THE ROLE OF SUB-STRUCTURE IN PHASE TRANSFORMATIONS

R. M. Fisher

Edgar C. Bain Laboratory
For Fundamental Research
United States Steel Corporation

Abstract

Lattice defects, particularly dislocations, play important roles in the nucleation and propagation of phase transformations and so plastic deformation prior to or during transformation provides a possible means of controlling the kinetics and the resulting microstructure. The available experimental evidence and the present status of our understanding of these effects will be reviewed for transformations from austenite, formation of sigma phase and the development of anti-phase domain structures in ordered alloys.

Introduction

Sub-structure can play several different roles in phase transformation or precipitation processes as it can be involved in both the nucleation and propagation of the new phase and also may itself be generated by the transformation process. Because of the ambiguity of the term 'sub-structure', in this report it will be taken to mean any dislocation array and these various roles will be discussed and related to some of the previous work on the decomposition of austenite, ordering transformations and the formation of sigma phase.

Most of the conceivable roles that dislocations might play in phase transformation and precipitation are illustrated schematically in Figure 1. As shown in Fig. 1a, the nucleation sites for the formation of a second phase (β) may be at either dislocations (top sketch) or in the case of f. c. c. crystals at stacking faults. The detailed features of these processes will depend on the crystal structures of the parent and product phases as well as any lattice expansion or contraction which may be involved and in many cases nucleation will occur only on specific dislocation configurations such as pure screw or edge segments, jogs, etc.

In body-centered cubic metals, the precipitation of carbon or nitrogen at low temperatures is usually observed to occur along dislocation lines. Figure 2 shows an example of carbon precipitation on a dislocation network in vanadium and other examples of such precipitation in iron can be found in the review paper by Keh, Leslie and Speich in this symposium.

Observations of the precipitation of carbide on stacking faults in f.c.c. stainless steels have been reported by Hatwell and Votava[2] and van Aswegen and Honeycombe[3].

Possible roles of dislocations in the propagation or growth of a phase transformation are illustrated in Fig. 1b. In the case of diffusionless or martensitic transformations, the atomic rearrangement occurs by shear processes and the interface between the parent and product phases consists of an appropriate dislocation array as indicated at the top of the β region in the figure. The transformation in this case proceeds by the movement of the dislocations in the array. If the transformation occurs by diffusion and results in a volume change, nearby dislocations can act as sources or sinks to supply or absorb vacancies required to accommodate such volume changes as illustrated at the bottom interface of the β phase in the sketch.

The inverse of the processes shown in Fig. 1a, b can also be expected to occur, i.e., the generation of dislocation sub-structure during the growth of the new phase and several different possibilities are illustrated in Fig. 1c. At the right of the β phase region is shown the case where the volume change during the transformation is negative (i.e., shrinkage). Here vacancy loops may be produced[4] which then move away from the particle by a combination of glide and climb (absorption of vacancies). An example of such vacancy loops observed by Smallman[5] in Al-3.5pctMg alloys is shown in Figure 3. A detailed analysis of such dislocation loop configurations in these alloys has been carried out by Embury[6] and Nicholson. At the left side, a positive volume change is shown which will result in the formation of interstitial loops. These loops may move away from the particle by glide as before, but in this case they will shrink by the absorption of vacancies from the lattice. An example of such loops produced during the precipitation of chromium carbide in an 80pct Cr- 20pct Fe alloy is shown in Figure 4.

Interface dislocations as shown schematically at the top of the β region in Fig. 1c may be produced to accommodate the misfit between the two lattices when coherency is lost. This structure has been observed along the cementite-ferrite interface in pearlite[18] and after cellular precipitation of Ni_3Ti in an austenitic Fe-30 Ni-6 Ti alloy (Speich)[7].

Finally as shown at the bottom of the β region in Fig. 1c, defect structures particularly stacking or sequence faults may be generated in the growing phase itself as illustrated in the figure. These may be formed during transformation directly or they may result from the presence of sub-structure i.e., dislocation arrays in the parent phase. Examples of these effects have been observed and will be discussed further in other sections.

Formation of Sigma Phase

The pronounced effect of cold-work in accelerating the rate of formation of sigma-phase in iron-chromium alloys is very well-known. It was first observed by Cook and Jones[8] and has been used extensively since then to hasten the approach to equilibrium in alloys where sigma phase might be expected to form.

The effect of cold work is very large even for transformations within the single phase field, i.e., where no long range diffusion is required. As an example, a heavily rolled sample of 46pct Cr-Fe will transform completely to sigma in several hours at 650°C whereas annealed samples will require several hundred hours. The results of quantitative measurements of the transformation kinetics by Pomey and Bastien[9] and Williams and Paxton[10] are summarized in Figure 5. In both investigations the alloys contained approximately 46 wt.pct Cr; Pomey and Bastien cold-rolled their materials 90 pct. and determined the extent of transformation by quantitative dilatometric measurements, whereas Williams and Paxton used filings and followed the reaction by magnetic measurements.

These data show that the transformation rate is increased by approximately a factor of 100 although whether it is the nucleation or the growth of sigma that is affected is not apparent. A detailed investigation has been initiated on this subject and some of the preliminary results will be outlined briefly in this report as well as some other aspects of the role of sub-structure in the transformation which have been observed.

The effect of cold-work on the growth rate was determined by measuring the diameter of a number of the largest particles that could be found in the sample following the procedure frequently used in studying the pearlite reaction. The results of the measurements on specimens deformed varying amounts by cold-reduction are shown in Figure 6 and it is clear that the growth rate is increased substantially. The apparent inversion between 85 and 90 pct. is puzzling; possibly it is related to the fact that 90 pct. samples were deformed using a different set of rolls and under different conditions or it may be a real effect as will be discussed further.

Measurements of the nucleation of sigma phase indicated that cold work does not have a pronounced influence. The results suggest that a particular amount of cold work introduced a fixed number of nuclei and that even for 95 pct. reduction the increase over the annealed specimens is less than a factor of five. Thin foil observations are in accord with this conclusion. Figure 7 shows a transmission electron micrograph of a specimen deformed 5 pct. and then aged for 16 hours at 650°C. Unlike the case of precipitation (Vanadium Figure 2) shown previously, there is no evidence of transformation beginning at the dislocations. Polygonization and recrystallization occurred in specimens more heavily deformed (90 pct.) and aged 30 min. at 650°C as shown in Figure 8 with no evidence for sigma nucleation in most regions.

Feng and Levesque[11] have reported sigma formation along deformation twins in rhenium - molybdenum alloys. Deformation twins were produced in annealed samples of the 46 pct. alloy used in this study by means of hardness indentations or punch marks on previously polished surfaces. Twinned areas were photographed and then after aging in hydrogen at 650°C the identical area was located and re-examined. An optical micrograph of the specimen after etching with glyceregia (the recommended etchant for sigma) is shown in Figure 9. From a preliminary examination of such areas it appeared that as reported, the twins had transferred to sigma. However, after further aging and using different metallographic procedures it was found that such twins were not sigma. Occasionally, definite sigma particles could be identified which were associated with the twins particularly at intersections. An example of this is shown in Figure 10. Thin foil studies of deformation structures in these alloys have shown that very intense localized deformation often occurs at twin intersections as illustrated in Figure 11. The rate of growth of sigma was also found to be enhanced along some of the twins as shown in Figure 12 causing the particles to have rather irregular shapes. In heavily cold-rolled specimens, the sigma particles maintain a more spherical shape.

Thin foil observations of partially transformed specimens show that some recovery and polygonization occurs ahead of the growing sigma phase. Figs. 14a and 14b show examples after 15 min. and 30 min. at 650°C following 90 pct. cold reduction and it is clear that the subgrains are becoming more perfect as aging proceeds. The growth measurements indicated that the rate was decreasing during this period. The apparent discrepancy in growth rate between samples deformed 85 and 90 pct. may be associated with more rapid and pronounced recovery in the samples given the greater cold reduction.

It may also be noted in these figures that the sigma particles contain faults parallel to the growth direction. These have been studied in detail by Marcinkowski and Miller[12] and found to be sequence faults. A large number of different fault configurations are possible because of the complex crystal structure of sigma. Marcinkowski and Miller suggest that these faults are generated during the transformation and this idea was borne out by these observations. Figure 15 shows an example of a fault corresponding to a dislocation subboundary in the ferrite.

Discussion

These preliminary results indicate that sigma phase is nucleated at regions of very high dislocation density, possibly when recrystallization begins at these points. From a study of sigma formation in a series of austenitic stainless steels, Lena and Curry[13] also concluded that there was a correlation between the effect of cold work on sigma formation and on recrystallization. In annealed specimens sigma formation begins at certain points along the grain boundaries where specific orientation relationships exist between the grains so that the sigma nucleus can be coherent with both grains simultaneously. (These results will be reported in detail separately.) However, despite this restriction on nucleation and the apparent connection with recrystallization, it must be emphasized that cold work appears to influence growth far more than it does nucleation.

The origin of the effect of dislocation density on the rate of growth of sigma phase is not clear. In some respects the growth of sigma particles in the single phase field where no composition change occurs is similar to recrystallization and grain growth. This similarity is suggested by the micrographs in Figure 14 showing the interface between sigma and the ferrite matrix. The difference, of course, is that the recrystallized 'grain' has a different crystal structure than the deformed matrix.

The increase in growth rate in heavily deformed specimens (approx. 100X) is of the same order of magnitude as the effect of cold work on grain growth in deformed as compared to annealed specimens. An Arrhenius-type plot of the time for 50 pct. transformation at different temperatures (from the data of Ref. 9 and 10) gives the identical slope of 31,000 calories for both annealed and deformed specimens. This value is comparable to measured activation energies of recrystallization. However, its interpretation as with similar measurements of recrystallization is complicated by the possibility of recovery occurrring in the lattice ahead of the growing interface so that the driving force is decreasing with time. This effect is clearly evident from a comparison of Figs. 14a and 14b, but might not have been as pronounced in the references cited.

The stored energy of cold-work recovered when sigma is formed, even in the most heavily deformed specimens, would not be more than 200 cals/mol. If this stored energy becomes the dominant driving force for growing sigma phase then the chemical free energy involved must be unusually small. Sigma is a more dense phase than ferrite and the strain energy developed by the volume change could result in a substantial reduction in the effective driving force. Any detailed analysis of the sigma transformation will require more experimental information than is now available, but it is apparent that substructure plays important roles in the formation of sigma phase.

Decomposition of austenite

Sufficient information is not available as yet to indicate the role of substructure in the decomposition of austenite in any detail, but the results of a number of investigations suggest that a close relationship does exist. Studies have been made of the effect of applied stress on the pearlite[14, 15], bainite[15, 16], proeutectoid ferrite[16, 17] and martensite[15] transformation and in all cases above a threshold stress level, a marked acceleration of the rate of transformation was obtained. Without going into a detailed discussion of the experimental observations and their interpretation, it seems quite clear that these transformations can be nucleated by plastic deformation of austenite. There appears to be little effect of stress in the propagation or growth rate of the transformations but further study of this point is desirable.

Dislocation sub-structure is generated during transformations from the austenite. This is evident as extra-plasticity which occurs during transformation under stress[15] and in the case of the pearlite reaction, metallographic effects may also be noted[18]. Here, even in the absence of an externally applied stress, sufficient deformation of the austenite occurs to cause appreciable polygonization ahead of the transformation which results in the formation of small angle subgrains within the pearlite colony. It has also been observed[18] that the dislocations in the polygonized boundaries can block the growth of the cementite lamellae but not the ferrite. Finally it appears[18] that sub-structure in the form of closely spaced stacking faults is generated in the cementite particles during the pearlite transformation.

Currently much interest is concentrated on microstructures produced by extensive plastic deformation during or prior to transformation, i.e., treatments usually referred to as ausforming or thermomechanical treatment. Our lack of a full understanding of the relation between dislocation sub-structure and transformation, handicaps attempts to interpret such structures. For example Figure 16 shows a carbon extraction replica of an ausformed sample of an experimental steel (composition listed below) kindly supplied by Dr. Victor Zackay[19]. This specimen was deformed 90 pct. at a temperature of about 500°C i.e., in the temperature range between the C curves for pearlite and bainite formation. From the micrograph it is clear that carbide precipitation has occurred along the deformation bands but it is impossible at the moment to choose between the several mechanisms that are conceivable. These are:

(1) carbide precipitated from the austenite on dislocations introduced by the deformation,

(2) the deformation accelerated the bainite reaction,

(3) the deformation raised the M_s temperature so that martensite formed which immediately tempered.

The first mechanism has been suggested by Grange[20] and the latter two are both consistent with observations on the effect of deformation on the bainite[14, 15] and martensite[15] transformation discussed below.

These brief remarks are intended to emphasize that dislocation substructure does appear to have an important role in transformation from the austenite and that insufficient experiments specifically designed to investigate these effects have been carried out. Such studies would be very valuable as they might shed considerable new light on the mechanisms of the transformations and also lead to more effective thermo-mechanical or ausforming processes.

Composition of ausformed steel

3 Cr 1.5Ni 0.75Mn 0.5Mo 1.5Si 0.63C

Formation of Superlattice Domain Structures

Dislocation sub-structure has an important and rather unique role in the formation of superlattice domains during ordering. The reason for this is that in many structures, the unit of slip, i.e., the Burgers vector responsible for anti-phase domain boundaries and an interaction can occur; in $AuCu_3$ for example these are both $1/2\ a_o\ \langle 110 \rangle$. That is, the extra half plane of atoms which constitutes the dislocation can eliminate the out of step boundary which otherwise would be present and terminate the anti-phase boundary at the slip plane. This effect is illustrated in the schematic drawing by Marcinkowski[21] shown in Figure 17. This figure also shows that the movement of individual slip dislocations in an ordered structure creates new anti-phase boundaries. The energy associated with this process results in strong coupling between pairs of dislocations which greatly reduces the stress necessary to drive dislocations through an ordered lattice.

The termination of anti-phase boundaries on dislocations present in the specimen prior to formation of the domain structure has been observed by Pashley[22] and Marcinkowski[21] previously. A difficulty that is encountered here is that the contrast conditions are such that only two-thirds of the boundaries are revealed[23] in any particular micrograph. Thus, most of the apparent terminal points of boundaries in micrographs are due to this reason rather than a true termination of the boundary. The point indicated in Figure 18 of a specimen of $AuCu_3$ slowly cooled from above the critical ordering temperature (approx. 385°C) corresponds to a point where termination on a dislocation has taken place. The extended boundaries running across the micrographs were produced by movement of single dislocations in the thin foil. This deformation occurred during handling of the thin foil specimen and boundaries of this sort would not normally be formed in bulk specimens.

If the dislocation density within the specimen prior to ordering is very high it can markedly influence the size of the anti-phase domains since their size will be essentially equal to the dislocation spacing. The rate of growth of the domains will also be retarded since this will involve dislocation climb processes. Roessler, Novick and Bever[24] have recently studied the annealing of $AuCu_3$ after cold work using electrical resistivity and X-ray techniques and noted the retardation of domain growth as discussed above.

A similar study of the effect of sub-structure on domain size is currently underway in this laboratory[25] using transmission electron microscopy. It has been found that domains formed during slow cooling of heavily cold-rolled $AuCu_3$ are only 1/30 to 1/10 to size of these in annealed specimens given the same cooling treatment. Since the strength of ordered alloys only depends strongly on domain size if they are very small, means of achieving very small domains are of considerable interest.

Summary

Dislocation sub-structure can be expected to take several important roles in phase transformations and these are discussed in connection with the nucleation and propagation or growth of precipitation or phase change. In the case of precipitation from solid solution, nucleation or dislocations on stacking faults has been observed in many systems although detailed analysis has not been carried out as yet.

Observations of the effect of plastic strain on decomposition of austenite suggests that dislocations introduced by deformation of the parent austenite can serve to nucleate the pro-eutectoid ferrite, pearlite and bainite reactions, although a direct connection has been demonstrated. The importance of these effects in developing ausforming processes is pointed out.

The effect of cold work on accelerating the formation of sigma phase in approx. 50-atomic percent Fe-Cr alloys is found to be mainly due to increasing the growth rate. It is suggested that the strain energy stored in the lattice by cold-work and released by the transformation makes a very large contribution to the driving force.

The unique relation between dislocations and the domain configuration in

ordered alloys is discussed and the manner in which dislocation density controls domain size is pointed out.

The various mechanisms by which sub-structure may be generated by phase transformation are described. Examples are shown of vacancy or interstitial loops generated by volume changes during precipitation and of growth faults in the new phase due to defects in the parent lattice.

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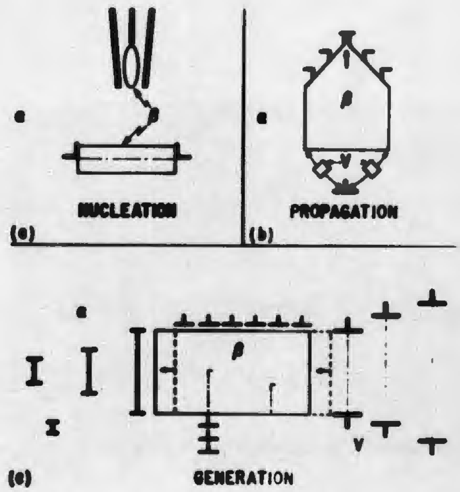

Fig. 1. Schematic Illustration of roles of dislocation sub-structure in phase transformation. a) in nucleation b) in propagation c) generation of sub-structure by the transformation.

Fig. 2. Carbide precipitation on dislocation network in Vanadium.

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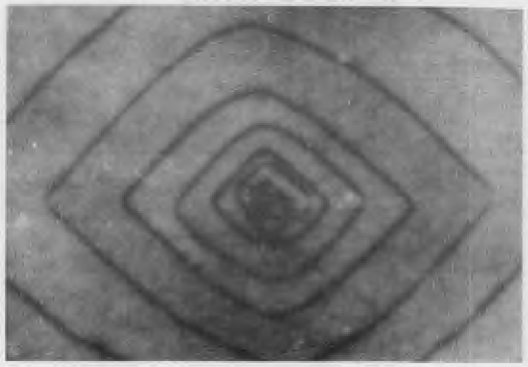

Fig. 3. Vacancy loops formed during precipitation of Al- 3.5pct.Mg alloy (Smallman[5]).

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Fig. 4. Interstitial loops formed during carbide precipitation in 80 pct,Cr- Fe at 600°C.

40,000X

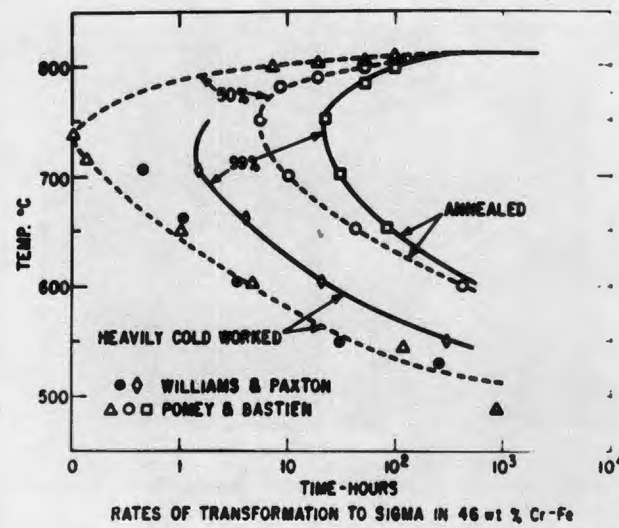

Fig. 5. Effect of cold work on formation of sigma phase.

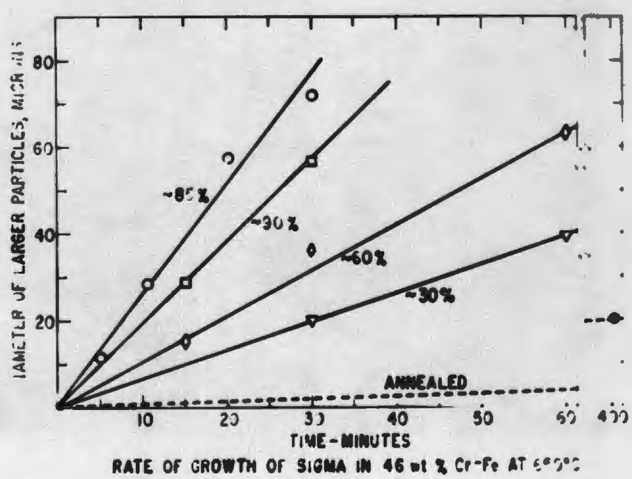

Fig. 6. Effect of cold work on growth rate of sigma phase.

Fig. 7. 46 pct. Cr- Fe cold-rolled 5 pct. and annealed 16 hours at 650°C.

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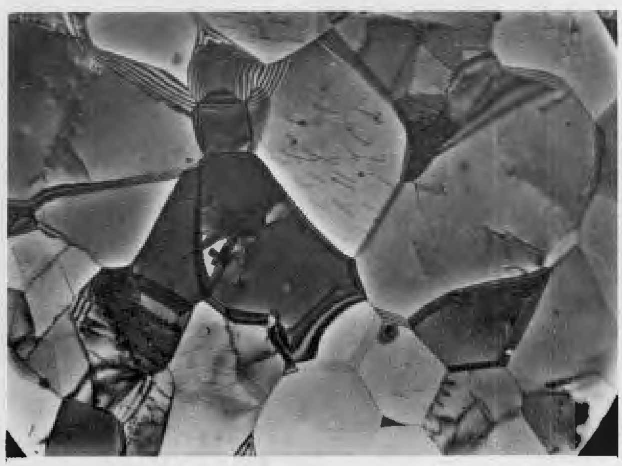

Fig. 8. 46 pct. Cr -Fe cold-rolled 90 pct. and annealed 30 min. at 650°C.

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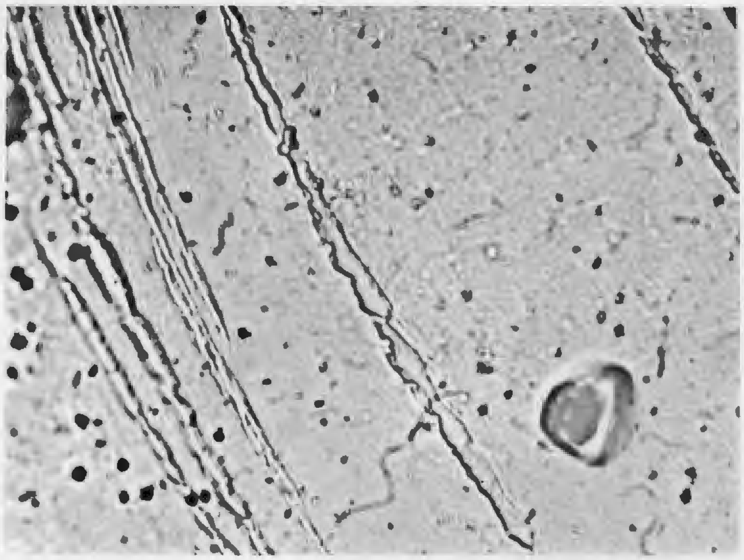

Fig. 9. 'Apparent' sigma formation along deformation twins in 46 pct. Cr - Fe during annealing at 650^{o}C.

1000X

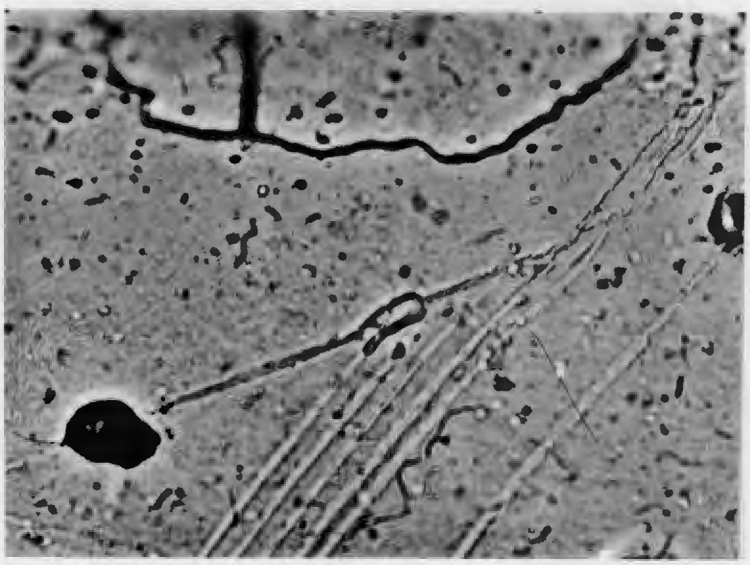

Fig.10. Sigma formation at intersection of deformation twins in 46 pct. Cr - Fe during annealing at 650^{o}C.

1000X

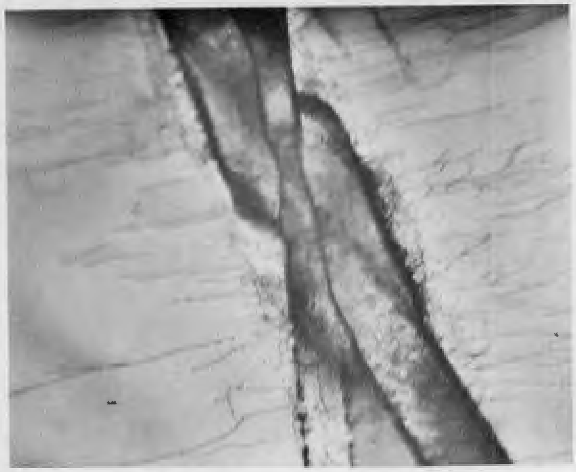

Fig. 11. High dislocation density at intersection of deformation twins in 46 pct. Cr - Fe.

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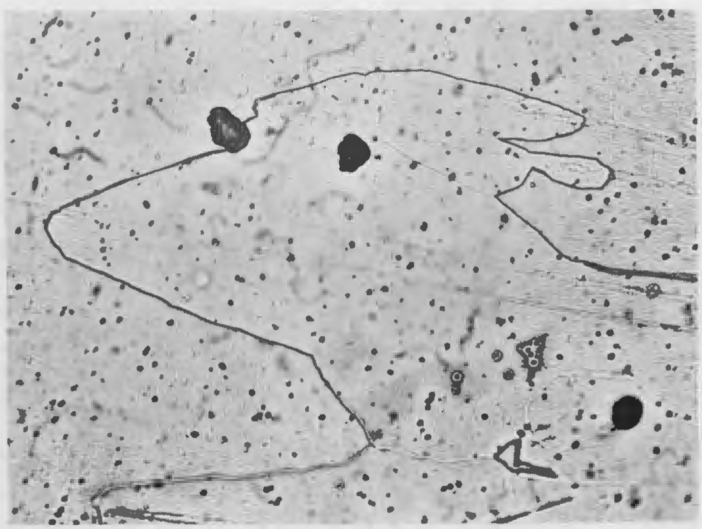

Fig. 12. Rapid growth of sigma phase along deformation twins in 46 pct. Cr - Fe during annealing at 650°C.

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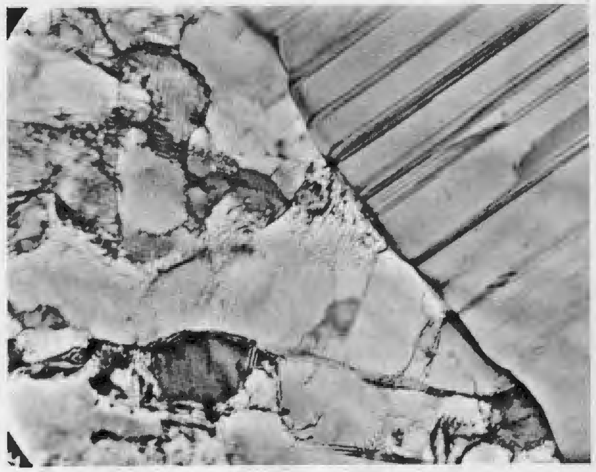

Fig. 13. Interface between sigma phase and deformed matrix in 46 pct. Cr - Fe annealed for 15 min. at 650°C.

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Fig. 14. Interface between sigma phase and deformed matrix in 46 pct. Cr - Fe annealed for 30 min. at 650°C.

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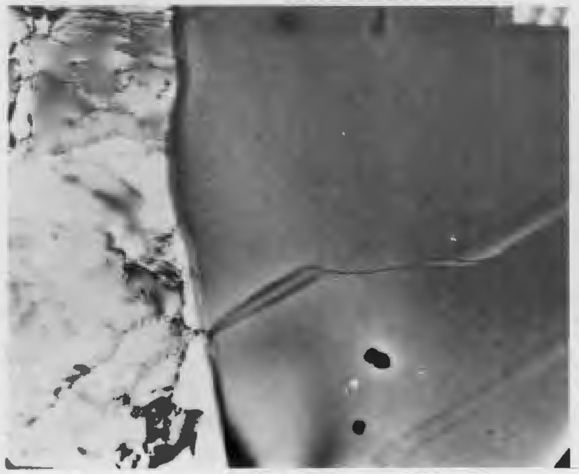

Fig. 15. Growth fault following sub-structure during growth of sigma at 650°C.

20,000X

Fig. 16. Carbon extraction replica showing carbide precipitation along deformation band in ausformed steel 18.

15,000X

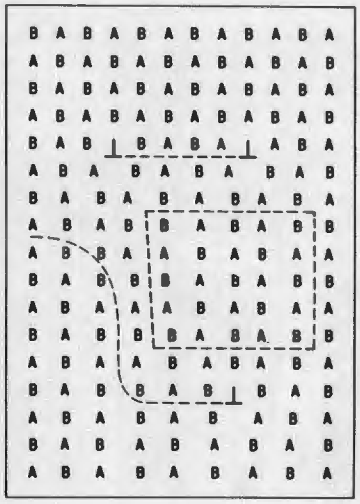

Fig. 17. Schematic illustration of relation between dislocation sub-structure and anti-phase boundaries in ordered structures[20].

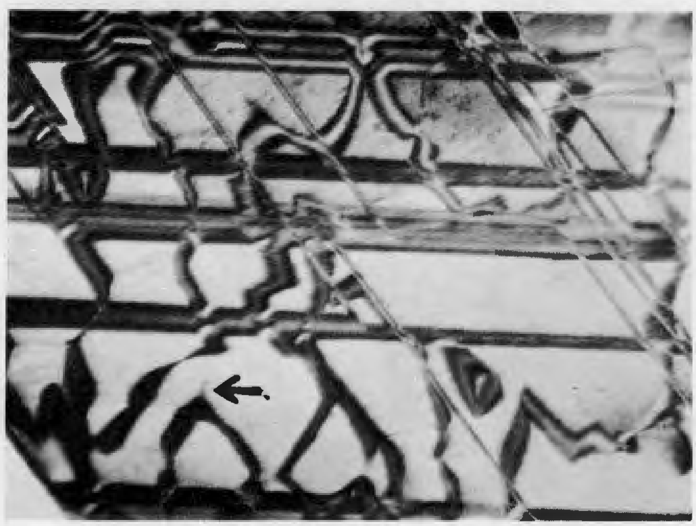

Fig. 18. Termination of thermal anti-phase boundary on dislocation.

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