, B.E.Met., Ph.D., is now with English Steel Corporation, Ltd.

TABLE I

Comparison of Carbide-Coarsening Rates during Static Tempering and during Tensile Deformation at 700°C

Steel	Heat-Treatment	Carbide	Coarsening Rate ($10^{-8}\mu^3$.sec^{-1}) Static	Dynamic	Dynamic Rate / Static Rate
0·87%Cr	Tempered 10 h	M_3C	2·56*	1400	550
0·87%Cr	Recrystallized	M_3C	0·496	540	1100
6·1% Cr	Tempered 10 h	M_7C_3	0·525	1200	2300
4·2% Cr	Recrystallized	M_7C_3	0·0903	890	9900

* Tangent to $\bar{x}_{G2}^3$ vs. time curve at 10 h as this plot is non-linear.

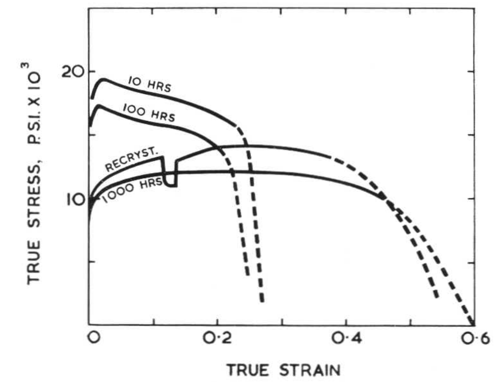

Fig. 1 *Tensile stress/strain curves at 700° C for 0·87% Cr, 0·2% C steel after tempering for different times and after tempering for 10 h, cold swaging 51% reduction, and further tempering for 21 h to give a recrystallized matrix structure.*

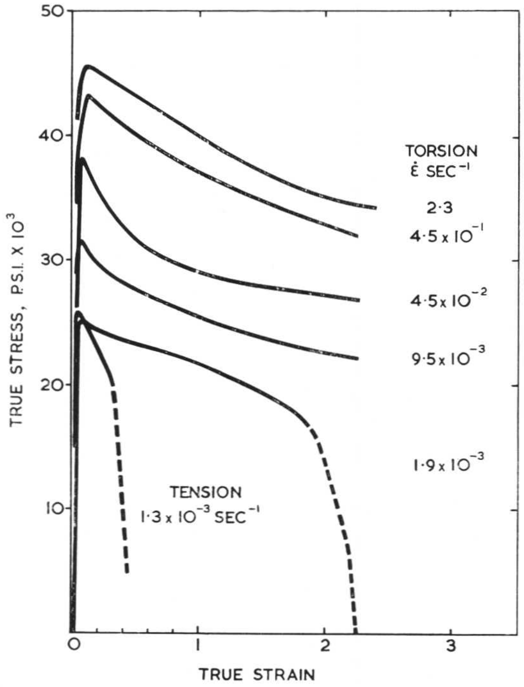

Fig. 2 *Torsional and tensile stress/strain curves at 700° C for 6·1% Cr, 0·2% C steel tempered for 10 h.*

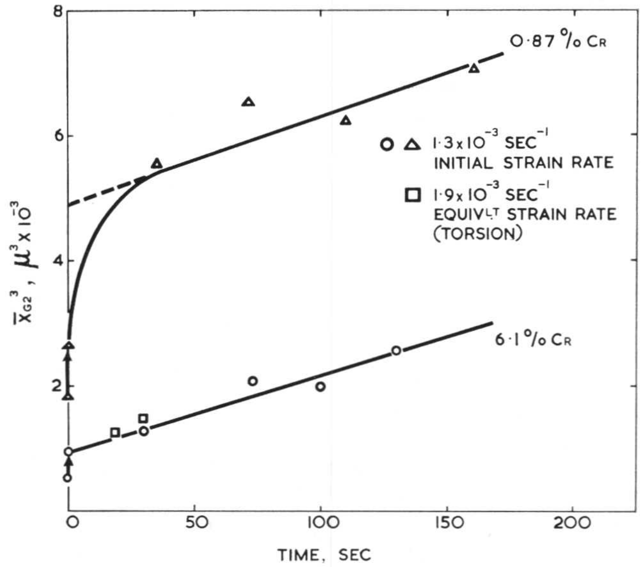

Fig. 3 *Relationship between the cube of the geometric volume mean particle dia. and time during deformation at 700° C of 0·87% Cr, 0·2% C and 6·1% Cr, 0·2% C steels tempered for 10 h. Arrowed points at zero time show size before reheating.*

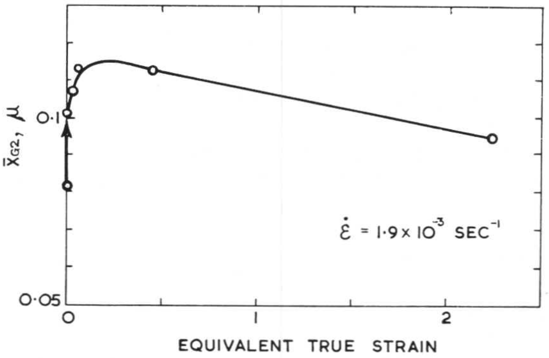

Fig. 4 *Change in geometric volume mean particle size with strain during torsion testing at 700° C of 6·1% Cr, 0·2% C steel tempered for 10 h.*

the mechanism is not clear. The enhancements in the recrystallized steels are greater than in the as-tempered steels, as might be expected because the static coarsening rates are enhanced in the latter by the presence of an unstable dislocation substructure. However, as greater dislocation rearrangement, resulting in work-softening, takes place in these steels, the differences cannot be simply interpreted.

The effect of higher strains in torsion on particle size is shown in Fig. 4. After the initial enhanced coarsening, similar to that in tension, the particle size decreases with strain so that the size after a strain of 2·25 is similar to the initial size. Identical observations were made after this strain at all the strain rates examined. This unexpected effect of large strains is similar to the decrease in particle size observed at large total strains in fatigue at 700° C and found to be associated with resolution of some of the carbides.[3] In neither case can this be accounted for by general adiabatic heating due to deformation as this is very small at most of the strain rates involved.

A further point of note from the results shown in Figs. 3 and 4 is that reheating the specimens for testing (heating rate $\sim$ 20 degC. min^{-1}) causes a significant increment in carbide size. As specimens were quenched after prior tempering, this effect can be associated with general precipitation of excess carbon on the existing carbides during the early stages of reheating, followed by preferential dissolution of the smaller carbides during the later stages to obtain the equilibrium carbon in solution at 700° C. This effect is not observed when specimens are reheated rapidly in a lead bath, but could be of considerable importance at thermal cycling rates which may occur in commercial applications. Combination of thermal cycling and deformation could then cause a very marked reduction in the stability of the structure.

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Discussion

Professor M. Hillert (Royal Institute of Technology, Stockholm, Sweden): I would like to comment on this systematic fluctuation in particle size near grain boundaries suggested by Professor Greenwood. I suppose that the distance between the particles is usually much smaller than that expected for a random-walk distance during this process and that is why you do not get these fluctuations. One would expect the fluctuations if a particle is aware only of its closest neighbours. We did experiments on this some years ago and, as expected, we found that close to the grain boundary, where the larger particles occur, you get a zone that is free of particles and, of course, the width of this zone increases with time. The width of the zone is much greater than the average distance between the particles.

Professor G. W. Greenwood (University of Sheffield): I appreciate that this fluctuation should be quite small, but I mentioned it to show that there may be some circumstances in practice that require a theory quite different from one which deals with an overall statistical pattern where there is no size-distribution difference in different regions. Although I agree that there will be a zone denuded of particles near the grain boundary, there is some protection, as it were, for the particles not adjacent to the denuded zone. Particles in one plane would tend to grow and particles in the next plane would tend to dissolve, and so on. The rates of dissolution and of denuded-zone growth would not be quite as rapid as one would imagine, because any particle that dissolves provides so much solute concentration that there would have to be some simultaneous local growth that would slow up the denuded-zone growth. Any experimental details of the kinetics of denuded-zone formation would be very exciting but I agree with your comment that the diffusion distance is generally very much greater than the separation between particles and that is why this systematic size variation should be a rather small effect.

Professor V. Gerold (Max Planck Institute, Stuttgart Germany): I should like to ask a question on the general theory of particle coarsening, referring to equation (3) in the paper by Professor Greenwood. In this equation the rate of volume change of the particle is related to the solute concentration gradient near its surface. In my opinion this equation must include the solute volume fraction in the particle because it influences the rate. So if X is the solute fraction inside the particle one has to multiply the left-hand side of this equation by this factor X and this finally appears in equation (22) as a factor $1/X$ on the right-hand side.

Professor R. B. Nicholson (University of Manchester): In all the γ' systems one uses equation (1) of Greenwood's paper and puts the molar volume of Ni_3Al instead of the atomic volume, so that you consider a solution of moles of Ni_3Al in nickel, not aluminium in nickel. Then you can use equation (1).

Professor Greenwood: This is correct but there are other complicating factors when one considers particles containing two components. For example, we have not argued about the actual value of Ω in the equations. Now, Ω is just taken to be an atomic volume, the atomic volume of any atom in the particle being exactly that of the solute atom in the matrix. We leave out conditions of strain and we leave out conditions of change in diffusivity, but I think it is fair to say that in most of the systems examined the approximations are justified, since the solubility of the particles is fairly small.

Professor J. Nutting (University of Leeds): On the same point about the use of Ω, one is really using the Thomson–Freundlich equation which is derived from a consideration of droplets in equilibrium with their vapour. The parameter Ω is then the molecular volume of the species with which you are concerned. I would have thought that this parameter Ω has no real physical significance in the solid-state situation.

What one should be concerned with is the change in molecular volume associated with the transfer of a solute element from the dispersed phase to the continuous phase. This, of course, gets you into all sorts of difficulties subsequently, when you start considering the growth of phases where changes in volume can occur that lead to strains associated with growing particles and problems arise of absorbing vacancies near particles that are shrinking.

Professor **Greenwood**: I was simplifying by putting Ω in terms of atomic volume. I generally like to think that all atoms are of very nearly the same size. People do, in fact, tend to assume that the equations are far more rigorous than they really are.

I would strongly disagree that Ω has no significance; it is true, however, that equation (1), as I have written it, is really strictly true only: (1) for a particle having atoms of the same size as the matrix, (2) where there are just two components in the system, and (3) if the particle consists entirely of one species of atoms. My justification for doing this is that once one considers strain and mutual solubility, differences in atom sizes, solubility dependent on solute concentration, and the diffusion-dependence of both solute concentration and strain, the modification equation (1) to incorporate gram molecular volumes will not really ease the situation.

Professor J. W. **Cahn** (Massachusetts Institute of Technology, Cambridge, U.S.A.): Surely equation (1) is just a simple equation of thermodynamic equilibrium with certain approximations in it. If we take $kT\log(S_r/S)$ and replace it by the chemical-potential difference between the actual solid solution and a saturated solid solution and replace Ω by the partial molar volume in the particle, which is also a precise quantity, then I think there is one other approximation and that is that the material inside the particle is effectively incompressible and that we are dealing with a particle in a fluid. Then equation (1) is absolutely precise and rigorous thermodynamically. So it is not at all difficult to generalize this to any number of components and it is only a little bit more difficult to generalize it to the case where one solid is within another solid. But we are, after all, dealing here with a thermodynamic equilibrium and that was settled precisely many, many years ago.

Dr. J. **Barford** (Central Electricity Research Laboratories, Leatherhead): May I attempt to put this topic in its true historical perspective by pointing out that in 1921 Professor F. C. Thompson, late of the Manchester University Department of Metallurgy, used equation (1) in Greenwood's paper to determine the interfacial energy between iron carbide and iron.*

Secondly, Professor Greenwood indicated in his introductory paper that there is no experimental proof of the theory for particles growing on grain boundaries. There is some work by Day and myself on the growth of iron carbide in iron,† in which there appeared to be a change in the time-dependence of the growth of particles from a cubic relationship in the early stages to a quartic relationship at later stages. This was observed at a temperature of 675° C. On ageing at high temperatures one observes a cube relationship throughout the same time period. I would stress that this is the only indication that we have so far found that a grain-boundary growth mechanism of the kind proposed recently by Speight‡ might occur in a solid system.

Professor **Hillert** (*written discussion*): It may be worth while pointing out that the Thomson–Freundlich equation, which constitutes the theoretical basis for particle coarsening, also enters into the theory of ordinary precipitation and eutectoid reactions. In that field it is often necessary to consider systems where the matrix has a high solute concentration and the precipitate contains both elements. A generalized Thomson–Freundlich equation must then be used. A convenient approximate form is given by equation (7) in my paper at this conference. Using the relation

$$\Delta G^{\beta} = p^{\beta} V_m{}^{\beta} = 2\sigma V_m{}^{\beta}/r$$

for spherical particles, we obtain

$$(X^{\gamma} - X_e{}^{\gamma})/X_e{}^{\gamma} = 2\sigma V_m{}^{\beta}/rRT[X^{\beta} - X^{\gamma}(1 - X^{\beta})/(1 - X^{\gamma})]$$

The ordinary Thomson–Freundlich equation may thus be generalized by dividing by the term in the bracket, where X^{β} and X^{γ} represent the mole fraction of the solute in the precipitate phase, β, and the matrix phase, γ, respectively.

It may also be worth while pointing out that the ordinary Thomson–Freundlich equation is derived assuming that the pressure difference due to capillarity is acting on the precipitate particle only and thus $p^{\beta} = 2\sigma/r$. This is true when the matrix phase is a liquid. In solid-state systems, on the other hand, the matrix phase could carry part of the pressure difference. In this case, equation (10) in my first reference§ yields a more generalized equation,

$$\begin{aligned}(X^{\gamma} - X_e{}^{\gamma})/X_e{}^{\gamma} = {} & p^{\beta} V_m{}^{\beta}/RT[X^{\beta} - X^{\gamma}(1 - X^{\beta})/(1 - X^{\gamma}]) \\ & + p^{\gamma} V_m{}^{\gamma}/RT[X^{\gamma} - X^{\beta}(1 - X^{\gamma})/(1 - X^{\beta})]\end{aligned}$$

where $p^{\beta} - p^{\gamma} = 2\sigma/r$ for spherical particles. Unfortunately, it seems very difficult to predict the individual values of p^{β} and p^{γ}. For example, a large difference in diffusivity of the two elements in a binary system may result in a local increase or decrease of the overall pressure at the precipitating particle, an effect related to the Kirkendall effect. The precipitation of graphite from austenite or ferrite provides a striking example of this case and the more generalized form of the Thomson–Freundlich equation was applied in an attempt to account for the rate of graphitization in ferrous materials.‖

Dr. F. G. **Wilson** (British Steel Corporation, Rotherham): Hall and Haworth find the diffusion coefficient, D, to be independent of concentration, but in the Al–Cu system it has been found that D varies by a factor of 2 with composition.¶ How do you account for this?

Dr. C. W. **Haworth** (University of Sheffield): I think it varied by about a factor of two over a rather larger range of composition. Here the total range of composition is only $\sim 2\%$.

Dr. **Wilson**: Do you get a Kirkendall effect?

Dr. **Haworth**: Yes, but we have not included it here.

Dr. H. I. **Aaronson** (Ford Motor Co. Research Laboratory, Dearborn, U.S.A.): In support of Hall and Haworth's results, Murphy** collected all the interdiffusion data on the

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* F. C. Thompson, *Trans. Faraday Soc.*, 1921, **17**, 391.

† R. V. Day and J. Barford, *Nature*, 1968, **217**, 1145.

‡ M. V. Speight, *Acta Met.*, 1968, **16**, 133.

§ M. Hillert, *Jernkontorets Ann.*, 1957, **141**, 747.

‖ M. Hillert, *ibid.*, p. 67.

¶ F. N. Rhines and R. F. Mehl, *Trans. Amer. Inst. Min. Met. Eng.*, 1938, **128**, 185.

** J. B. Murphy, *Acta Met.*, 1961, **9**, 563.

α phase in Al–Cu and added some of his own very carefully produced data and it looks as if, in the composition range of interest, there is not a great deal of variation of the interdiffusion coefficient with composition.

Dr. N. SEN (Imperial College, London): I should like to ask Mr. Bower what is the effect of titanium on the diffusion coefficient?

Mr. E. N. BOWER (University of Sheffield): There are so few data available on this system that we are unable to answer this at present and since we do not know the diffusion coefficient—in fact we do not even know the solubility—it is impossible at this stage to work out the surface energy.

Professor NUTTING: Could the errors mentioned in your paper be avoided by using surface rather than extraction replicas? With an extraction replica it is extremely difficult to get good quantitative results, whereas with a surface replica and some fairly elementary statistical treatment of the results afterwards, accurate results can be obtained.

Mr. BOWER: It is possible, but because of the complexity of this system we have had in any case great difficulty in preparing replicas.

Dr. L. DELAEY (University of Leuven, Belgium): In the paper by Mukherjee and Sellars the deformation velocities are rather small compared with those in industrial deformation processes. What happens with high strain rates, and can the authors give a procedure to obtain very fast spheroidization of pearlite in wire and plate material?

Dr. C. M. SELLARS (University of Sheffield): We have, in fact, observed fast spheroidization, not in these steels, of course, because they are not pearlitic. We have looked at a wide range of strain rates in torsion, which go up to commercial working rates, but one certainly gets very little overall effect. We have not yet studied the effect of increments on strain. That is why I was very careful to plot particle size against time only during deformation.

Mr. K. THOMAS (National Physical Laboratory, Teddington): Has the author tried this method on any system that failed to give these effects?

Dr. SELLARS: No. At the moment we have worked only on the tempered chromium steels and we seem to get similar effects independent of the chromium content, so that presumably they occur in all the chromium carbides. Whether this is a peculiar property of carbides or not, I would hesitate to say.

Dr. J. KITTL (Comision Nacionale Energia Atomica, Buenos Aires, Argentine): The effect described could also be due to changes in diffusion in the matrix. In all the models considered in the paper you assume volume diffusion, but on going to low temperatures other diffusion modes could exercise more influence. Recent work* has shown that other diffusion modes could be of importance at low temperatures.

Dr. SELLARS: We have not gone below 600° C in these experiments and although we have not measured any activation energies during deformation, as yet in the different structures described in our paper, we have found an activation energy of $\sim$ 60 kcal g-mole^{-1}, independent of whether there is a substructure or not. Therefore we feel that the coarsening is diffusion-controlled by a self-diffusion process in the temperature range in which we are concerned, even when a dislocation structure is present. When a static dislocation structure is present it looks as if the factor of $\sim 2\frac{1}{2}$ increase in coarsening rate could be accounted for by an increased solubility of carbon in the region of dislocations. That is why I say that these effects may be rather peculiar to carbides. I do not think we can talk in terms of this sort at all for an enhancement factor of 1000 or more during concurrent deformation, and any suggestions as to a plausible mechanism would be welcome.

Dr. R. D. DOHERTY (University of Sussex): Just a brief comment on Mr. Thomas's question about effects in systems other than those containing carbon. In a study with Dr. Martin on the recrystallization of two-phase Al–Cu alloys,† we found that, in alloys that had been rolled 60% and then annealed at 300° C, the θ phase coarsened very much faster than in the undeformed structure. We observed this effect under static conditions and thought that the dislocations between the particles had provided short-circuit paths for diffusion, but there was no real evidence of this.

Dr. SELLARS: In your case did this treatment not change the particles from coherent to incoherent?

Dr. DOHERTY: No, they were all aged at over 400° C to start with, so the θ particles were incoherent.

Dr. SELLARS: I am very interested to hear that you got the effect in Al–Cu. There is another point that tends to eliminate dislocation enhancement. If one has sub-boundaries through which the diffusion is occurring, then the kinetics of the equation should be altered and would probably tend to r^4. I agree that it is very difficult to distinguish between an r^3 and an r^4 law from experimental points, but we feel that we are still getting results that follow quite closely an r^3 law.

Mr. L. G. T. DAVY (University of Birmingham): I am afraid all I can do is to throw a bit of confusion into this discussion. Figs. D.III.1 and D.III.2 show some of the effects of alloy additions and substructure in Fe–Mn–C alloys. The heat-treatments were all the same. Alloy (*a*) shows considerable greater particle growth than alloy (*b*), which has a slightly higher manganese content. Alloy (*c*), containing 1% Mn, shows even less particle growth and alloy (*d*), with 2% Mn, has very small particles. This shows the effect of alloy content, but what is perhaps more significant is that there is a changeover in behaviour on rolling. For low manganese content the tempered and rolled specimens coarsen much more rapidly than those of higher manganese contents, whereas at the higher manganese contents, undeformed specimens (i.e., just tempered martensite) coarsen more rapidly than the rolled specimens. So there is a reversal in the effect of alloy content induced by prior deformation.

Mr. N. E. RYAN (University of Oxford): This question is directed to Dr. Sellars and concerns the refinement of particle sizes at high strains. I should like to suggest that you are actually getting resolution and perhaps reprecipitation during these processes.

Dr. SELLARS: As regards Mr. Davy's comment I think the effect of manganese is analogous to that of chromium when we still have M_3C as the carbide. The first small addition of chromium reduces the coarsening rate of Fe_3C or M_3C.

Answering Mr. Ryan's question about possible dissolution, in the fatigue work we have carefully measured the volume fraction and density of particles, and this is precisely what happens. The volume fraction goes down, but the density of particles goes up, so one has dissolution and precipitation at the same time in a structure that looks very uniform in terms of dislocation density. The relation between these

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* A. F. Smith and G. B. Gibbs, *Metal Sci. J.*, 1968, **2**, 247.

† R. D. Doherty and J. W. Martin, *A.S.M. Trans. Quart.*, 1964, **57**, 873.

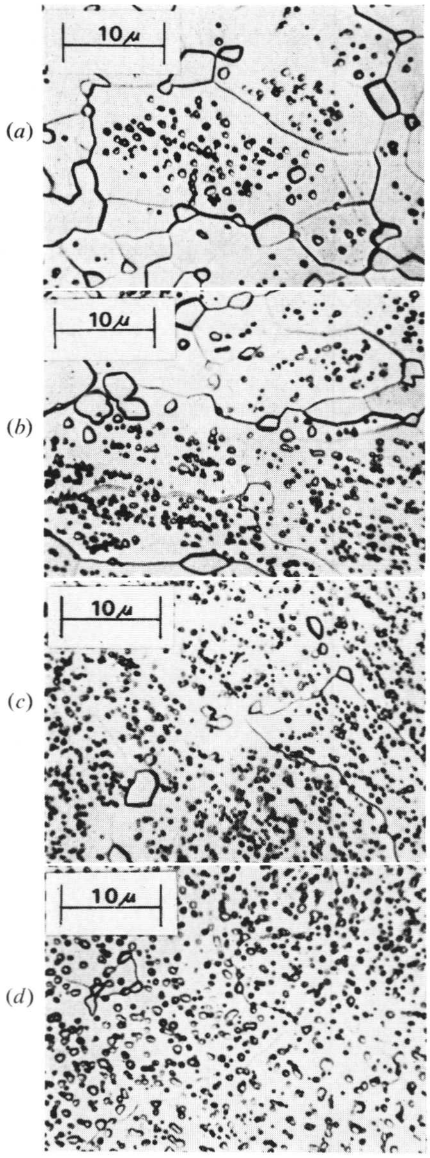

*Fig. D.*III.1 *The effect of manganese content on carbide particle size after* 10 *days at* 648° *C. The steels contained* 0·45% *carbon and:* (a) 0·23%, (b) 0·55%, (c) 1·13%, (d) 1·92% *manganese.* (Davy.)

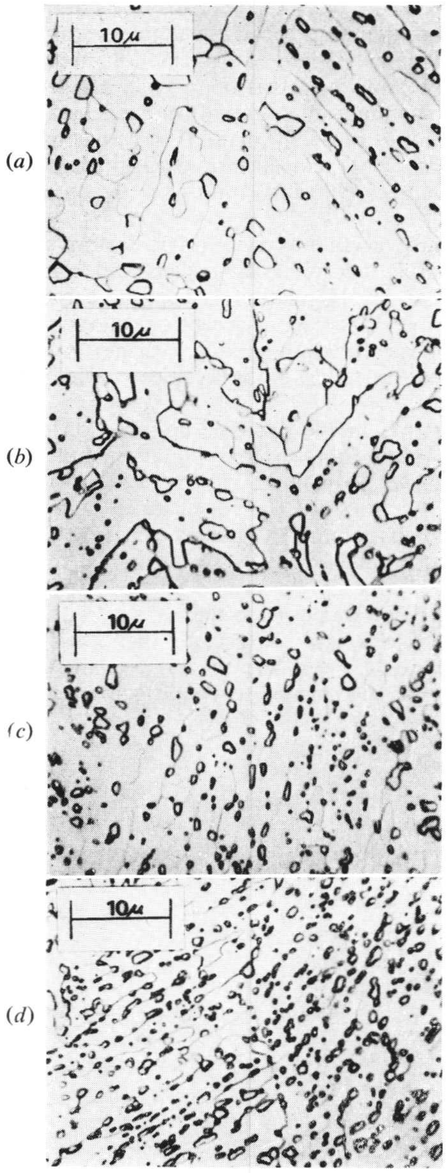

*Fig. D.*III.2 *As for Fig. D.*III.1*; specimens cold rolled* 50% *before coarsening treatment.* (Davy.)

individual precipitation and dissolution events and the dislocation structure is not clear.

Dr. D. H. Warrington (University of Sheffield): Could I ask Dr. Sellars what is the particle spacing in the torsion tests where this decrease in particle size occurs? Is it comparable with the slip-band spacing?

Dr. Sellars: The spacing is ~ 2 μm. At the moment I am quite happy to accept anybody's interpretation!

Mr. R. Hobbs (University of Manchester): I was surprised to learn from Stumpf and Sellars' paper that they found no difference in grain size between the tempered and recrystallized samples. I wonder whether this was because they were working at 700° C, a high temperature. Dr. Barford does mention that he found this effect only at lower temperatures.

Dr. W. E. Stumpf (University of Sheffield): Yes, I quite agree with that. As Dr. Sellars mentioned, we found the activation energy of ~ 60 kcal g-mole^{-1} for coarsening in a substructure, which indicates that between ~ 600 and 700° C there is no short-circuiting down sub-boundaries or grain boundaries. However, this may well occur at lower temperatures.

Professor Cahn: So very often the coarsening rate is much faster than expected from the Lifshitz–Wagner equation and this is usually reported as an absurdly high surface energy but it could, of course, equally well be a much larger diffusion coefficient. Is there ever agreement between theory and experiment? Are these experiments bad, or is it short-circuiting, or what is going on?

Professor **Greenwood**: I should like to take up this question of short-circuiting because I agree with Dr. Sellars that some dynamic aspect of deformation needs to be invoked. The reason for this is that, while it is true that dislocations can conduct solute rapidly and efficiently, there is a high constraint because the path is very narrow. I think that at almost all the temperatures used in the papers under discussion lattice diffusion must be the predominating mechanism.

Consequently, I was interested in Dr. Barford's comments, which do suggest that he has been successful in getting some indication that the r^4 relation is correct, because I think it is a case where one cannot accept one theory without the other. I believe the grain-boundary theory is every bit as watertight as the lattice-diffusion theory which gives the r^3 relation.

I consider that in the dynamic deformation experiments we are in a much more exciting situation, but one that is also more difficult to analyse.

Professor **Nicholson**: Can I make a comment about Professor Cahn's point? I think one can see two classes of behaviour here but it depends on what one means by an absurdly high value of the surface energy. In most of the systems where one gets a value that is, say, within an order of magnitude of what is expected, the other parameters that can be used to test the theory, e.g. the particle-size distribution, also give moderately good agreement. I believe that in this situation we have really just made minor mistakes in assessing the precise magnitudes of the parameters in the Lifshitz–Wagner equation, particularly for non-spherical particles. However, there is also a completely different set of results where one is incorrect by several orders of magnitude. Here, other tests of the theory, such as particle-size distribution, fail miserably. For instance, in the θ'/Al system which Boyd and I investigated,* the size distributions are skewed in the wrong direction and I do not feel that one is justified in applying the Lifshitz–Wagner equation and then saying that some parameters are wrong by several orders of magnitude. I feel that if the particle-size distributions are so far from those predicted, one really has no right to apply the analysis at all and so get apparently absurd values of the surface energy. Some other analysis is required. Quite why these size distributions are produced in certain situations is difficult to explain. My own feeling at the moment is that it may be the sort of situation that Dr. Aaronson† has looked at in the θ' case where, although growth is not diffusion-controlled, neither is it interface-controlled in the meaning of the Lifshitz–Wagner formulation. One has some rather complex local-diffusion situation occurring around the particle itself.

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* J. D. Boyd and R. B. Nicholson, to be published.

† H. I. Aaronson and C. Laird, *Trans. Met. Soc. A.I.M.E.*, 1968, **242**, 1937.

Session IV

Martensitic Transformations: A Current Assessment

J. W. Christian

Most of the work summarized in this paper has appeared since the 1965 Scarborough Conference on Martensite and Bainite. The topics include the significance of a shape change and its relation to a lattice correspondence; the pre-existing-embryo and the lattice-defect theories of nucleation; the effects of pressure on transformations and substructures; the present status of the crystallographic theories; the fine structures of various types of martensite; the significance of the dilatation parameter; the nature of the interface; thermal stabilization; reverse transformation from martensite to austenite; and transformation induced by shock waves. The importance of autocatalytic nucleation is emphasized, and it is concluded that there is little evidence to support the embryo theory. Although the crystallographic theory has had some notable successes there are still many unsolved problems, and the fine structures revealed by electron microscopy are frequently more complex than expected.

In this paper, I shall attempt to survey recent progress in the theory of martensitic transformations, with especial attention to work that has appeared since the 1965 B.I.S.R.A. Conference on Martensite and Bainite at Scarborough. The definition of a martensitic transformation will be taken to be the existence of a lattice correspondence with no diffusive mixing of the atoms other than the shuffles needed to complete the structural change.[1] I shall also discuss some work on non-martensitic military transformations, but these will not be considered in detail in view of Aaronson's separate paper on bainitic changes.[2]

Many review articles dealing both with the crystallography of martensite[1,3–9] and the kinetics of martensite formation[1,3,9–13] have been published, and it is not my intention to cover this familiar ground again. However, it is worth recalling that the currently accepted theories of crystallography were published less than 15 years ago, and that the first electron micrographs to show the fine structure of martensite were obtained less than 10 years ago. Thus the whole subject is still very much in a state of transition, and any selection of important topics and problems must necessarily reflect to some extent the writer's personal prejudices.

At the Scarborough Conference, much of the discussion centred around problems of morphology and fine structure. The confusion that had arisen from different usages of the terms " massive structure " and " massive transformation " was clarified considerably,[1,14–15] although no-one signed a convention on future terminology. The old distinction between *schiebung* and *umklapp* martensite in iron–nickel alloys was revived, and attention was directed to further problems arising from the identification of a surface transformation.[14,16] Among the many difficulties revealed by recent investigations of fine structure, mention might be made especially of the very irregular interfaces found in untwinned or partially twinned {259} plates of Fe–Ni martensite.[14]

Kinetics was not neglected at Scarborough, but progress has been less rapid, and early hopes that electron microscopy would give direct information on nucleation processes have proved to be too optimistic. It appears likely, however, that the theory of the kinetics of martensite formation will be relatively much more important in the present conference, and I shall attempt to give it correspondingly greater weight in this introduction.

The Lattice Correspondence, the Atomic Shuffles, and the Shape Change

It has generally been assumed, though without formal justification, that any lattice correspondence which is maintained during the growth of a phase will be characterized by small values of the principal strains of the lattice deformation, and specifically that the preferred correspondence will be that for which $\Sigma\eta_i^2$ is a minimum, where η_i are the principal deformations.[17,18] In most military transformations this minimum-strain correspondence is obvious from inspection, but a trial-and-error procedure may have to be used in complex cases, for example in uranium alloys.[18] A further difficulty is that with large primitive cells only a small fraction of the atoms can be transferred from one structure to the other without additional shuffles, the number and complexity of which naturally increases with the size of the basic unit of transformation. Considerable progress has been made in classifying the main shuffles in twinning,[9,19,20] but the transformation problem is much more difficult because of the distinction between lattice and shape deformations. At the present time, we have little understanding of such shuffle mechanisms, even in relatively simple cases. Certainly the displacements must be very complex when there are 30 atoms involved, as in the structural transformation from β- to α-uranium. Further work on the kinetics of both nucleation and growth for this transformation in two uranium–chromium alloys containing

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0·16 and 0·2% Cr, respectively, has recently been reported by Bar-Or and Kimmel.[21] These workers believe that their growth results are consistent with a thermally activated shuffle mechanism, although it is not clear that other possibilities previously advanced to account for the slow growth can yet be eliminated.

In addition to the structural change from β- to α-uranium, there are many non-martensitic transitions involving thermally activated growth processes in which it is nevertheless believed that a lattice correspondence is maintained during growth. The observation of a change of shape in the transformed region is the generally accepted criterion for a military transformation of this type, but in view of Aaronson's stimulating and challenging remarks,[2] it is perhaps appropriate to re-examine this question. The personal view which I shall now develop is that a lattice correspondence may justifiably be inferred from a shape change, but only provided that the shape change conforms to certain conditions. The problems of interpretation may be illustrated by recalling Eshelby's series of virtual operations to produce a particle enclosed by a matrix.[22,9]

Let a region of whatever shape be cut out of the matrix and be transformed to a product by a lattice deformation. If this product is now reinserted into the hole by application of elastic stresses the two phases are coherent, but if atoms are transferred from some regions of product to others before reinsertion the phases are incoherent. A semi-coherent particle is obtained if the product is deformed by slip or by twinning before reinsertion, as in the theory of martensite crystallography. These are the only operations allowed if the number of atoms is conserved during formation of the new phase.

Unless the phases have the same specific volume, all three operations will produce a change of shape in the transformed region. Eshelby's calculations show that the strain energy per unit volume is large if there is appreciable misfit between product particle and matrix hole along any major dimension of the particle. Thus equiaxed shapes are likely only for small, fully coherent particles or for transformations with very small changes in volume.

Reasonably large particles for which there are measurable changes of shape on formation will generally be expected to be in the form of flat plates, with no appreciable change of dimensions in the plane of the plate. This ensures good accommodation of the product in the matrix, i.e. a reasonably low strain energy, and also implies that the observed shape of the product when constrained by the matrix is not very different from its unconstrained shape immediately before the virtual operation of reinserting it into the hole. Needle-shaped particles, which fit the matrix only along a line rather than over a plane, can be accommodated less readily in the matrix, and in principle should not be observed if there is a change of shape or volume. However, this theory applies only to a perfect lattice; conditions might be modified appreciably if the new phase grows on a dislocation because of the energy of the strain field of the dislocation.

It follows from the above discussion that *all* measurable shape changes of plate-shaped product regions are invariant plane strains, irrespective of whether the product is coherent, semi-coherent, or incoherent. However, if the particle is incoherent, only a component of strain normal to the plane of the plate should be observed, there being no shear component of shape deformation produced by unco-ordinated atom-by-atom growth. Thus, the observation of a shape change with an appreciable shear component indicates a lattice correspondence, although the converse is not necessarily true. It has perhaps not been sufficiently emphasized in the past that attempts to deduce transformation mechanisms from observations of transformation rumpling of a free surface are really justified only when the shape change has been measured carefully and shown to be of the expected type.

At high temperatures, atomic mobility may be sufficient for the transformation to be non-conservative. There are then additional virtual processes in which atoms are added to or removed from the product particle before reinserting it into the matrix. This should lead to incoherent particles with no shape change and no strain energy, but in principle semi-coherent particles could also be produced by the orderly addition or removal of planes of atoms from the product without further rearrangement.

Theories of martensite crystallography assume that the habit-plane interface is either fully coherent, or (more usually) is semi-coherent with discontinuities that can move conservatively with the interface in either direction. The interface motion is in principle glissile, although it may also be slow, for example in order–disorder changes of the military type. There is also the possibility that a semi-coherent interface might move by non-conservative processes (climb of interface dislocations) and this corresponds to the last of the virtual operations detailed above. If the lattice transformation contains a shear component on the habit plane, this would then remain in the observed shape change. Thus, the observation of a shear component allows the probable existence of a correspondence* to be inferred, but does not prove that the interface is of the martensitic (glissile) type. In a previous discussion of this question,[23] I suggested that it is improbable that crystals will grow non-conservatively in the manner just described. If atoms have to migrate through large distances as the interface moves, they should also be able to produce a net flow parallel to the interface, thus eliminating any shear component. This means that if the number of atoms is not conserved during growth, it is difficult for a correspondence to be maintained.

Laird and Aaronson[24] have recently investigated the dislocation structure of the broad faces of γ (h.c.p.) plates precipitated from the f.c.c. matrix of an aluminium–15 wt.-% silver alloy. They found the dominant structure to be partial dislocations of type $a/6\langle 112\rangle$ in edge orientation and arranged in: (1) parallel configurations with one Burgers vector, (2) intersecting configurations with two Burgers vectors, and (3) networks with three Burgers vectors. They propose that these dislocations accommodate the misfit between the two lattices, and also that they are unable to climb. The boundary structure is thus stated to be wholly immobile, and thickening of the plates is supposed to occur by a mechanism of formation and migration of ledges; the partial dislocations themselves are suggested as possible ledges. A surface-relief effect, stated to be of the martensitic type, was found to accompany the formation of the plates, and this is attributed to the " *de facto* climb " of the partial dislocations by the ledge mechanism. It is suggested that as long as a dislocation structure exists at an interphase boundary, displacement of the boundary will produce a shape deformation, which is described as a " geometric surface relief ".

This important but controversial paper raises many issues which I am forced to ignore, but which will perhaps arise in

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* Correspondence here means a correspondence of lattice sites, irrespective of the occupancy of these sites.

the discussion of Aaronson's paper.[2] In my opinion, the authors do not distiguish properly between localized regions of misfit in a planar interface (interface dislocations) and atomic steps or ledges (sometimes called transformation dislocations). Moreover, the restrictions on the climb of Shockley partial dislocations in a free lattice may not apply to dislocations that are correcting a mismatch in the interface. However, in the present context the important point about the observations is that they provide evidence of a shape deformation in a transformation that involves long-range diffusion, and in which (although the authors do not make this point) growth is presumably non-conservative. A similar difficulty in accounting for the reported non-ferrous " bainites " has previously been noted,[23] although the interface has been assumed to be martensitic in this case. It is clear that diffusional growth processes with accompanying shape changes are geometrically possible; the difficulty is to explain why this shape change is not automatically removed during growth since the atoms are so mobile. More definitive evidence of the nature of the shape change would now be welcome.

As Aaronson[2] points out, bainite in steels can be all things to all men, but the usual mechanistic description of this reaction,[1,2,9,25,26] supposes a lattice correspondence and a martensitic-type semi-coherent interface. This seems reasonable at low temperatures because of the low mobilities of individual iron atoms, and there is experimental evidence both that the shape deformation is of the required type and that the crystallography is in fair agreement with the martensite theory. On the other hand, a martensitic-type change is not so probable at the rather high temperatures at which pro-eutectoid ferrite can form, and it would be helpful to know whether the shape changes reported for this reaction meet the above condition of an invariant plane strain with a shear component.

We should next consider the possibility that a martensitic-type lattice correspondence is established in the early stages of a nucleation-and-growth reaction but disappears in the later stages of growth. There has been little work in this field since the paper on copper–beryllium alloys by Bowles and Tegart,[27] but an alternative recent suggestion is that a non-martensitic correspondence at the nucleation stage of a transformation may be inferred solely from the existence of an orientation relationship between product and matrix. Ryder and Pitsch[28] suppose that nucleation of a new phase may be described by the co-operative movement of a small number of atoms, i.e. by a homogeneous lattice deformation, and they assume that the nucleus is plate-shaped with the plane of the plate being an unrotated plane of the lattice deformation and containing one unrotated direction. In the interior of a grain, the unrotated plane and direction are chosen to be a close-packed plane and a direction of nearly equal repeat distance in the two lattices, but for grain-boundary precipitates the unrotated plane and direction are determined by the local boundary orientation. This gives a restricted range of possible orientations for any given correspondence. For f.c.c. → b.c.c. transitions, for example, the orientation relations must lie within 11° of the relation that is given by the Bain strain alone, i.e. parallelism of corresponding principal axes in the two structures.

In a recent investigation of precipitation on grain boundaries in a cobalt–20% iron alloy, Ryder, Pitsch, and Mehl[29] found that the precipitates had an orientation relation lying within the predicted Bain region for at least one and sometimes both of the austenite grains on each side of the boundary. This can scarcely be coincidental, since they estimate the probability of a random orientation lying within this region as only $\sim 4\%$. Thus, they conclude that a correspondence exists at the nucleation stage.

If an orientation relation, even with an appreciable spread, does signify an initial correspondence, this is of considerable interest in the general theory of transformations. It is of course quite plausible that many transformations begin with a coherent nucleus, although the special assumptions made by Ryder and Pitsch require more detailed justification. However, the assumption of a correspondence must remain speculative at present, since it is conceivable for there to be a preferred-orientation relation even with an incoherent nucleus. This could arise at the nucleation stage; for example, from anisotropy of elastic constants or of surface free energy, or alternatively by growth selectivity from initially randomly orientated nuclei. On the other hand, when it is *known* from other information (e.g. a shape change) that a correspondence does exist, the orientation relations provide a useful guide to the possible correspondences. This method, used by Lomer[30] in the uranium transformation, depends on the assumption that the principal strains and the relative lattice rotations, which together make up the lattice deformation, are not too large. Corresponding planes and directions in the two structures then make relatively small angles with each other.

Nucleation

A major difficulty in developing a satisfactory theory of the nucleation of martensite is the uncertainty about the critical stage of the process. The simplest assumption is that the shape deformation and interface structure of a nucleus are the same as for a macroscopic plate. If Knapp and Dehlinger's estimate[31] of the interfacial energy of martensite in steels is accepted, the critical nucleus of classical theory then contains $\sim 10^6$ atoms and has an energy of ~ 6000 eV.[10,11] Thus, the classical theory of homogeneous nucleation by thermal fluctuations immediately fails for this transformation. It does not seem probable that the position can be improved by choosing a lower surface energy appropriate to a fully coherent nucleus, since the strain energy would then have to be calculated from the shape change of the lattice deformation and would be correspondingly higher. Moreover, even if both surface and strain energies are arbitrarily assumed to be small, classical theory still cannot explain the very low M_s temperatures in some alloys.

It follows that nucleation must be assisted by heterogeneities of some kind, and these are presumably dislocations and/or internal-stress fields, since nuclei clearly do not form mainly on existing interfaces. The theories in the literature are of two kinds. One assumption is that embryos of martensite of a maximum size, r_m, are formed at high temperatures and become activated at low temperatures where $r_m > r^*$, the size of the critical configuration at the saddle-point in free energy. It has generally been assumed that the order of magnitude of r^* and hence of r_m is given by the classical theory of homogeneous nucleation. The alternative theories suppose that a region of martensite can form spontaneously by some kind of dislocation reaction or rearrangement, and in a formal sense (though this is not usually stated explicitly) this means that the critical nucleus size of classical theory is very small.

The Kaufman–Cohen theory of pre-existing embryos depends on rather special assumptions. A semi-coherent interface of the dislocation type is formed from existing lattice dislocations (the mechanism is not specified), and the strain energy of the lattice dislocations is assumed to be released to aid nucleation. This gives an effective negative surface energy and a minimum total free energy at a finite embryo size, even when the chemical free energy of martensite is greater than that of austenite.† This quasi-equilibrium embryo size increases with decreasing temperature, and would eventually become infinite when martensite has the lower free energy. There would then be no barrier to nucleation. However, the change of size with temperature presupposes some mechanism of embryo growth or coalescence, and it is further assumed that this ceases to operate at some temperature, T_f, so that the distribution of embryos is frozen-in at T_f and lower temperatures.

The condition for rapid athermal growth is assumed to be that the embryo exceeds a size r_c, where r_c is larger than r^* but decreases with decreasing temperature in the same way as r^*. In the temperature range where $r^* < r_m < r_c$, thermally activated nucleation will be observed if the embryo can increase in size from r_m to r_c by fluctuations. At slightly lower temperatures r_c will have become smaller than r_m, and athermal transformation will take place followed by isothermal activation of those embryos in the distribution that are initially smaller than r_c.

Experiments intended to test the embryo hypothesis may be divided into direct attempts to see embryos, and measurements to examine indirect predictions of the theory. An early claim that large embryos had been detected in the electron microscope[32] was later shown to be incorrect, and to be due to spontaneous transformation which often occurs above the bulk M_s as foils are thinned.[33–35] In principle, it might be possible to overcome the difficulty by suitable choice of T_f and M_s, but there have been no reports of successful experiments. The alternative direct experiment is to use a high-voltage electron microscope to examine thicker foils, more representative of bulk material. No work of this kind has yet been reported.

Probably the most informative indirect experiments are measurements of the effects of high hydrostatic pressures on the initiation of transformation. The application of pressure depresses the equi-free-energy temperature, T_0, and reduces the difference in free energy of the two phases at temperatures below T_0. This leads to a lowering of M_s under pressure, which was measured by Radcliffe and Schatz[36] for a series of high-purity iron–carbon alloys and for some plain carbon steels. Their results and those of other workers on iron alloys all show a depression of M_s by between 4 and 8·5 degC/kbar. The measured changes in M_s for the iron–carbon alloys and for an iron–10% nickel alloy are in good agreement with the theoretical changes calculated on the assumption that the net driving force at M_s is independent of pressure. According to the embryo theory, this result is expected only if the size of the largest pre-existing embryos is not changed by the pressurization. However, the model used by Kaufman and Cohen implies a second effect of pressure, namely, a reduction in the equilibrium embryo size at T_f. In consequence, the required driving force at M_s should be considerably increased, causing a further decrease in M_s which, it is estimated, should be several hundred degrees. The discrepancy might be caused by a change in the strain energy or a lowering of T_f under pressure, but it is difficult to avoid the conclusion that the observed lowering of M_s is much smaller than that predicted by the embryo theory. A similar difficulty arises from the observation that the driving force at M_s is independent of composition in iron–carbon alloys.[37]

In contrast to these negative results, there is one series of experiments that supports the theory. Kaufman, Leyenaar, and Harvey[38] investigated the effects of pressure and annealing cycles on the transformation behaviour of an iron–32·4% nickel alloy and found the results to be consistent with $T_f = 625 \pm 25^\circ$ C at ~ 25 kbars and $T_f = 525 \pm 25^\circ$ C at ~ 50 kbars. Thus, for example, cooling under pressure from T° C to 100° C was found to have no effect on the transformation on subsequent sub-zero cooling at 1 atm if $T < T_f$, but to suppress transformation when $T > T_f$. The discrepancy between these results and those of the experiments on direct transformation under pressure has not been explained, nor do there seem to have been further experiments of the kind just described. Despite the apparent success of the embryo theory in this one instance, however, it seems unlikely to be correct in its present form. The details of the theory, including the assumption of a large critical nucleus size, are difficult to justify; large embryos have not been observed and most of the thermodynamic evidence does not support the concept of a quenching-in temperature.

There are a number of other recent experiments that relate to the nucleation stage. The concept that M_s depends only on the net driving force is supported by the work of Satyanarayan, Eliasz, and Miodownik,[39] who showed that the change of M_s in a magnetic field is correctly predicted by including the magnetic-energy term. As pointed out previously,[3,9] the change of M_s in an elastic shear-stress field is consistent with the view that at the critical stage the shape deformation is already that of a macroscopic plate. The importance of the strain energy of the transformation constrained by the matrix is illustrated by the recent work of Goldman and Robertson,[40] who measured the supercooling, $T_0 - M_s$, in an iron–30% nickel alloy and in various Fe–Ni–X alloys in which the nickel content was adjusted to keep M_s in the temperature range 215–260° K. The results show that the various elements raise or lower the net driving force, assumed proportional to $T_0 - M_s$, according to their effect on the matrix shear modulus, i.e. on the strain energy, in the isotropic approximation. Cobalt was the only element to raise M_s and the only element to decrease the shear modulus.

Many observations show that previously formed martensite plates are probably the most effective agents yet identified in promoting transformation, but the implications for nucleation theory have not been fully examined. By analogy with the effect of externally applied stresses, one possible nucleation effect is simply that the mechanical energy of interaction of the internal stress field of one plate with the shape deformation of a new nucleus should be added to the overall energy balance. In an investigation of burst transformation in single crystals of an iron–31·7% nickel alloy, Bokros and Parker[41] found that the most effective mechanical coupling takes place among a group of plates with four nearly parallel habit-plane normals centred on matrix ⟨110⟩ directions. When crystals were deformed before transformation, the group of habits with normals clustered around the two ⟨110⟩ directions in the primary slip plane at 60° to the slip direction were preferred, but plates nearly normal to the slip direction itself did not form. Recently, this result

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† In effect, the usual calculation is reversed. The volume and surface free energies are of opposite sign and there is a minimum in free energy, not a maximum. Some objection may be made to the minimization procedure, but this only introduces small factors into the equations for the equilibrium radius and diameter of the embryo.

has been indirectly confirmed by Borik and Richman[42] in an investigation of the preferred orientation of martensite produced in a steel rolled to 93% reduction before transformation. In contrast, however, Defilippi and Paxton[43] reported that in deformed single crystals of a 25% nickel maraging alloy, the principal group of plates formed in the burst transformation had normals centred on the $\langle 110\rangle$ direction at 35·3° to the poles of both the primary and conjugate slip planes and at 60° to the primary slip direction.

In both these single-crystal investigations, the burst temperature M_b was raised by small deformations, although it was lowered again in the maraging alloy when the deformation was continued beyond the Lüders region into the work-hardening part of the stress vs. strain curve. This effect cannot be due to autocatalysis from stress-induced martensite, and it must be concluded that the deformation introduces defects or internal-stress fields that aid nucleation. The preferred group(s) of habit-plane variants may be due to the anisotropy of the dislocation substructure, and the discrepancy in the results might be attributed, though perhaps not very convincingly, to different substructures in the two alloys. One possible reason for the Bokros and Parker result is that the dislocation substructure lying mainly in primary slip planes resists growth nearly parallel to these planes more readily than growth normal to them. A possible reason for the alternative result is that nuclei form from dissociations of Shockley partials which tend to lie in the slip plane and thus give habits as nearly as possible parallel to the slip plane.

Further support for the conclusion that martensite is nucleated by defects comes from recent experiments on the transformation of small (100–300 μm dia.) single-crystal spheres of iron–nickel alloys,[44] and of very small (200–1300 Å) spherical or cubical particles of austenite precipitated in copper.[45,46] The Fe–Ni crystals containing $>$ 30% Ni transformed in a burst that began at a very variable temperature, typically − 12 to − 196° C, presumably because of variations in the defect structures of individual small crystals. For the coherent and semi-coherent precipitates of iron in copper, there is apparently no spontaneous transformation on cooling to 1·4° K,[45] even though the M_s temperature of the bulk Fe–Cu solid solution is ~ 600° C. Easterling and Miekk-oja[46] used transmission electron microscopy to study the transformation that is induced by deforming the specimens. The transformed precipitates show a banded structure, which is interpreted as discs of martensite nucleated by dislocations that have cut through the precipitates. These experiments are perhaps the most direct evidence we have that defects are necessary to nucleate martensite.

Models for the athermal formation of martensite nuclei from existing dislocations remain speculative, apart from the special case of f.c.c. $\rightleftharpoons$ h.c.p. transformations where an ordinary stacking fault may be regarded as a two-dimensional nucleus of another phase.[47] No single dissociation of this kind can produce a b.c.c. or b.c. tetragonal phase from f.c.c., but lattice shears that give approximations to the structural change in steels have been expressed in dislocation terms, and suggested as possible nucleation processes. The best known of these theories follows the Kurdjumov–Sachs two-shear model for martensite formation, and involves a half-twinning shear on $\{111\}$, which could be produced by "quarter-dislocations" of type $a/12\langle 11\bar{2}\rangle$.[48] A more recent suggestion, based on hard-sphere models of the two structures, begins with a one-third twinning shear produced by $a/18\langle 11\bar{2}\rangle$ dislocations.[49] Both theories require further shears and dimensional changes, and it is by no means obvious how these are achieved, or how a nucleus is evolved from the original stacking fault. Some electron-microscope evidence that martensite may be nucleated at stacking faults on austenite $\{111\}$ planes, at least in an iron–32% nickel alloy, has been provided by Dash and Brown[50] but partial dislocations of the above types were not identified.

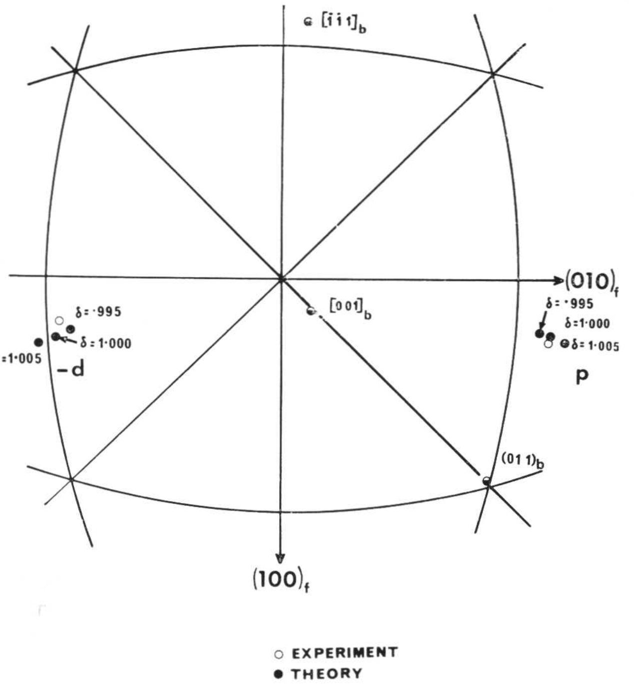
It seems probable that real nucleation processes are more complex than those envisaged in these simple theories and involve the interaction of several dislocations. Although some kind of dislocation reaction is clearly a possibility, the nucleation process might more simply take place in the high internal stress field of a suitable dislocation configuration. The formal description of such a process would include a negative energy term due to the strain energy destroyed, as discussed by Cahn[51] for incoherent nucleation on a single dislocation, or (equivalently) to the work done by the internal stress field in creating the nucleus. In either case, this could lead to much smaller critical nucleus size and energy than are envisaged in the embryo theory and to the disappearance of the energy barrier at sufficiently high driving forces. This type of nucleation is akin to Orowan's theory of mechanical twin formation in high internal stress fields, and seems to fit in well with the known facts about the burst phenomenon and the autocatalytic effects of existing plates.

Crystallography

Despite some difficulties and unsolved problems, confidence in the validity of the modern theories of the crystallography of martensite has been high ever since these theories were first formulated in 1953. In the present conference we are avoiding detailed discussion of formal aspects of the crystallography, but it is impossible to consider the mechanism of transformation and the fine structure of the product without giving some attention to crystallographic theories. Naturally, we shall be concerned mainly with the unsolved problems, but it may be appropriate first to record an outstanding success, namely, the recent investigation by Efsic and Wayman[52] of the crystallography of transformation in an iron–platinum alloy.

Greninger and Troiano were the first to determine the specific variants of the habit plane and orientation relations associated with an individual martensite plate, and this information is essential if a detailed comparison of theory with experiment is to be attempted. When the product is twinned, the assumptions of the theory can be further verified by determining the variant of the twinning plane. Finally, it is very desirable to measure the direction and magnitude of the displacement in the shape deformation in order to complete the comparison with theory. The shape deformation is difficult to measure accurately, however, and has received relatively little attention until quite recently. In 1964, Bowles and Morton[53] devised a method of determining the direction **d** and the magnitude m of the shape strain from the displacements of at least three non-parallel scratches. The shape strain is assumed to be an invariant plane strain plus a small dilatation, and the procedure in principle then also allows the dilatation parameter, δ, to be determined.

Efsic and Wayman used this technique to determine the shape deformation in an iron–24·5 at.-% platinum alloy, with an M_s temperature (in the disordered state) of ~ − 5° C. The plates were large and had very planar boundaries. Habit planes were determined for six separate plates, shape defor-



[*Courtesy Amer. Inst. Min. Met. Eng.*

Fig. 1 *Comparison of experimental values of the habit plane* **(p)** *and the direction of displacement in the shape deformation* **(d)** *in an Fe–24·5 at.-% Pt alloy with the theoretical predictions for three different values of the dilatation parameter* (δ).[52]

mations (at least three independent measurements for each plate) for five separate plates, and orientations for two plates. The authors emphasize that for the first time the habit plane, orientation relations, and shape strains were all measured for the same plate.

Fig. 1 shows a comparison of the mean values of the experimental quantities with the theoretical predictions for three different values of δ. The individual habit-plane normals were all within a scatter circle of 4° radius on the projection, and the directions **d** were similarly all within a 6° circle. The mean habit-plane normal is (.191, .760, .621), which is comparable with the habits in iron–nickel alloys generally described as of $\{259\}$ type. Thus, it is natural to assume that the usual $\{112\}$ $\langle 11\bar{1} \rangle$ twinning system of the martensite gives the elements of the lattice invariant shear, and the theoretical predictions are based on this assumption. It will be seen that the exact invariant plane-strain condition ($\delta = 1$) gives best agreement with the mean habit plane normal, **p**, but $\delta = 0{\cdot}995$ gives slightly better agreement with mean **d**. Consideration of the orientation relations in detail, however, confirms that best agreement is obtained for $\delta = 0{\cdot}995$. There is a very slight discrepancy in the magnitude of the shape strain, which is predicted as $m = 0{\cdot}239$, and has a mean measured value of 0·216, although individual measurements up to 0·249 were obtained. Apart from this the agreement is extremely good and certainly constitutes the most impressive confirmation of the theory yet obtained in iron alloys. The experimental evidence for a value of δ smaller than unity is of especial theoretical interest and is further discussed below.

Turning from this success story, we must consider what progress has been made in the long-outstanding problems of martensite crystallography in steels. These problems are: (1) the experimental scatter of habit planes over a wide region of the stereographic triangle, (2) the habit planes of $\{225\}$ type found in some steels, and (3) the transformations in nearly pure iron which have been variously described as having a needle- or lath-like morphology, with habits or pseudo-habits of $\{111\}$ or $\{112\}$ types. The prediction of the simple theory may be varied in two different ways to explain these divergent results, namely, by changing the elements of the lattice invariant shear or shears, or by relaxing slightly the condition that the habit plane is an invariant plane of the shape deformation. Both these approaches have been pursued in considerable detail and it is possible now to assess whether convincing claims can be made in favour of either hypothesis.

First, it should be emphasized that much of the experimental scatter reported in the literature may not be real. Breedis and Wayman[54] first showed that habit planes measured from mid-rib traces are much more consistent than those measured from the edge of the plate, and the structural investigations of recent years have made it clear that the interfaces of untwinned or partially twinned plates are very irregular. The scatter is not removed completely, especially in carbon-containing alloys, but many of the earlier results can now be discounted. Recent habit-plane determinations by Reed[55] on twinned martensite plates in iron–nickel alloys containing 29–35% Ni, for example, are consistent with previous measurements by Greninger and Troiano[56] and by Krauss and Pitsch,[57] but not with some other published data.

In earlier reviews of martensite in steels, it was often stated (*a*) that there is rather a sharp crystallographic transition from habits of $\{259\}$ type to those of $\{225\}$ type, and (*b*) that the habit plane probably depends on the temperature of formation of the plate, rather than on the composition of the alloy. The first statement was disproved by Johnson and Wayman,[58] who found an intermediate habit in an Fe–Cr–C alloy, but the second has been generally accepted. However, Reed's work gives strong indications that, in iron–nickel alloys at least, the habit (mid-rib) plane changes continuously with nickel content. He found that as the nickel content decreases, the pole of the habit plane moves from near the $\{110\}$ – $\{111\}$ great circle towards $\{225\}$. In contrast to iron–carbon alloys, however, habits near $\{225\}$ are not observed and the product apparently ceases to have a plate-shaped morphology below $\sim$ 29% nickel. The M_s temperature also depends on composition, but at fixed nickel content can be lowered appreciably by prestrain at room temperature. In a 31% Ni alloy with a normal M_s of − 20° C, the habit plane was unchanged when the M_s was lowered by prestrain to temperatures between − 40 and − 195° C, thus indicating that the habit is a function of composition rather than temperature or strain.

A comment on this result might be that the theory predicts that the habit plane depends on the lattice parameters of the two phases, which change with both temperature and composition. The coefficient of expansion of the 31% nickel alloy is very low, so that any temperature variation might be unusually small. Reed's results support the conclusion that the habit is determined only by the principal strains η_i, inasmuch as the scatter of the experimental habits lies almost exactly along the Bowles–Mackenzie line for varying dilatation (or varying principal strains). Unfortunately, the lattice parameters of the martensite phase as a function of composition are not known with sufficient accuracy to judge whether the change in habit can be attributed entirely to change in η_i, or whether a change in δ must be invoked.

The alternative approach of varying the elements of the lattice invariant shear has been investigated most systematically by Crocker and Bilby.[59] They supposed that this shear corresponded to one of the usual deformation modes of parent or twin, or to combinations of two such modes having either a common direction or a common plane. Even with these rather general assumptions, they were unable to account completely for all features of the experimental results. More recently, Crocker[60] has considered that the net lattice invariant shear might be resolvable into two component shears plus a rotation; the two component shears then must have the same plane of shear (i.e. plane normal to K_1 and containing η_1). Variation in the relative amounts of the two shears thus leads to a curve on the stereogram representing the loci of habit planes, and since one of the component shear systems is the usual product twinning system, this curve intersects the Bowles–Mackenzie dilatation curve at the exact prediction of the simple theory (one shear system and no dilatation). The observed two-dimensional scatter of habit-plane poles can be explained in principle by combining a variable shear with a dilatation, but there is a natural reluctance to increase the number of assumptions in this way. Crocker suggests that a theory that would explain the scatter without any dilatation might be obtained by discarding the condition that the two component shears have the same plane of shear and considering instead a combination of the product twinning shear with any secondary slip system.[*] A theory of this type has not been fully developed, however, and evidence at present seems stronger for a dilatation or some more general relaxation of the invariant plane strain condition.

The situation in respect of {225} habits remains confused. In early work, the best agreement between theory and experiment was obtained either by assuming a maximum value of the Bowles–Mackenzie dilatation parameter[61] or by adopting Frank's model of the interface,[62] which amounts to an anisotropic distortion from a macroscopically invariant plane and gives the best fit for some experimental results obtained on an Fe–7·9% Cr–1·11% C alloy.[63] However, later and more accurate work on this same alloy[64] has shown that the exact parallelism of close-packed directions of the two phases, which is assumed in Frank's model and was previously reported, is not observed. Moreover, almost all recent determinations of individual habit planes in both Fe–C and Fe–C–Cr alloys[53,63,64] show that the plane is not exactly of the {*hhl*} type. This means that a close-packed ⟨101⟩ direction does not lie in the habit plane, and the mathematical degeneracy of the crystallographic theory, formerly assumed, strictly does not exist.

Bowles and Mackenzie[65] used the reverse crystallographic calculation first suggested by Lieberman[66] to evaluate the dilatation and the elements of the lattice invariant deformation. Accurate measurements of the shape deformation are critical for this procedure, and were made recently for an iron–1·13% carbon steel by Bowles and Morton[53] and for the Fe–Cr–C alloy by Morton and Wayman.[64] Both investigations indicate that the shape deformation includes a volume change other than that contained in an invariant plane strain, and thus give experimental support for the assumption that the habit plane in such transformations is not an invariant plane of the shape deformation. Morton and Wayman conclude that an anisotropic distortion of the interface is unlikely, but their results are such that complete agreement between theory and experiment has not been attained with any of the assumptions of the theory in its present form. Thus, the observed habit plane and orientation relations can be predicted, but the predicted direction of the shape deformation then does not agree with experiment; alternatively, the habit plane and complete shape deformation can be predicted but there is then a discrepancy in orientation relations.

The orientation relation found by Morton and Wayman shows that nearly parallel close-packed directions of the two phases differ by 0·53° and nearly parallel close-packed planes by 0·45°. The authors point out that both deviations are in the same sense as those observed for {259} martensites; the directions are more nearly parallel for {225} plates and the planes for {259} plates. This supports the idea that there is some form of continuity in the crystallographic transition from one habit to another.

An alternative theory of {225} crystallography, not involving a dilatation, has recently been advanced by Lieberman and Bullough[67] and by Lieberman.[68] The theory is based on the experimental observation that martensite plates are partially twinned, and on the theoretical conclusion[69] that a lattice rotation is associated with the termination within one orientation of a row of twins of another orientation. The matching of the matrix with a " smeared-out " average lattice of a composite or partially twinned plate is considered and it is claimed that this concept gives good agreement with experiment. The theory is extremely controversial[70] and I do not propose to comment further on it here.

The final steel problem is the difficult question of the non-plate-like morphologies found in iron alloys of low nickel and low carbon content. There is still great confusion about the correct description of these structures, but most workers have reported that bulk martensite is in the form of sheaves of parallel laths with a habit near {111} and a long axis along ⟨1$\bar{1}$0⟩,[71–74] whereas surface martensite grows in {112} planes with wide scatter. Numerous attempts at predicting shape deformations with invariant planes near {111} have been unsuccessful, and it is tempting to assume that these needles or laths do not satisfy the ordinary crystallographic theories of martensite when formed singly, but do so approximately in pairs. This would represent a form of self-accommodation, not for the shear component of the shape deformation as is usual in banded martensite but for the habit misfit itself. A somewhat similar suggestion is made in the paper by Bryans, Bell, and Thomas.[75]

Because of space limitations, much recent work on non-ferrous martensites cannot be included here, but some of it is surveyed by Lieberman.[76] Perhaps the most important progress has been made in the transformations in titanium alloys.[77–80] Various authors have reported a cubic product phase but it seems rather probable that this may be caused by hydrogen contamination. The transformation to the usual hexagonal product is noteworthy because the lattice deformation is a close approximation to an invariant plane strain. The product in pure titanium is untwinned but {10$\bar{1}$1} twins are observed in impure titanium[79] and in a titanium–5% manganese alloy.[80] This strongly suggests a Bowles–Mackenzie Class A transformation and according to the work of Hammond and Kelly both $(\alpha^+\omega^+)$ and $(\alpha^-\omega^+)$ solutions should be observed. These authors made a detailed

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[*] This " two-shear " theory is quite distinct from the old two-shear theories of the lattice deformation. In a purely formal crystallographic theory, the lattice invariant deformation can be a simple shear with any elements, rational or irrational. Crocker is considering the possibility that this net shear is resolvable into two components, one of which is the twinning shear for which there is experimental evidence and the other an undetected slip shear.

comparison of theory with experiment for the ($\alpha^-\omega^+$) transformation, where least scatter was observed, and concluded that a dilatation parameter is needed to explain the results.

The deviation from a lattice-matching condition increases with solute content in alloys that stabilize the β phase. Hammond and Kelly suggest that this change is accommodated first by changing the dilatation parameter, but eventually the amount of lattice invariant shear is increased and $\{10\bar{1}1\}$ twins appear in the product. Thus, in contrast to some earlier crystallographic results, there may be a continuous transition from {334} to {344} habits, with both plates having habits nearly normal to the hexagonal basal plane, and possessing equivalent variants of orientation relation, shape deformation, &c. The product plates might be described as {334} type until twinning begins (or is first obvious), after which they could be called {344}. The electron metallography of {344} plates shows some interesting features in the structure of the interface and these are discussed below.

The Martensite Interface, the Fine Structure, and the Dilatation Parameter

The crystallographic theories predict that martensite plates should either consist of a uniform stack of fine parallel twins, or else should not possess any particular substructure. Electron microscopy has shown that some martensites are twinned as expected, while others are untwinned or are partially twinned. The untwinned regions of the plates frequently have a complex dislocation substructure. Moreover, there sometimes appears to be a relation between the substructure and the external morphology.

Planar interfaces are observed in single-interface transformations of single crystals and in banded martensites where neighbouring parallel plates produce opposite (self-accommodating) shape deformations. The products in the known transformations of these types are fully twinned. A martensite plate that is constrained by the matrix is expected to have a lenticular shape and the habit-plane interfaces should again be nearly planar. Wayman[14] has pointed out that the traces of the interfaces in micrographs of {259} plates of Fe–Ni alloys are straight when the plates are fully twinned but are irregular for untwinned or partially twinned plates.

A detailed investigation by Patterson and Wayman[81] has shown that plate-like martensite in Fe–Ni alloys is always at least partially twinned, and the amount of twinning increases with increasing nickel content or decreasing M_s temperature. Partially twinned plates in this system are twinned along a region extending outwards from the mid-rib, and the boundary of the twinned region is often quite planar even when the interface of the whole martensite plate is irregular. This helps to explain the greater consistency of habit planes determined from mid-rib traces, and indicates that the macroscopic mid-rib itself is visible because it is a twinned region. The mid-rib is not fully understood, however, since it can usually be distinguished even in a fully twinned plate.

The observed twins are always those expected from the usual crystallographic theory, and interference measurements of surface topology showed that the shape deformations in twinned and untwinned regions of a partially twinned plate are identical. Observations of twin intersections were interpreted as evidence that the plates grow in two stages, with the twinned regions forming first and most rapidly. The transition in growth behaviour is attributed to the temperature rise produced by the nearly adiabatic growth of the twinned region. This suggestion agrees with the conclusion that the internal structure depends on the temperature of formation, and with the increase in the extent of twinning as the M_s decreases. An experimental measurement of the temperature rise produced by a burst of transformation in a iron–31% nickel alloy led to an estimate that the local temperature rise produced by rapid transformation is ~ 33 degC.

Although vague comparisons are sometimes made with the transition in deformation behaviour from slip to twinning as the temperature is lowered, it is not at all clear why a transition should be expected in transformation substructure. Moreover, although the percentage of twinned product may increase with decreasing M_s in any one system,[82,83] this behaviour has been firmly established only for Fe–Ni and Fe–Ni–C martensites. Certainly the absolute temperature at which fully twinned plates are observed is very variable,[84] ranging from + 200° C in Fe–C alloys to ~ − 196° C in an Fe–Cr–C alloy. It should also be noted that an implication of the Patterson and Wayman explanation of the growth transition is that the untwinned part of a martensite plate forms by a mechanism which is related to that of the lath or needle-shaped *schiebung* martensite. According to Huizing and Klostermann,[44] surface martensite, angle-profile martensite, massive martensite, and the untwinned part of a martensite plate formed after a burst are all morphologically different types of martensite, but may be formed by a common mechanism. They quote a result of Krauss and Pitsch[85] to conclude that untwinned martensite can form at temperatures as low as − 50° C, even in Fe–Ni alloys.

The equivalence of the shape deformations in the two parts of a martensite plate strongly suggests that the untwinned part is formed by the motion of a dislocation interface, with the interface dislocations giving a lattice invariant shear corresponding to that produced by the twinning. The substructure of the untwinned parts of the plate seems to consist of intersecting arrays of $\langle 111\rangle$ screw dislocations, and it has been stated that all four $a/2\langle 111\rangle$ Burgers vectors are involved. The likeliest explanation of this substructure is that it is due to accommodation slip forced by the matrix constraints; the interface dislocations should not contribute to substructure unless they have non-lattice Burgers vectors, in which case stacking faults would be left. No evidence of extensive accommodation slip or twinning has, however, been observed in fully twinned plates.

Not all partially twinned martensites have the twinned region confined to the mid-rib. Plates of an Fe–Cr–C alloy with approximately a {225} habit, for example, have very variable substructures.[64] Twins frequently extend right across the plates but occur in patches, with large untwinned regions. Both fine and coarse twins are observed and in this case the habit-plane interfaces are fairly straight. The twins are once again the specific variant expected from the crystallographic theory, so that it is difficult not to associate them with the transformation. A tentative suggestion might be that the plates are initially fully twinned on a fine scale, but that some growth or coalescence of twins takes place during preparation of the thin foils as the matrix constraints are relaxed.

A very interesting observation, first made by Nishiyama, Oka, and Nakagawa[79] and repeated by Hammond and Kelly,[80] concerns the structure of the interface in twinned specimens of titanium alloy martensites. Fig. 2 shows one of Hammond and Kelly's micrographs, from which it will be seen that the actual interface consists of two alternate plane sections, one for each twin orientation. While the

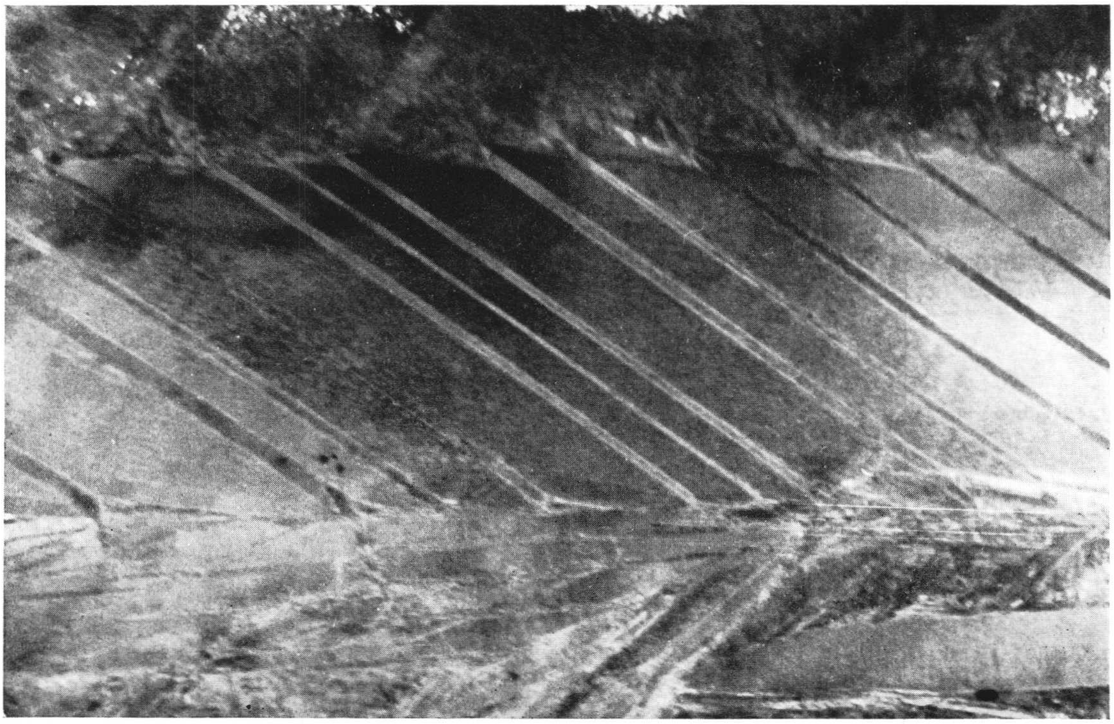


Fig. 2 Dark-field electron micrograph of a Ti–5% Mn alloy, water-quenched from 850° C and aged at 400° C for 2 h.[80] *The α (hexagonal) plate is twinned on* $\{10\bar{1}1\}_\alpha$ *and is in a β matrix. The habit plane of the plate is* $\sim\{344\}_\beta$ *but the individual interfaces of the two twin orientations are* $\sim\{334\}_\beta$. × 20,000.

average interface is a $\{344\}_\beta$ plane, the jagged sections are $\{334\}_\beta$ planes which represent nearly invariant planes of the lattice deformations producing the two twin orientations. Thus, each twin orientation has a local interface that is similar to the habit of untwinned titanium martensites, but because the misfit along this plane is larger than in pure titanium it has to be periodically compensated by a neighbouring region of the other orientation.

The concept that the atomic interface differs from the average interface is certainly not contrary to the crystallographic theory, but the titanium situation is unusual. When the lattice deformation is not a close approximation to an invariant plane strain, as in steels, there may be less tendency for the atomic interface to differ appreciably from the (irrational) macroscopic interface. Moreover, the scale of the inhomogeneity at the interface must be finer in steels, so that it may be more difficult to resolve a stepped interface.

The irregular interfaces observed in partially twinned {259} iron–nickel plates contain many mutually parallel planar sections and it is tempting to speculate that these also may represent planes of near atomic fit. Patterson and Wayman[81] used interference techniques to show clearly that the invariant plane of the shape deformation is the midrib plane and not the plane of the faceted segments. The habit plane of these sections is near {112},[81] and it is noteworthy that needles of surface martensite also grow in {112} austenite planes.[16,86] Klostermann has suggested that this crystallography is governed by an approximate atomic matching condition in which close-packed rows are parallel in the two lattices and {112} austenite planes are parallel to {321} martensite planes, but the validity of this assumption for the quite large interface segments seen in the plates seems doubtful. We have to admit that no convincing explanation for this morphology is currently available. Possibly a more satisfactory explanation might be found in the analogous irregular interfaces of some mechanical twins, caused by emissary and accommodation slip.

As already indicated, the fine structure of massive or *schiebung* martensite formed in low-carbon, low-nickel ferrous alloys consists of sheaves of parallel fine laths, of average width 0·2–0·4 μm. Adjacent laths have been reported to be approximately twins of each other but to have relative orientations differing by up to 10–15° from the exact twin relation.[87,88] The needle or lath structure is associated with a high dislocation density but the regular arrays of screw dislocations found in the untwinned regions of martensite plates have not been reported.

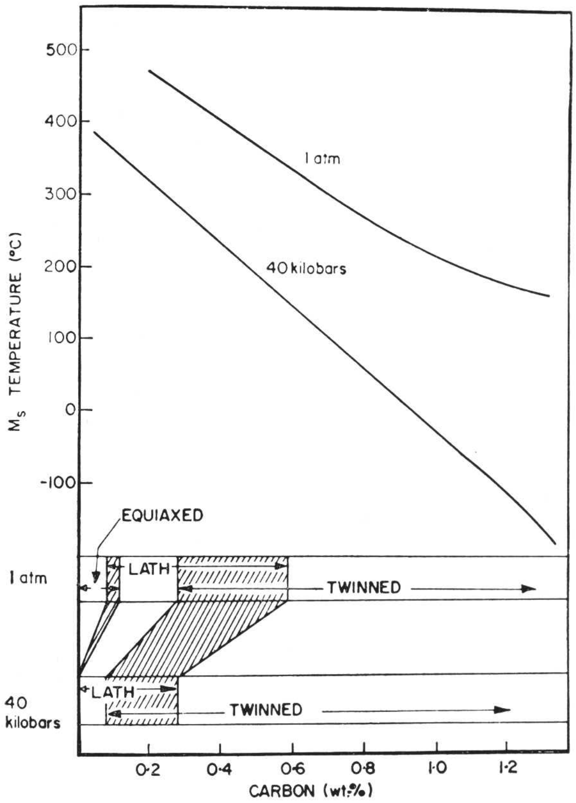
Recently, Vyknal and Radcliffe[88] have reported an electron-microscope investigation into the effects of transformation under pressure on the fine structure of pure iron and of Fe–C martensites. They found that with a pressure of 40 kbars, the non-martensitic transformation to equiaxed ferrite is suppressed in pure iron by a cooling rate of only 100 degCsec^{-1}, whereas, according to Bibby and Parr,[89] a cooling rate of ~ 30,000 degCsec^{-1} is needed to obtain the same result at atmospheric pressure. The iron transformed under pressure had a lath structure, similar to that of martensite in low-carbon steels and almost identical with the structure found recently in thin discs of pure iron quenched at very high rates (~ 100,000 degCsec^{-1}).[90] The suppression of the equiaxed transformation under pressure is believed to be due both to the depression of the $\gamma \rightarrow \alpha$ transformation temperature and also the direct effect of pressure on self-diffusion rates.

Changes in fine structure were also found for Fe–C alloys transformed under pressure. An alloy with 0·24% carbon contained very little twinned martensite when quenched at atmospheric pressure but consisted mainly of twinned plates after quenching at 40 kbars. Similarly, there were no twinned plates in an iron–0·09% carbon alloy transformed at normal pressure, but there was a large proportion of such plates after transformation under pressure. Fig. 3 shows the M_s temperature as a function of carbon content at pressures of 1 atm and 40 kbars, respectively,[36] and also indicates schematically the structures formed after quenching under these two conditions. The two carbon alloys discussed above have M_s temperatures at 40 kbars that correspond to those of ~ 0·7% and 0·5% C alloys, respectively, at one atmosphere, and also have structures under pressure similar to those of the higher-carbon alloys at normal pressure. The results thus tend to support the suggestion that the transition from lath martensite to twinned martensite is determined mainly by M_s temperature.

I should like to conclude this section by discussing briefly the possible significance of the dilatation parameter. The crystallographic results provide a steadily mounting body of evidence that in many transformations it is necessary to assume that there is a deviation from the invariant plane strain shape deformation in the form of a uniform dilatation, as originally postulated by Bowles and Mackenzie. The dilatation does not seem to be related in any simple way to the overall volume change; it occurs in titanium and its alloys where the phases have nearly equal specific volumes and in steels where the volume change is quite large. At one time it seemed possible that the assumed dilatation is always opposite in sign to the overall volume change (i.e. it increases the normal component of the invariant plane shape deformation that remains after removing the dilatation). This is contradicted, however, by the results on iron–platinum alloys[52] described above.

A dilatation parameter has never been invoked in a single-interface transformation and, although such transformations are admittedly rare, it seems probable on other grounds that the dilatation is connected with the matrix constraints on the shape deformation. Since the dilatation modifies both the shape deformation and the amount of the lattice invariant shear, it might be important at the nucleation stage, either in reducing the strain energy of the constrained shape change or the surface energy of the semi-coherent interface.[91] Thus, we should expect δ to differ from unity either in the sense that reduces the macroscopic shape shear or in the sense that reduces the lattice invariant shear, and if possible both.

The clearest evidence that the second of these factors can operate comes from the previously mentioned work on the transformation in titanium–manganese alloys.[80] In pure titanium the dilatation parameter that best fits the experimental data is in the same sense as the overall volume change, whereas in the 5% manganese alloy it is in the opposite sense. In both cases, however, the dilatation acts so as to diminish the magnitude of the lattice invariant shear. In pure titanium, the lattice misfit is accommodated almost entirely by the dilatation, and the usual theory implies a very small lattice invariant shear which is presumably obtained by widely spaced interface dislocations. In the alloy, the lattice parameters have changed in such a way that a larger lattice invariant shear is now required and the structure is twinned. The dilatation parameter still acts so as to reduce the amount of lattice invariant shear or twinning and to improve the atomic fit on the {334} planes of the faceted interface.



[*Courtesy "Acta Met."*

Fig. 3 *The upper part of the figure shows the variation of* M_s *temperature with composition at pressures of* 1 *atm and* 40 *kbars, respectively. The lower part is a schematic representation of the type of structure formed on quenching to room temperature at these pressures.*[88]

The difficulty in generalizing this interpretation of the dilatation is that in most transformations the lattice deformation does not allow anything approaching a plane of good atomic fit, even when a dilatation parameter is incorporated. Thus, although the sense of the dilatation may often be such as to improve atomic fit across a lattice plane forming part of the interface, there is at present no evidence for the existence of such interfaces in other than titanium alloys.

Thermal Stabilization

The phenomenon of thermal stabilization of austenite in steels is very complex, and there is space only for a brief mention of some recent work. Stabilization is usually investigated by first quenching to an arrest temperature, T_A, below M_s, then ageing at T_A or at a higher temperature T, and finally cooling and observing the progress of the transformation which begins again at a temperature M_s'. The temperature interval $\theta = T_A - M_s'$ is a measure of the magnitude of the effect. It is well established that the presence of interstitial solutes is essential for stabilization, that θ varies with time and temperature in the manner expected from controlling mechanisms which are thermally activated, and that stabilization is usually reversible in the sense that θ approaches the value characteristic of the last of a succession of ageing treatments.

Previous work has established that θ generally increases with time at constant ageing temperature to a maximum value, after which it decreases again and becomes constant. A second increase after long ageing times is sometimes observed, but is believed to be associated with bainite formation and is treated as a separate phenomenon. As the temperature is increased, the time taken to attain the maximum in θ and the height of this maximum both decrease. More complex behaviour, however, was found by Priestner and Glover[92] in an Fe–5% Ni–1·43% C steel with an M_s near room temperature. After ageing at temperatures above 50° C, the value of θ continued to decrease beyond the maximum until it became negative, after which it passed through a minimum and increased again.

Various theories of stabilization all involve the migration of interstitial solutes, but may perhaps be divided into three main groups. The first model ascribes the effect to locking of the martensite/austenite interface by solute atoms,[93] the second to destruction of the autocatalytic effect of previously formed plates,[94] and the third to the strengthening of the austenite matrix by strain-ageing processes.[95] Priestner and Glover used this strain-ageing model to account for their experimental results and they attributed the negative θ to softening caused by over-ageing. More recently, Kinsman and Shyne[96] have proposed a variant of the interface-locking mechanism that is based on the embryo theory of nucleation: the activation of embryos pre-existing in austenite is assumed to be made more difficult by solute segregation to the interface.

The available experimental evidence strongly suggests that different mechanisms may be operative in different alloys and recent work also shows that there is probably a change in mechanism with temperature. Kinsman and Shyne[97] made tests on three different Fe–Ni–C alloys with sub-zero M_s temperatures, and found that at low ageing temperatures (up to 50–100° C depending on composition) the behaviour was reversible and had the general characteristics described above. The authors state that these results agree with the predictions made from their model. At higher temperatures, however, θ was initially constant and then increased at long times except for the highest-carbon alloy which had a maximum value of θ. The magnitude of θ after any ageing treatment was always increased by subsequent ageing at a higher temperature and the stabilization was not reversible. If successive ageing treatments at different temperatures were given to the alloys, θ always approached a value characteristic of the highest ageing temperature used.

Clearly, the high-temperature ageing results do not support the embryo-locking model and there is at present no very convincing reason for the change in mechanism. Although the low-temperature results are consistent with the embryo model, they do not provide conclusive evidence in favour of pre-existing embryos. All models of stabilization make somewhat similar assumptions about segregation of carbon or nitrogen atoms to nucleation sites, embryos, strain fields, matrix dislocations, &c., and it seems very difficult to distinguish between them on kinetic grounds.

One prediction of the embryo model, as well as of some other models, is that stabilization should occur by ageing above M_s without any previous martensite formation. The evidence for and against this effect has always been difficult to evaluate. Kinsman and Shyne[97] plotted the maximum value of θ for various ageing temperatures against the amount of pre-existing martensite obtained by varying T_A. Extrapolation to zero martensite content indicated that there should be a small stabilization effect above M_s, but the scatter of individual results was too large for this to be established directly.

Martensite–Austenite Transformation and Pressure-Induced Transformations

Transformations in which coherency at the glissile interface is not destroyed (single interfaces, banded martensite, thermoelastic martensite) are often completely (crystallographically) reversible on heating. In other cases the high-temperature phase may have to be renucleated in the low-temperature martensitic phase and the nature of the heating transformation then depends on the temperature of transformation and the heating rate. It is difficult to study the reverse transformation from martensite (α) to austenite (γ) in steels because of the intervention of tempering reactions, but several investigations of the $\alpha \rightarrow \gamma$ change in iron–nickel alloys have been made in recent years. Moreover, reversed reactions in steels may be studied by changing the pressure rather than the temperature.

Various workers have used metallographic techniques and observations of surface relief to show that a martensitic-type transformation is obtained when specimens of Fe–Ni alloys with 30–33% nickel are partially transformed to α and then rapidy reheated to temperatures in the γ phase field.[98–104] The reverse transformation begins at the interfaces between α-martensite and retained austenite, and new austenite plates subsequently form in the interior of the α-martensite. The rate of heating seems to have relatively little effect on the temperatures A_s and A_f, at which transformation starts and finishes. Kessler and Pitsch,[103,104] for example, report A_s = 300–310° C and A_f = 400–420° C for iron–32·5% nickel, with heating rates varying from 0·3 degCmin^{-1} to 6000 degCmin^{-1}. At the faster rates transformation is complete at A_f, but at the very slow rates there is some form of stabilization and the reverse transformation is interrupted. It resumes again by a thermally activated mechanism above 475° C. An acoustic technique was used to demonstrate that individual martensite plates form in $< 10^{-2}$ sec, and electron microscopy has shown that the new γ phase contains dense dislocation networks.[101,104] Speich, Szirmae, and Fisher[90] have also demonstrated both that the heating transformation is rapid and that the austenite has a high defect density. They used a laser device to heat thin discs of iron–31% nickel at 10^6 degCsec^{-1} and found complete transformation followed by partial recrystallization after pulse-heating to 725° C for 0·02 sec, and complete recrystallization after 0·4 sec at this temperature.

Kessler and Pitsch also investigated the crystallography of the reverse transformation[102–105] and obtained good agreement between measured and predicted habit-plane normals. The theoretical predictions were made on the assumption that the lattice invariant shear utilizes an austenite slip system $\{111\}_\gamma \langle 10\bar{1}\rangle_\gamma$, which does not correspond to either of the shear systems usually invoked to account for the $\gamma \rightarrow \alpha$ transformations. In this respect the results differ from those obtained in pressure-induced $\alpha \rightarrow \gamma$ transformation.

Pressure-induced transformations produced by shock loading two Fe–C alloys (0·095 and 0·01% C) and two Fe–Ni–C alloys (30% Ni, 0·026% C and 28% Ni, 0·1% C) have recently been investigated by Bowden and Kelly.[106] The Fe–Ni–C alloys were cooled to sub-zero temperatures to give ~ 60% martensite and were then shock-loaded at room temperature to peak pressures of 100, 160, and 200 kbars. At the lowest pressure a small proportion of the α-martensite transformed to γ, whereas at the two higher pressures transformation to γ was virtually complete; in all cases the austenite was retained after the shock. In the 100-kbar specimens it was possible to investigate the orientation relations and the habit planes of the retransformed γ. The orientations were all consistent with the Kurdjumov–Sachs relation and ten habit planes of type $\{523\}_\alpha \equiv \{225\}_\gamma$ and three of type $\{121\}_\alpha \equiv \{112\}_\gamma$ were observed.

The crystallography is discussed in terms of the alternative shear systems $\{110\}_\gamma \langle 1\bar{1}0\rangle_\gamma \equiv \{112\}_\alpha \langle 11\bar{1}\rangle_\alpha$ (I) and $\{111\}_\gamma \langle \bar{1}2\bar{1}\rangle_\gamma \equiv \{101\}_\alpha \langle \bar{1}01\rangle_\alpha$ (II). System I is the usual lattice invariant shear for the cooling transformation in Fe–C and Fe–Ni–C alloys, whereas System II for $\gamma \rightarrow \alpha$ transformations is apparently confined to steels of low stacking-fault energy.[17,18] Most of the austenite regions formed by the 100-kbar shock-loading were consistent with a System-I transformation, and the results indicated that this was probably an exact reversal of the $\gamma \rightarrow \alpha$ transformation that originally produced the α-martensite. The twins in the α-martensite were not inherited by a System-I region of austenite, but were inherited by a System-II region where exact reversibility is not possible. At the higher pressures it was not possible fully to determine the crystallography but it is probable that the transformation is of Type II. The most characteristic feature was the presence of internal twinning on austenite $\{111\}$ planes as previously reported.[107] The twinning plane was observed to be nearly normal to the habit plane, as required by a Type-II transformation, but the density of twins is too low to produce an invariant habit plane without some accompanying slip.

The observation of a System-II $\alpha \rightarrow \gamma$ transformation is unexplained at present, although it might be suggested that there is a general tendency for the lattice invariant shear system to be a possible twinning system of the product phase. Bowden and Kelly point out there is evidence that $\alpha \rightarrow \gamma$ transformation produced by severe deformation,[108] or by heating iron whiskers,[109] may also follow a System-II path, so that there is no reason to suppose that this type of crystallography depends on pressure. On the other hand, the results of Kessler and Pitsch indicate a different lattice invariant shear.

The pressure-induced transformation in the Fe–C alloys studied by Bowden and Kelly was from the α phase to the ε (h.c.p.) phase, which is a solution of carbon in the high-pressure form of iron. In this case a shock wave of 200 kbars peak pressure resulted in a complete cycle of transformation $\alpha \rightarrow \varepsilon \rightarrow \alpha$, and the authors rely on earlier work for the assumption that the high-pressure phase is h.c.p.[110,111] Only indirect conclusions about the crystallography are possible, based on measurements of the relative orientations of α plates in doubly transformed specimens and of the habit planes of these plates. The results of this analysis are all consistent with a crystallography in which the $\alpha \rightarrow \varepsilon$ change essentially involves an invariant plane strain on $\{112\}_\alpha$ plus a small uniform dilatation. Individual habit planes showed some deviation from $\{112\}$, and are consistent with a smaller dilatation plus a small amount of lattice invariant shear. The $\varepsilon \rightarrow \alpha$ transformation is believed to be a simple reversal of the $\alpha \rightarrow \varepsilon$ change.

Conclusion

Investigations of martensite formation have now reached the stage where attention has frequently to be directed towards the details and complexities of individual transformations rather than to broad general principles. A few years ago it seemed possible that the very substantial advances made in the crystallographic theory and in the electron-microscope techniques for experimental investigation of martensite might lead to a period of consolidation, but this has proved not to be the case; the new experimental techniques have solved some problems but have revealed many new difficulties. There is still intense activity in all branches of the subject but it seems likely that future progress will be both difficult and slow. Perhaps the next big advance will come from the use of high-voltage electron microscopy.

Many important aspects of the subject have been omitted from the above survey, either for lack of space, or because of inability to deal adequately with them. " Qui s'excuse s'accuse ", but perhaps it will help to lessen the bias of my personal selection if I now mention some of these topics, with appropriate references to recent work. They include coherent transformations between close-packed phases;[112–117] transformations in carbon-free iron alloys,[118–124] in steels[125–131] and iron–nitrogen alloys,[168] in β-phase copper alloys,[132–146] and in intermetallic compounds;[165–167] the effects of prior deformation and of defects in austenite;[147–151] the kinetics of transformation;[160–164] bainite in steels,[152–156] and in non-ferrous alloys.[157–159] This list is not intended to be exhaustive and certain subjects (strength and fracture of martensite, ausforming, tempering, maraging) are deliberately excluded because of the large number of references.

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The Nucleation and Growth of Slow-Growing Martensite in Fe–30% Ni

J. A. Klostermann

Slow growth, impediment of growth in deformed austenite, and polarity of growth of surface martensite in Fe–30% Ni have been observed. An interpretation of these phenomena is given. X-ray work with a texture goniometer shows that the surface martensite has a very well-defined orientation relationship. However, the Invariant Plane Strain theory is not applicable to this type of martensite. Instead, the fit on an atomic scale is thought to be important. New needles are often systematically nucleated at one of the boundaries of a surface martensite needle.

The martensite transformation is one of the older subjects in the study of solid-state phase transformations. However, many problems remain, especially in connection with the mechanism of nucleation and growth, for instance for the transformation f.c.c. to b.c.c. (or to body-centred tetragonal) that occurs in iron alloys and steel and is of great technical importance.

The phenomenological theory of martensite transformations independently proposed by Bowles and Mackenzie[1] and by Wechsler, Lieberman, and Read,[2] often called the Invariant Plane Strain theory, was a great advance. With this I.P.S. theory it has become possible, for instance, to correlate successfully the experimentally determined orientation relationship, habit plane, and shape deformation for martensite with a " {259} habit " in steel. After the I.P.S. theory, many predictions of habit planes were made which sometimes necessitated the introduction of rather artificial propositions.[3] Nevertheless, the I.P.S. theory was undoubtedly a very elegant result. However, we think that it holds only for a minority of martensite transformations. Moreover it tells us nothing, or next to nothing, about the actual mechanism of the transformation.

A difficulty in the study of the martensite transformation in iron alloys is that it proceeds very fast (the speed of growth of individual needles is about one third of that of sound as measured by Bunshah and Mehl[4]), so that nucleation and growth cannot be studied readily. However, besides fast-growing martensite, slow-growing types of martensite have also been observed in iron–nickel alloys. Slow-growing surface martensite was found by Honma[5] and by Klostermann and Burgers.[6] The present author[7] also observed angle-profile martensite which appears to be related to surface martensite. Both types of martensite show very peculiar characteristics with respect to nucleation and growth and the I.P.S. theory does not appear to be applicable. In this paper more extensive information about the subject is given.

Experimental

Single crystals of composition 30·2%Ni, 0·04%C, 69·76%Fe, were prepared by the method of Czochralski. Single-crystal slices of known orientation were obtained by the method described by Bogers.[8] Surface martensite formed spontaneously after mechanical polishing with emery paper and subsequent electropolishing on a Disa-electropol apparatus (electrolyte A2, 36V). X-ray orientation determinations were performed with a Siemens texture goniometer. Measurements of high accuracy were obtained by reconstructing the apparatus in such a way that for every revolution of the specimen the tilt was 0·25° (orientation determinations were reproducible within 0·25°).

Characteristics of Surface Martensite

Some important features of surface martensite have been reported elsewhere.[6,7] They will be summarized here by reference to a few micrographs. In addition many new facts will be reported.

Surface martensite needles can develop spontaneously after electropolishing; they can also be nucleated by scratching. Fig. 1 shows a surface martensite needle which grew on a specimen with a {100} orientation. Several interesting features are clearly shown in this photograph. The accommodation of the austenite can be observed from the slip lines. Fig. 2 shows that growth has occurred, in one direction only, in both the length direction and in the direction perpendicular to this. The growth in length is much faster than the sideways growth. The growth in the length direction can vary from 100 mm/sec to < 0·001 mm/sec. If an obstacle such as an inclusion is encountered, the growth stops and then continues again some time later. In the region of the obstacle the sideways growth does not continue and the needle remains narrow. In Fig. 2 the boundaries of the needle are classified as Types I, II, and III. In Fig. 1 it can be seen that the shape deformation must be very small, as the needle is in focus over its full breadth (the relief is exaggerated by the interference contrast). Measurements with an interference microscope combined with observations of the deflection of scratches showed that the shear angle of the shape deformation in the immediate region of boundary I amounts to approximately $8\frac{1}{2}°$. The measured direction of the shape deformation of surface martensite is indicated by S_e in Fig. 9. However, the shape

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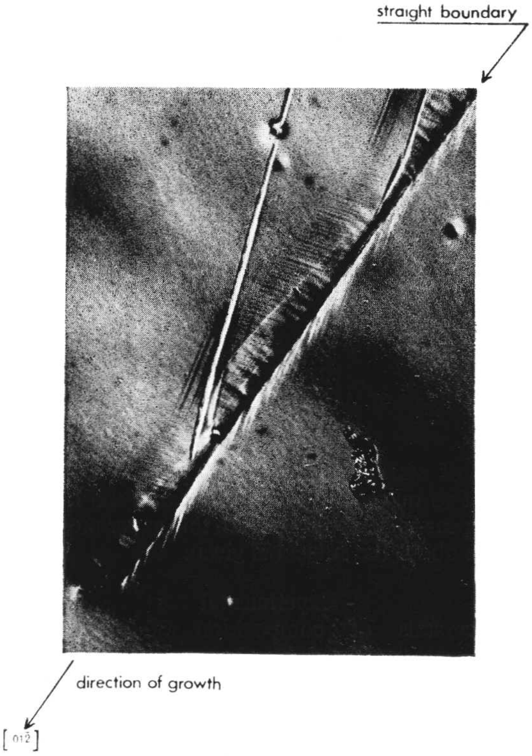


Fig. 1 *Surface martensite needle with polar direction of growth. Specimen surface* (100). *Interference contrast.* × 150.

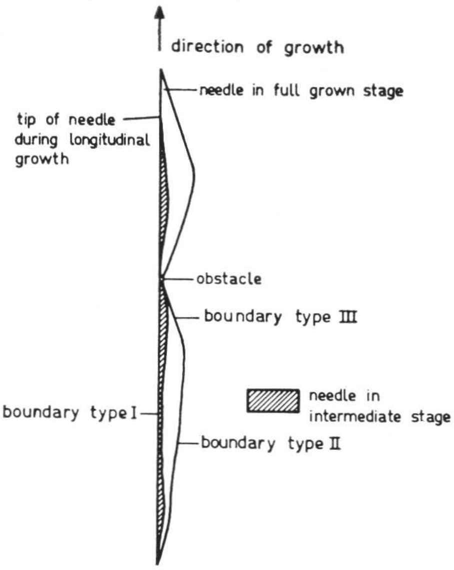
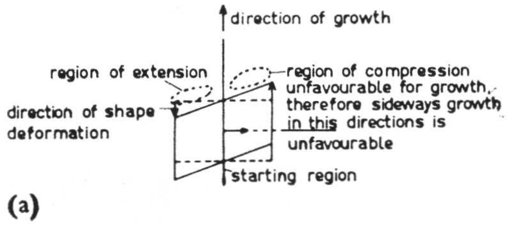


Fig. 2 *Type I, II, and III boundaries in a surface martensite needle. Influence of an obstacle on growth.*

deformation is not homogeneous and the overall shape deformation is nearly zero. The sideways growth on one side only may be interpreted as follows. Because of the greater specific volume of the α phase, the transformation will be promoted by a " hydrostatic " tensile stress and suppressed by a hydrostatic compression. In Fig. 3(*a*) the shape deformation is shown schematically as a simple shear on the habit plane. The direction of the shape deformation is indicated, as is the region where there will be a " hydrostatic " component of the tensile stress. If a very narrow needle has formed, it will broaden only in the direction for which the



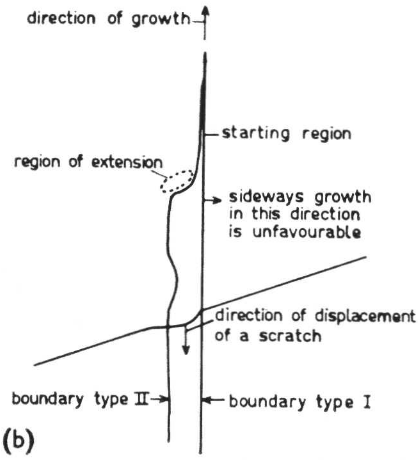


Fig. 3(a) *Shape deformation shown schematically as a simple shear on the habit plane. Growth is promoted in a region of hydrostatic tensile stress.*

Fig. 3(b) *Growth in region of hydrostatic tensile stress results in broadening on one side only.*

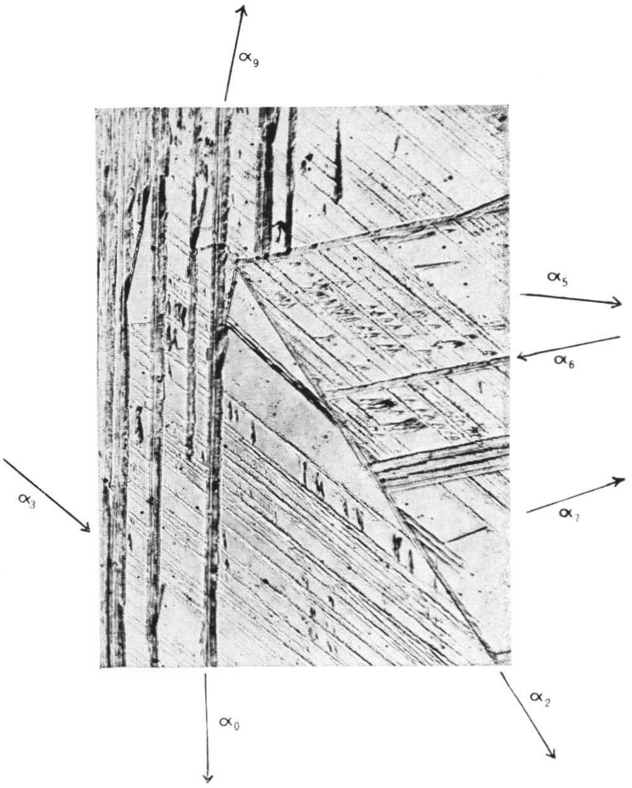


Fig. 4 *Systematic branching of surface martensite. Specimen surface* ($\bar{1}21$). × 30.

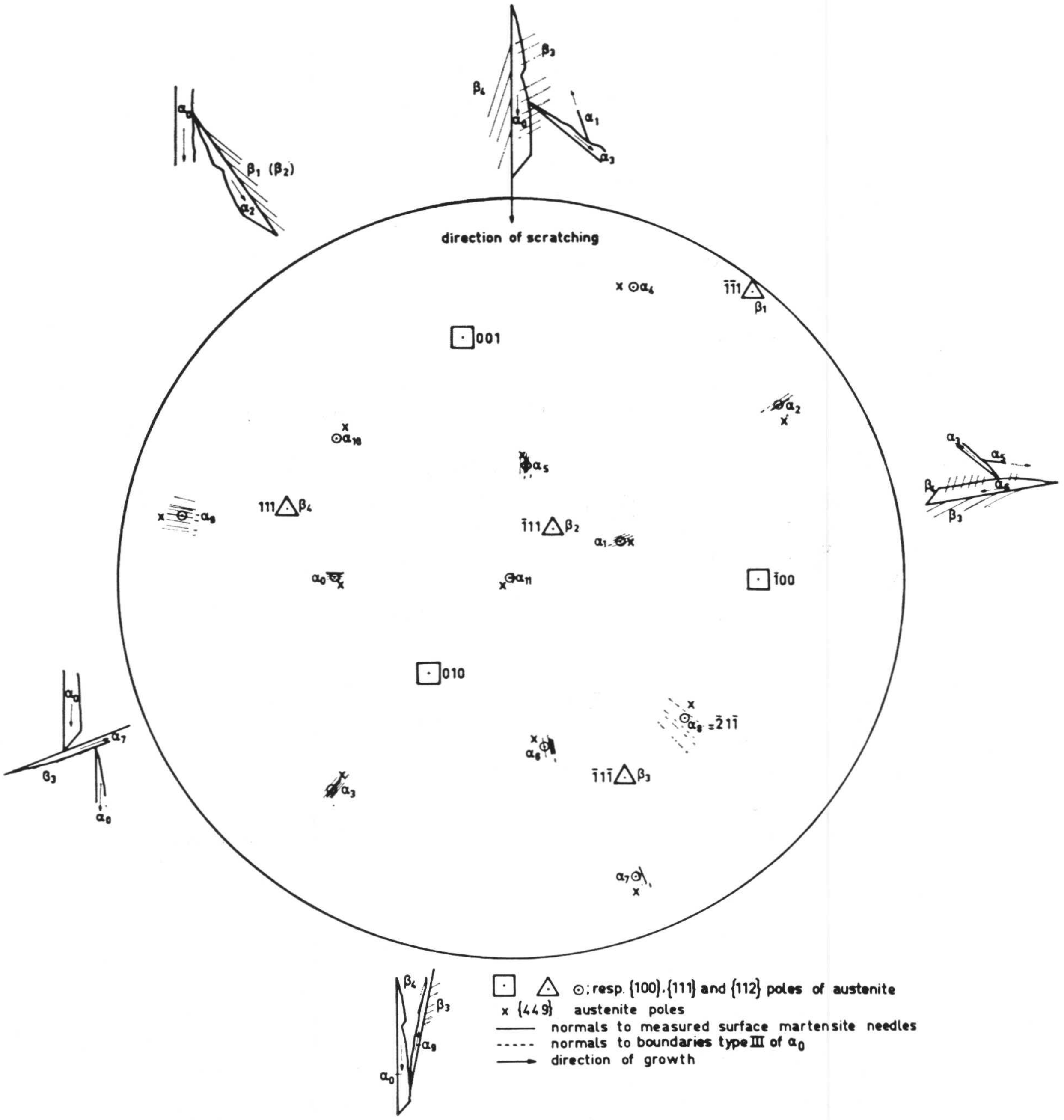
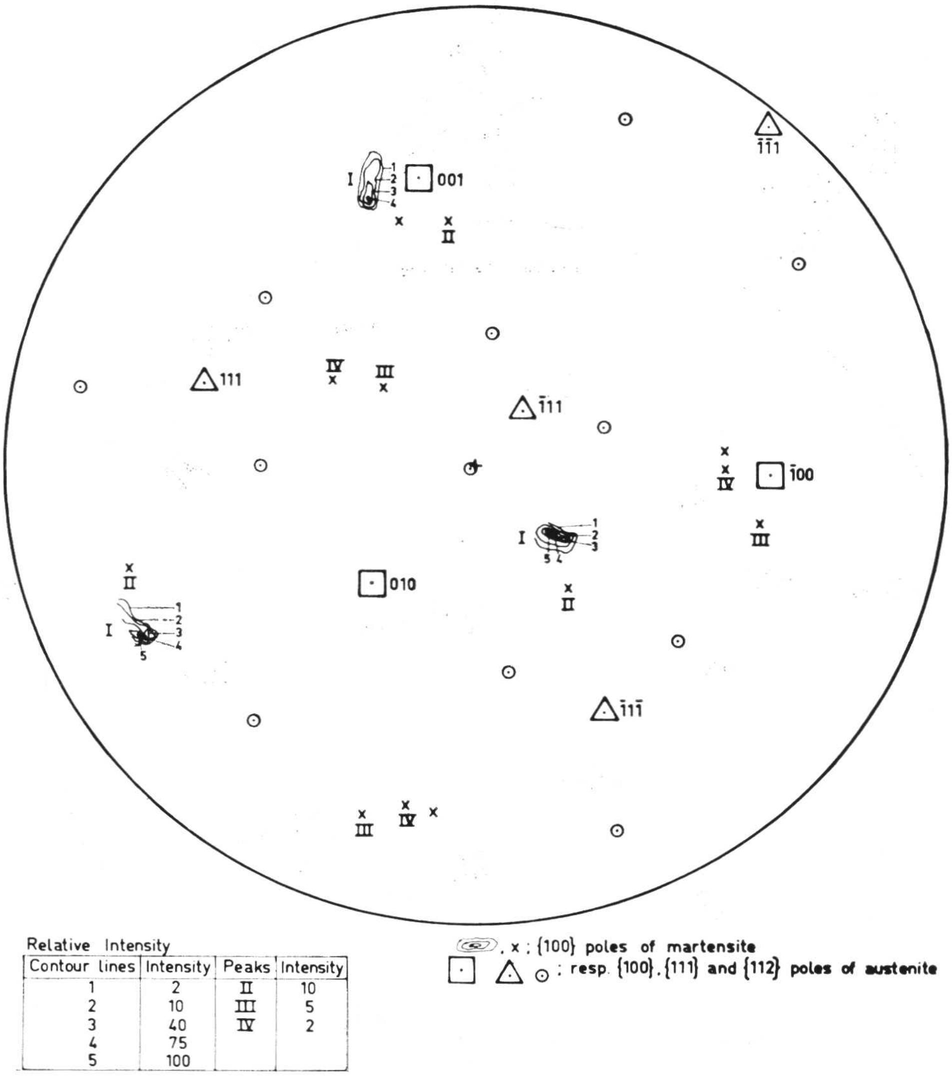


Fig. 5 Showing the austenite orientation, habit planes, Type-III boundaries, and manner of branching for the specimen illustrated in Fig. 4.

shape deformation promotes a hydrostatic tensile stress (see Fig. 3(*b*)).

An interesting feature of surface martensite is the formation of branches in a systematic manner. This is illustrated by Figs. 4 and 5. In Fig. 5 the mode of branching of the surface martensite needles of the specimen shown in Fig. 4 has been indicated schematically. The austenite orientation of the specimen, the normals to the surface martensite needles, the accommodation slip lines, and some normals to Type-III boundaries are also indicated in Fig. 5. The normals to the surface martensite needles are close to the {112} poles of the austenite. From the specimen shown in Fig. 5, which had a (112) orientation, and from other specimens with (100) and (111) orientations, it was concluded that the habit plane of surface martensite differs from $\{112\}_A$ by 2° at most. X-ray work showed that, surprisingly because of large accommodation shears, the martensite orientation was very well defined. Fig. 6 shows the sharp peaks obtained for the $\{200\}_M$ reflections for the specimen shown in Fig. 4. This is perhaps the first martensite orientation determination for which it has been possible to obtain the distribution in space of the orientations of a single martensite variant. The distribution



Relative Intensity

Contour lines	Intensity	Peaks	Intensity
1	2	II	10
2	10	III	5
3	40	IV	2
4	75		
5	100		

, x : {100} poles of martensite

□ △ ⊙ : resp. {100}, {111} and {112} poles of austenite

Fig. 6 *Orientations of surface martensite in the specimen shown in Fig.* 4.

of the martensite intensities is indicated by contour lines. (Orientation I). In this figure the orientations of weak reflections that originated from branches of the main needles are also shown and indicated by II, III, and IV, respectively. The combination of martensite orientations and habit planes is given in Fig. 7. The orientation relationships of the martensite variants I, II, III, and IV are brought together in " standard orientation " in Fig 8.

Still more astonishing than the sharply defined martensite orientation is the fact that the orientation relationships of the four variants lie close together in spite of the fact that they belong to different habit variants on the same specimen. Three of these habit planes have an orientation to the specimen surface that is different (habit planes I, II, and IV; see Fig. 7). One would expect that the orientations of the related martensite variants should differ because the accommodation of a needle by the surrounding austenite would be different.

As already mentioned, the overall shape deformation of surface martensite is nearly zero. This means that the lattice deformation is almost completely compensated by the lattice invariant deformation.

The I.P.S. theory may be formulated as

$$\mathbf{F} = \mathbf{S\,R\,P}$$

In this matrix equation **F** is the shape deformation, **S** the lattice invariant deformation, which must be an invariant plane strain, and **R P** the lattice deformation written as the product of the " pure " strain **P** and a rotation **R**. Now in the case of complete compensation of the lattice deformation **S** must be the inverse of **R P**. Consequently **S** cannot be an invariant plain strain, and calculations with the I.P.S. theory are of no use. However, it may be supposed that the slight shape deformation is a consequence of the accommodation in the austenite and that in an initial stage a needle in the form of a very narrow lath grows under conditions that satisfy the I.P.S. theory. Starting from this supposition, the application of the theory was attempted. The graphical method developed by Lieberman[9] was used because for this method a " best fit " procedure is possible. The invariant line is found from the intersection of the initial Bain cone B_i and the rotated final Bain cone B_{fr}. For the orientation re-