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ABSTRACT

Substructures of conventional and ausformed steels based on Fe-25% Ni-0.3%C, with carbide forming alloying elements (Cr, V and Mo) were examined by transmission electron microscopy in both austenitic and martensitic conditions. Precipitates and a high density of dislocations were observed in austenites and martensites of all 30% ausformed steels.

The higher strength resulting from ausforming is primarily due to the increased dislocation density. The precipitates play an important role by providing sites for dislocation multiplication and pinning. The role of carbon and alloying elements in strengthening was mainly through providing precipitates. No systematic variation of martensite plate size with ausforming parameters was found.

The extent of twinning in martensites decreased with increasing amount of ausforming. The absence of twinning and the high density of dislocations probably accounts for the better ductility of ausformed steels. For maximum strength and ductility the total alloy content should thus be chosen such that the final structure consists of small stable precipitates in a matrix containing a very high dislocation density ($\sim 10^{13}/\text{cm}^2$).

FIGURE CAPTIONS

Figure 1 Dislocation structures in undeformed and 8% deformed austenites. (A) and (B) show two different areas from steel 1410, showing that some dislocations remain after austenitizing. (C) for steel 1541 and (D) for steel 1402, show dislocations lying on slip planes after 8% deformation at 500°C.

Figure 2 (A) Bright field micrograph of austenite in steel 1398, 30% deformed at 500°C. The substructure shows dislocation tangles and precipitates which are clearly seen in the dark field micrograph (B), taken of the 111 spot A in the diffraction pattern (C). Notice faint streaks near the 200 and $0\bar{2}\bar{2}$ spots in (C). The diffraction pattern is in $[01\bar{1}]$ orientation.

Figure 3 The diffraction pattern from another area of 30% deformed steel 1398. Notice the faint rings from carbides and increased intensity of these rings near matrix spots, e.g. near $\bar{2}00$, $\bar{2}20$, etc. The diffraction pattern is in [001] orientation.

Figure 4 A very thin edge of 30% deformed austenite in steel 1398 after polygonization in the electron microscope due to slight beam heating. Some of the precipitates are seen to reverse contrast when the dark field micrograph (B) is taken of A. The ring diffraction pattern in (C) proves that austenite is polygonized and the carbides are of random orientations. The MoC precipitates here are larger compared to Fig. 2.

Figure 5 Polygonized area in a very thin foil of 30% deformed austenite in steel 1541. The dark field (C) is taken from A at the first ring of the diffraction pattern (B), while the dark field (D) was taken from inside this ring.

Figure 6 Mechanical twinning in austenite of steel 1398, deformed 30% at 100%C.

Figure 7 Twinned and untwinned structures in martensites of undeformed and 8% ausformed steel 1410. The size of the martensite plates has not undergone much change as can be seen by comparing the substructures in (A) and (B) for undeformed and 8% ausformed steel, respectively. Notice the dislocation substructures in the martensite plates also. In (C) and (D) twinned plates with midribs are shown from these steels. In (D) a dark field micrograph shows the discontinuity of the twins along the twinning direction corresponding to the trace of the slip plane. The twin density is seen to decrease away from midrib.

Figure 8 (A) VC precipitates in martensite of 30% ausformed steel 1402. The precipitates are not visible in bright field but are clearly seen in the dark field micrograph (B). The precipitates are from 50-150Å in size about 150-250Å apart.

Figure 9 Retained austenite (γ) and martensite (M) in 30% ausformed steel 1402, both showing precipitation and a high dislocation density. Notice the non-uniform shape of martensite plates in (B).

Figure 10 (A) Diffraction pattern and its analysis (B) of the circled area in (C) from steel 1402 ausformed 30%, containing martensite and retained austenite. (D), (E), and (F) show the dark field micrographs from A, C, and B, respectively.

Figure 11 (A) and (B) showing presence of some transformation twinning in martensite after 30% ausforming in steel 1410 and 1398, respectively.

Figure 12 (A) Martensite containing fine cementite particles after slight tempering in 30% ausformed steel 1410.

(B) Another area after tempering for longer time, showing that the Fe_3C precipitates have grown into a Widmännstatten pattern.

Figure 13 Diffraction pattern from a tempered area in 30% ausformed steel 1410, used to verify the orientation relationships. The foil orientation is $[211]_\alpha$ which is parallel to $[001]_{Fe_3C}$.

INTRODUCTION

There are various thermal mechanical treatments for alloys which are now being developed for obtaining higher strength and toughness. Ausforming is one such treatment in which metastable austenite is deformed without recrystallization before transformation to martensite. The deformation is confined to a limited 'bay' region in order to prevent decomposition to non-martensitic products. The ausforming process has been the subject of numerous investigations which have been recently reviewed by Phillips and Duckworth (1), and Marshall (2). The main metallurgical interest has centered around optimizing the process parameters so that the best combination of strength and ductility is obtained. These parameters (viz., temperature of deformation, amount of deformation, carbon content, alloy content, tempering time and temperature, and austenitizing conditions) are, however, intimately related and it is difficult to make generalizations about the process (see e.g. Phillips and Duckworth (1)). A number of factors are thought to be important in controlling the strength, e.g. precipitation and/or solution hardening and work hardening. Opinion is divided regarding macroscopic factors such as martensitic plate size (3,4,5).

From the results of Floreen et al. (6) on stainless steel it is clear that ausforming is not beneficial in the absence of carbon. The exact role played by carbon has been rather unclear although a number of suggestions regarding precipitation hardening have been recently put forward (3,5,7-10). No direct evidence for precipitation was found until preliminary results of the present work were reported at the Berkeley Conference (10). Carbon may also act as a solid solution strengthener (11), although it has a deleterious effect on ductility (12).

With deformation of austenite there is an increase in dislocation density. It is possible that these dislocations are retained during the transformation from austenite to martensite, though some dislocations or twins will be produced during the phase transformation. Dislocations introduced into austenite could aid in inducing precipitation by increasing, directly or indirectly, the diffusivity of alloying elements. It is also known that carbon atoms form atmospheres about dislocations (Cottrell atmospheres). Depending on the temperature and amount of deformation, the nucleation of carbides may be very high, but the growth rate would be limited. From thermodynamical considerations, alloy carbides rather than cementite are likely to precipitate under the usual ausforming conditions. The alloy carbides formed would therefore be very small, finely dispersed, and difficult to detect. Previous thin foil, and extraction replica work have not been successful in determining the existence of such carbides (5,7). Thus, so far, there has been no direct evidence for carbide precipitates.

Twinning has also been regarded as a possible mode of martensitic strengthening by Kelly and Nutting (13). In the absence of any detailed substructural investigations of ausformed steels, the exact role of twinning in this case is not known, although other observations indicate that twinning may not be an important mode of strengthening. For example, Speich and Swann (14) have shown in the case of Fe-Ni martensites that internal twins are not an important strengthening mechanism, because no sharp increase in strength was found for alloys of increasing nickel content which were internally twinned. Work on explosively deformed nickel (15) also showed that twinning did not appreciably increase the strength.

It is apparent that most of the work done on ausformed steels has been either on mechanical properties or on explaining these on the basis of some metallographic and extraction replica work, but little attempt has been made to study the substructure in detail. The present work is an attempt in this direction.

EXPERIMENTAL

Steels were designed so as to provide a range of temperatures for deformation and to enable examination of both metastable deformed austenite at room temperature, and martensite obtained by quenching these austenites in liquid nitrogen. A base composition of Fe-25% Ni-0.3%C was utilized. With a constant carbon content of 0.3%, the alloying elements and nickel content were adjusted to provide a favorable M_s. Based on strength considerations (10) three different alloying elements, V, Cr and Mo, were used. Three important parameters were chosen for this work, viz. degree of deformation (undeformed, 8% and 30%), temperature of deformation (100° and 500°C), and composition. The steel compositions and their M_s temperatures are given in Table 1. The steels were provided by the Ford Motor Company who carried out the thermal mechanical treatments. The mechanical properties of these steels have been reported elsewhere (10), and will be referred to where necessary.

For this electron microscopy investigation, 10 samples were taken from each steel: two from steels with no deformation - one austenitic, and one transformed to martensite; four from steels deformed at 100°C -

TABLE 1

Heat No.	%C	%Ni	%Alloying Element	Austenitizing Temperature	M_s
1410	0.3	27.94	---	1200°C	- 8°C
1398	0.28	24.92	4.50 Mo	1200°C	Below-77°C
1541	0.32	16.40	4.72 Cr	1200°C	-16°C
1402	0.29	24.73	1.85 V	1290°C	- 3°C

two 8% and two 30% deformed, one each for each deformation in untransformed conditions; and similarly four from steels deformed at 500°C.*

Thin foils were prepared by electropolishing, using the window technique, in chromic acid-acetic acid solution (270 cc glacial acetic acid, 14 cc distilled water and 60 gm chromic acid). Foils were mounted in single or double tilt stages, and examined in a Siemens Elmiskop Ib microscope, operated at 100 KV.

The dark field technique was mostly used to study the precipitates, twins, or other fine structures. Dark field work is an absolute necessity in this type of electron microscopic investigation as has been discussed by Thomas (16). The dark field images can be obtained either by gun tilt or without gun tilt. Although it is quicker to obtain dark field images by using only the objective aperture, maximum resolution is obtained only when the electron gun is tilted so that the diffracted rays pass down the optical axis of the electron microscope. In this way spherical and chromatic aberrations are minimized.

In this paper emphasis is placed on a detailed metallographic analysis of the various substructural features in austenite and martensite. These include dislocation arrangements, precipitation, and microtwinning, and involved examination of many electron micrographs and

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*As was found later, the M_s of steel 1398 was too low and hence very little martensite was detected in the microscope. The M_s for steel 1402 was higher, and almost all steels showed the presence of martensite, more so in case of deformed steels because M_s is raised by prior deformation of austenite.

diffraction patterns. On the basis of these investigations some suggestions regarding strengthening mechanisms and the development of high strength alloys are made.

RESULTS

The steels will be referred to by their heat numbers (Table 1). When "alloy steels" are referred to, this means steels containing carbide forming alloying elements in addition to nickel and carbon (e.g. steels 1398, 1402 and 1541).

A. Structure of Austenites

1. 0 and 8% Deformation

Figure 1 shows four structures of austenites in various steels in the undeformed and 8% deformed steels. In many areas of undeformed samples very few dislocations are present (Fig. 1A), but some areas show a relatively high density (Fig. 1B). This indicates that the austenitizing treatment does not anneal out all of the dislocations, which is not surprising because of the relatively low temperature (Table 1). In 8% deformed steels (Figs. 1C and D), the dislocations lie along the traces of {111} slip planes. For all steels in these conditions (0 and 8% deformation) no evidence for any precipitation was observed. The structures are similar to dislocation substructures observed in other plastically deformed metals and indicate that the deformation normally takes place by slip and not twinning. The density of dislocations observed depends on the orientation of the area being examined and its relation to the deformation process, i.e. the amount of local resolved shear strain.

2. 30% Deformation

In contrast to the structure of 0 and 8% deformed steels, the structures of 30% ausformed steels were more complex, for example, in Fig. 2A (for steel 1398), dislocation tangles were observed. It was not possible to resolve any precipitates in bright field images. However, when dark field work was done, it became clear that small precipitates were present in the steels as shown in Fig. 2B. The dark field micrograph (Fig. 2B) was formed from spot A (Fig. 2C), which, as shown in the following, includes a precipitate reflection as well as the (111) matrix reflection. Reversal of contrast indicates the presence of small precipitates.

Some of the austenitic steels were also examined using the XRD-5 diffractometer. The results gave a lattice parameter of about 3.60Å for austenite, and showed no evidence for the presence of carbides. The electron diffraction pattern of Fig. 2C shows streaks near the 200 and 220 type spots, which are seen more clearly in Fig. 3, along with faint continuous rings. From measurements on the diffraction patterns the 'd' values corresponding to the extra reflections were calculated to be approximately 2.10Å and 1.45Å.

For austenites, d_{111} = 2.08Å, so that one of the carbide diffraction spots (with $d \approx 2.10$Å) will almost coincide with the matrix spot. Thus, precipitates will change contrast when the dark field micrograph is taken from a $(111)_\gamma$ spot (e.g. Fig. 2B), as well as at the streaks. Normally, however, the streak or ring is too faint to be seen on the microscope screen (Fig. 3), and the dark field micrographs are taken with the objective aperture placed over a 200 matrix spot which also includes the corresponding streak. The presence of precipitates in this steel is thus confirmed. Precipitates are not producing strain contrast because their dark field images are all of uniform intensity (Fig. 2 for steel 1398), i.e. not black-white "lobed" strain contrast images expected from coherent precipitates such as G.P. zones (17). It is concluded, therefore, that there is no coherency strain field associated with these precipitates.

Similar observations regarding the presence of precipitates were made on the other steels. It was observed from the diffraction patterns in all cases that the streaks or faint rings (as in Figs. 2C, 3) due to precipitates appeared again near the 200 and 220 spots. The observations of these streaks does not necessarily imply an orientation relationship because the intensity of precipitate reflections may be enhanced due to some overlap with matrix reflections (e.g. in Fig. 3 the intensity of the faint continuous ring is higher near the matrix spot than elsewhere). Also, there are insufficient reflections present to establish any possible orientation relationships which may exist.

Sometimes thin edges of the foil polygonized and in these regions the precipitates were observed to be larger than elsewhere. This is associated with the ease with which the dislocations anneal from very thin edges as a result of electron beam heating of the sample in the microscope. One such case is shown in Fig. 4 for steel 1398. The measurements from the ring pattern and the results therefrom are recorded in Table 2. The dark field image (Fig. 4B) from a Point A on the first ring (Fig. 4C) shows the contrast reversal for precipitates.

TABLE 2

Measurements from Fig. 4, for steel 1398

Ring No.	Observed Diameter of Rings in Cm	Austenitic Rings Ratios	Austenitic Rings hkℓ for Matrix	Probable Carbide 'd' values*
1	4	1	111	2.08Å
2	4.6	1.15	200	
3	5.6			1.46Å
4	6.55	1.63	220	
5	7.0			1.18Å
6	7.65	1.91	311	
7	8.0	2.00	222	
8	8.1			0.99Å
9	8.6			0.94Å
10	9.10	2.28	400	
11	10.0	2.50	331	
12	10.3	2.58	420	

*These values are calculated from the camera constant equation.

The carbide rings also include the same d-spacings as were obtained from the spot patterns (Figs. 2C, 3). Although the 'd' values of carbides obtained are not very accurate, it is possible to identify the carbides for steel 1398. In the literature (18), there are two carbides reported for molybdenum, viz. MoC and Mo_2C. Within the accuracy of the results in Table 2, both carbides show lines at 'd' values of 1.46Å and lower. However Mo_2C shows no line with a 'd' value in the neighborhood of 2.1Å. The existence of a 'd' value of ≈ 2.1Å proves that the precipitates are MoC and not Mo_2C.

Similar observations in the polygonized part of the foil were made for steel 1541 (Fig. 5). Calculations of 'd' values from the ring pattern and its comparison with the 'd' values obtainable from the ASTM card file (18) presented similar difficulties as for steel 1398 where the rings for lower 'd' values could not be used to identify the carbides definitely due to the limited accuracy of the calculated results. The line in the neighborhood of 2.1Å is present in all the three Cr-carbides reported (e.g. at 2.05Å for $Cr_{23}C_6$, 2.12 and 2.04Å for Cr_7C_3 and 2.12 and 2.10Å for Cr_3C_2). In this case, therefore, from these observations positive identification of carbides cannot be made. These results are, however, not in disagreement with extraction replica work on aged alloys (10), in which the precipitates were found to be $Cr_{23}C_6$. Similar diffraction experiments enabled the precipitates in steel 1402, to be identified as VC and in steel 1410 as cementite. These identifications are based on the best fit obtained from the comparison of the electron diffraction data of the present work with the previous published x-ray results (18). However, since only a few lines could be observed for each carbide the results of identification may not be conclusive.

In Fig. 5 two dark field micrographs are shown (C and D), one of which (D) is taken with the aperture inside the first ring. Most carbides have 'd' spacings which are higher than the minimum 'd' spacings for the matrix (2.1Å for (111) in the case of fcc austenite and 2.08Å for (110) in the case of martensites), e.g. there are six more lines with 'd' spacings higher than 2.05Å for $Cr_{23}C_6$. If enough carbides are present, these will give rise to some faint spots (which may not be easily visible) inside the first ring. A dark field micrograph inside the first ring may, therefore, under appropriate conditions, show contrast reversal for some precipitates. This is seen in Fig. 5D. It is obvious, however, that for such effects to show up, many precipitates of different orientations should be present. This is unlikely to be the case when precipitates are small and possibly not random.

Observations were made on steels deformed at 100°C also, and they showed similar evidence of precipitation. Due to the complexities of the structures observed, it is not possible to meaningfully measure and compare the sizes of the precipitates or dislocation densities obtained at 100°C and 500°C. From the observations there is very little difference in the structures observed after the 100°C and the 500°C ausforming. The precipitates are up to 150Å in size in the non-polygonized areas.

3. Twinned Austenites

In a few areas of 30% deformed austenites of steel 1398 some evidence of mechanical twinning was observed, both for 500°C and 100°C deformation. An example is shown in Fig. 6. The diffraction pattern (Fig. 6B) is close to [110] orientation and the twins lie on either (111) or $(11\bar{1})$ planes, so that the twin spots coincide with some of the matrix spots (19). The analysis of this pattern together with dark field work show that the structure is twinned. The dark field image of spot A (Fig. 6C) showed no contrast reversal for twins, but only for some precipitates and dislocations. Thus, reflection A is not a twin spot. At spot B, contrast reversal for twins takes place (Fig. 6D), as would be expected, because this $\bar{2}20$ spot remains the same after twinning on either of the {111} planes mentioned above.

Although very few twinned areas were found in Mo steel, no evidence for twinning was found in austenites of the other steels. This is the first time that mechanical twinning has been observed in austenitic steels that can undergo the martensitic transformation.

B. Structures of Martensites

1. 0 and 8% Ausformed Steels

During the transformation austenite to martensite, the lattice invariant shear occurs by slip or twinning. Previous work has shown that twinned substructures are preferred when the solute content is high. Thus, Kelly and Nutting (13) found internally twinned martensite plates in plain carbon steels, the relative number of which increased with carbon content. Swann and Speich (14) found some twinning in Fe-Ni alloys above 25% Ni. There is not a sharp transition from dislocations to twinning and both are usually observed.

The structures of steels ausformed 0 and 8% showed substructures similar to those reported from various other martensitic investigations (e.g. refs. 13, 14). The structures show both twinned and untwinned martensites (Fig. 7), and careful dark field work showed no evidence for precipitation. The twinned structures in these steels contained mid-ribs (13) which are actually regions of highest twin density usually near the center of the plate. The twin density decreases outwards to the edges of the plates (Fig. 7D). The fraction of twinned martensite plates was less in 8% ausformed steels than in unausformed steels.

2. 30% Ausformed Steels

The structures observed in martensites formed after 30% ausforming in all the steels contained precipitates. This is not surprising since the austenites after 30% deformation also showed precipitates (as already mentioned). Figure 8A shows a bright field image in which it is difficult to resolve precipitation. However, once the dark field micrograph (Fig. 8B) is taken, then, as in the case of austenites, precipitation is clearly evident. Furthermore, the individual martensite plates are more clearly resolved. By similar dark field work, it was proved that precipitates were also present in the other steels. There appears to be no change in the number or distribution of carbides from the austenitic to the martensitic state.

Extra rings and streaks were not observed in diffraction patterns from ausformed martensites, although contrast reversal for precipitates could be obtained by suitable dark field experiments. The reason for the non-observance of precipitate reflections is simply due to the fact that the d-spacings of precipitate and matrix are nearly the same; hence, both sets of reflections coincide (e.g. for the first two allowed reflections for martensites $d_{110} \sim 2.08\text{Å}$ and $d_{200} \cong 1.47\text{Å}$ and the observed d-spacings for carbides (Table 2) are 2.08 and 1.46Å).

The structures of these steels were, in general, very complex due to the effects of working and precipitation and because retained austenite was always present. Figures 9A, B show such complex structures for steel 1402, from which it is seen that the dislocation density for retained austenite (γ) is very high. The martensitic areas also contain a high density of dislocations, which may not be revealed in some areas, because of the orientation, and the specimen must be properly tilted in order to reveal all of the substructural features. The martensite plates, in general, had no uniform shape or size as can be seen from the micrographs (Figs. 8, 9). This is because the growth of a martensite plate is hindered by the presence of precipitates and/or other martensite plates in its path.

Because of the small size of martensite plates various orientations of the martensites and precipitates are illuminated. Thus, the diffraction patterns of these steels were very complex and showed very many spots. This was, at times, further complicated by diffraction from retained austenite. Figures 10A, B show such a diffraction pattern and its analysis, with the corresponding image (Fig. 10C) and dark field micrographs (Figs. 10D, E, F) from three spots. The dark field technique helps in the analysis of such diffraction patterns by enabling the separation of different regions contributing to the pattern. It is seen from the diffraction pattern (Figs. 10A, B) that the [110] axis for both M_1 and M_2 martensite plates is parallel to the [111] axis of the austenite. From other patterns this relationship (viz. $[111]_\gamma \parallel [110]_M$) was found to be observed within an accuracy of 3°.

Unlike unausformed and 8% ausformed steels the structure of martensites after 30% ausforming showed very little twinning. In some cases no evidence for twinning was found, while in others, very few areas were twinned. Figure 11 shows two such structures for steel 1410 and 1398. In all cases of martensite twinning the twin plane is one of the {112} variants. Dislocations and precipitations are always present in these martensites.

3. Beam Heating Experiments

The effect of slight beam heating during microscopy observation of martensites from 30% ausformed steels was also investigated. It was found that, in general, beam heating produced no visible change in the size of the precipitates or of distribution of dislocations in the three 30% ausformed alloy steels. However, such was not the case for 30% ausformed steel 1410. Figure 12A shows an area of martensites in steel 1410 with precipitates and dislocations after slight beam heating. On heating a little longer, the precipitates grow in size and give rise to precipitation on preferential planes resulting in Widmanstätten structure, as observed from a different area in Fig. 12B. The cementite precipitates lie on {112} planes. Figure 13 shows a typical diffraction pattern obtained from tempered areas similar to Fig. 12B from steel 1410. This pattern clearly verifies that the precipitates are cementite, as well as affording the following orientation relationships for cementite.

$$[211]_\alpha \parallel [001]_{Fe_3C}$$

$$[0\bar{1}1]_\alpha \parallel [100]_{Fe_3C}$$

$$[1\bar{1}\bar{1}]_\alpha \parallel [010]_{Fe_3C}$$

C. Summary of Results

1. Austenites

1.1 The dislocations lie along the traces of slip planes up to at least 8% deformation. This would probably continue to be so with further deformation unless precipitation takes place.

1.2 A critical amount of deformation is necessary to nucleate observable precipitates. The results suggest that in all the four steels examined this critical value lies between 8 and 30% deformation.

1.3 The deformation substructure consists of tangles of dislocations with precipitates after 30% deformation.

1.4 The precipitates are found to be Fe_3C (for steel 1410), VC (for steel 1402), and MoC (for steel 1398). The precipitates in the case of steel 1541 could not be uniquely identified, but are probably $Cr_{23}C_6$.

1.5 For alloy steels, it is not possible to reduce the dislocation density or increase the size of precipitates by slight beam heating of thick areas, but thin areas near the edges polygonize.

1.6 In the case of steel 1398, some mechanical twinning in austenite is observed after 30% deformation. This effect has not been reported previously.

1.7 The dark field technique has been shown to be of considerable significance in studying important substructures such as precipitates and twinning.

2. Martensites

2.1 As for the austenites, martensites from 0 and 8% deformed steels show no precipitation, while those of 30% deformed steels show precipitation.

2.2 The amount of transformation twinning decreases as the extent of deformation increases, until after 30% ausforming very little twinning is observed.

2.3 Retained austenite from 30% ausformed steels show precipitation and a very high density of dislocations.

2.4 Ausformed steel 1410 is found to be most susceptible to low temperature tempering in the microscope with rapid growth of Fe_3C precipitates. Ausformed alloy steels resist tempering, in that the precipitates do not grow appreciably and the dislocation density does not drop.

2.5 No generalizations can be made regarding the influence of temperature or change of size of the martensite plates, after the various ausforming treatments.

DISCUSSION

A. Precipitation and Structure of Austenite and Martensite

The experimental observations have shown that precipitation of carbides in austenite takes place in ausformed steels after a certain deformation. By thermodynamic arguments, previous workers (5, 10) have shown that the diffusivity for the various alloying elements involved is favorable for precipitation. In almost all investigations of precipitation on substructures in iron base alloys (reviewed by Keh et al. (20)), a high density of dislocations favors formation of fine precipitates, probably because dislocations provide a high density of nucleation sites, and/or that diffusion is increased as a result of high concentration of vacancies which are generated during plastic deformation. The absence of precipitation in steels deformed 8% or less and the comparatively lower mechanical properties of such steels prove that precipitation is favored by large deformations. The difficulty of precipitation is thus probably one of nucleation since when precipitation takes place on closely spaced nucleation sites, the volume of material in the matrix from which precipitating constituents can diffuse to a site is limited. Thus, nuclei, in order to grow, will have to redissolve and diffuse to other sites. This process is likely to occur only on tempering at high temperatures. In the absence of any tempering effect, the higher the amount of deformation, the greater are the number of nucleation sites possible, and this means that precipitates are finer and more closely spaced. Both of these favor high mechanical strength by providing sites for dislocation multiplication and pinning.

It is likely that some tempering takes place in the microscope during observation. It should be emphasized, however, that all the specimens in the electron microscopes are examined under identical conditions and, therefore, if precipitation occurred by beam heating alone, specimens deformed 0 and 8% would have also shown evidence for precipitation. Since this is not found, it is concluded that the precipitation observed is deformation dependent. The size and separation of precipitates is therefore dependent on the temperature and degree of deformation and subsequent tempering. After precipitates have reached their maximum size, no further change can take place, unless the steel is subjected to a temperature high enough to redissolve some of the precipitates so that others can grow.

The observations also show that precipitates are retained by martensite during the phase transformation. The effect of tempering on growing precipitates should be more rapid in the case of martensite than in the case of austenite, because the solubility of carbon in martensite is lower. In steel 1410 cementite precipitates are observed after ausforming, which easily grow into a Widmanstätten pattern when the foil is purposely heated in the microscope. As explained later, this easy growth accounts for the comparatively poor properties of steel 1410 (10). Similar experiments in the microscope on the other steels showed no evidence for growth of precipitates. This result is attributed to the fact that the temperature was not high enough to favor growth. Indeed, this is confirmed by the observed tempering behavior of ausformed steels where the mechanical properties are maintained to a temperature as high as 500°C (12).

Besides precipitates the structures observed in ausformed martensites include a high density of dislocations which can be inherited from the deformed austenite and/or can arise from deformation during the austenite to martensite phase transformation. It is estimated that the dislocation density in the martensites is about $10^{12}/cm^2$ or higher.

Twinning in body centered structures is known to be an important cause of fracture (21). From its almost complete absence in ausformed steels examined in this investigation, it would seem that the decreased amount of twinning is of considerable importance for enhanced ductility of ausformed steels. The high density of dislocations may prevent the nucleation of cracks or allows incipient cracks to close (22).

B. Twinning

The experimental observations clearly show that the extent of transformation twinning in martensites decreases with increasing amount of deformation of the metastable austenite prior to transformation. It is very likely that twins may be entirely absent for greater deformations. Two factors, viz. low M_s temperatures and higher stacking fault energy, have been shown to favor the occurrence of transformation twinning (14,23). As discussed elsewhere (24) the important factor in determining twinning is M_s temperature and not stacking fault energy. This agrees with the present work, because deformation of austenite as well as depletion of solutes from austenite by precipitation are known to raise the M_s temperature.

The observations of mechanical twinning in deformed retained austenites from steel 1398 (Fig. 6) can be explained on the basis of stacking fault energy alone. While there are no accurate measurements of the stacking fault energies of the alloys examined here, Mo is known to strongly lower the stacking fault energy of austenite (25), and in FCC metals the lower the stacking fault energy the greater is the tendency for deformation to occur by twinning (26,27). In the areas showing twinning the stacking fault energy may be low because of local solute segregation.

In steel 1398 since the removal of Mo from solid solution by precipitation during deformation of metastable austenite would raise the stacking fault energy and hence oppose mechanical twinning, it would indirectly seem (from the observation of precipitates within the twins in austenites, e.g. Fig. 6), that precipitation does not take place concurrently with deformation of austenite, at least in the early stages. This is supported by the observations of serrated yielding of austenite during tensile tests (10). Furthermore, no large precipitates were observed, even in steels deformed at 500°C. If the precipitation had taken place side by side or preceding the deformation, there would be at least some particles which would have been of comparatively large size or at least there would be a broad range of precipitate sizes observed. The observations (Figs. 2, 8) seem to suggest that this is not so. It is concluded that the nucleation starts during the later stages of deformation, with slow growth occurring with the passage of time. This issimilar to strain aging, with aging taking place in a short time.

C. Strength of Ausformed Steels

In this section substructure will be related to strength. Neglecting the inherent lattice friction stress τ_o, and solid solution strengthening due to substantial alloying elements, as they are comparatively small, there are five main factors which are important in strengthening. Substructural observations of the present work suggest the following about each of these five factors:

1. Martensitic Grain Size

Although optical metallographic examination of ausformed steels indicates a decrease in martensitic grain size with ausforming, when individual martensite plates are examined in the electron microscope, no such trend is apparent. In fact, martensite grain sizes (i.e. width of plates) were observed from as small as 300Å (some of the martensites in Fig. 12A) to a few microns and greater (e.g. as in Fig. 11, which shows single plates). This work would therefore indicate that there is no systematic variation of martensite plate size with ausforming, so that it is difficult to correlate grain size with strengthening. In view of other overriding parameters to be discussed in the following, it is concluded that this contribution is small.

2. Twinning

As already discussed, the almost complete absence of twinning in 30% ausformed steels would eliminate twinning as a factor in strengthening of ausformed steels. However, the absence of twinning appears to be favorable to enhanced ductility.

3. Carbon Content

Carbon is the most important factor in strengthening of conventional martensites, the strength levels achieved vary from 80,000 psi for 0%C to 280,000 psi for 0.8%C (11). The alloys used here had a carbon content of only 0.3%. Also, since ausforming results in precipitation of alloy carbides, carbon is depleted from the solid solution. The amount of carbon remaining in solution would be dependent on the amount of carbide forming element present, and on the extent to which precipitation has progressed (i.e. depending on the amount of deformation and temperature). For example, in steel 1398, where MoC precipitates, a simple calculation shows that the ratio of atomic percentages of carbon to molybdenum is 1:2; and thus, the probability of carbon remaining in solution is small. Furthermore, in practice, steels are subsequently tempered, so that almost all of the carbon would be removed from solid solution. Hence, the solution strengthening effect of carbon is probably negligible.

4. Precipitation

Dislocations and precipitates are the dominant features of the structures and thus presumably control the strength. Their contribution, however, is related in the same sense that creation of dislocations and accompanying point defects aid in precipitation, while creation of precipitates aid in increasing the dislocation density by pinning the dislocations and by providing sites for dislocation multiplication. To be beneficial in strengthening, the precipitate particles should be strong enough to resist shearing. Kelly and Nicholson (28) have shown that the critical size, r_c, of a particle which would resist shearing is given by $r_c = \frac{2G\,b^2}{\pi\gamma}$ where G is the shear modulus of the matrix b the Burger's vector, and γ which is the interfacial energy between particle and matrix, is dependent on the values of the shear moduli, G' and Burger's vector b' for the particle. They derive a value of r_c = 2b for G' = 10G and b' = b and r_c = 20b for G' = G and b' = b. As the particle size in the present case is higher than these values (though no data for G' of carbides are available, they are in the range of G - 5G) e.g., from Fig. 8 the carbide particle diameters are in the range 50 - 150Å it is unlikely that carbides will be sheared by dislocations. Since the values of G' and b' for carbides are not available, Thomas et al. (10) proposed that γ may be related to the bond energies of the carbides, and showed that even for the weakest carbide (MoC) the particle size would have to be less than about 70Å in order for them to be cut by dislocations.

Dispersion strengthening is usually considered in terms of the yield strength. For unsheared particles the strengthening will be essentially of an Orowan type. However, in the case of ausformed steels, since the carbides precipitate out in an already work-hardened matrix, it is meaningless to consider dispersion strengthening alone as controlling the yield stress. The contribution to strength of the particles must therefore be accounted for, not on the basis of Orowan yielding, but rather on their effect on the total dislocation density, as discussed below.

5. Dislocation Density

The substructural observations of ausformed steels on both austenites and martensite clearly indicate an increase in dislocation density with prior deformation of austenite. The total dislocation density is the sum of contributions from the effects of deformation, dislocation multiplication at the precipitates, and dislocations generated during the phase transformation. The structure is in a work hardened state and using the usual relationship for flow stress τ (neglecting the friction stress), $\tau = \beta\ G\ b\ \sqrt{N}$, where β is a constant $\simeq 0.4$ for iron (29), G is the shear modulus, b $\simeq$ Burger's vector of the dislocation and N the dislocation density (see e.g. Friedel (30)). In general, for plastically deformed metals, N has been observed to range from 10^{10} to 10^{12} lines/cm^2. In dispersion strengthened materials, provided the second phase is not cut by dislocations, the dislocation multiplication rate is greater than in the absence of dispersoids because of dislocation-particle interactions. Previous work has estimated that the rate is increased by about a factor of five (31-33). Allowing for this multiplication factor it is expected that the dislocation content of ausformed martensite is about 10^{13} lines/cm^2, which is consistent with estimates from the micrographs.

For $N = 10^{13}$, τ is of the order of G/50. For steels $G = 12 \times 10^6$ psi so that the strength is calculated to be about 240,000 psi. The maximum strength for the alloy steels is 210,000 psi (10). The agreement is close enough to state that the high strength of ausformed martensite is primarily due to the total dislocation density.

D. Parameters of Ausforming

From the present results and in agreement with previous work (7) there does not appear to be any influence of temperature of ausforming on the strength. The substructural differences between as quenched ausformed steels containing carbide forming alloying elements and steel 1410 were not found to be large. Precipitation of Fe_3C in ausformed 1410 increases the strength slightly over conventionally treated 1410 (10). However, the tendency for rapid growth of Fe_3C at low temperatures of tempering (i.e. overaging) causes a deterioration in strength. The differences between the various carbide forming alloying elements on the dislocation density and size and distribution of precipitates could not be established by substructural investigation alone. Thomas et al. (10), using thermodynamical considerations have shown that of the elements Mo, Cr, V, and Nb, Mo is the most beneficial and Cr least, which is in agreement with the mechanical property measurements. From the slight tempering work done in the microscope, it seems that the alloy steels are little affected, though systematic tempering experiments may be necessary to arrive at the full importance of this parameter.

The carbon content is of considerable practical importance. We have already established that deformation causes precipitation in ausformed steels. Theoretically, therefore, for a given size and distribution of precipitation desired, one can calculate the amount of carbon required, e.g. for MoC precipitation of average particle size of 50Å diameter, uniformly distributed at 100Å separation, the theoretical alloy content would be 1.75% Mo and 0.22%C. It would thus seem that in an alloy of say 3% Mo, a carbon content of 0.3% would be enough for complete MoC precipitation. Whatever excess carbon is present in solid solution will be an added benefit in solid solution strengthening. However, a higher percentage of carbon gives rise to twinning, poorer ductility and more retained austenite.

The observations suggest that in order to obtain good ductility twinned martensite should be avoided. The occurrence of transformation twinning depends on the M_s temperature which, in turn, depends on the amount of solute in solid solution. Most alloying elements which are beneficial in ausforming are also those which lower M_s and consequently favor twinning. Thus, alloys and composition must be chosen such that the amount of twinning is minimized. In addition, as observed in the present case for steel 1398, a large addition of a particular alloying element may lower the stacking fault energy of austenite and favor mechanical twinning during deformation. A high proportion of alloying elements may also lower the M_f temperature such that large amounts of retained austenite may be obtained.

The solid solution strengthening from solute elements is probably small, unless the stacking fault energy is changed appreciably (14).

One function of solutes is to cause a favorable M_s and a bay region in the TTT diagram for the process to be carried out at appropriate temperatures and for sufficient times without transformation. Secondly, enough of the most beneficial carbide formers should be present in order to provide a high density of small, stable precipitates. Some of the alloying elements will have to be controlled on the basis of other specific properties of steels, e.g. weldability, corrosion resistance, etc., but these are not considered here.

E. Control of Properties

In this section, in the light of previous and present observations, possible ways of achieving the highest possible engineering strength (i.e., high U.T.S. and desirable ductility) will be discussed. Obtaining higher strengths would require that as many barriers to dislocation motion be provided as possible, without introducing other substructures such as twinning which might impair the ductility. As shown in the present work, two effective barriers to dislocation motion are the high density of dislocations and precipitates.

As discussed in section C.4, the strengthening due to the dislocations is given by $\tau = \beta G b \sqrt{N}$. The maximum theoretical value for N is $\simeq 10^{16}$, in which case strengths of the order of G will be obtained. Since the theoretical strength limit is G/15, the maximum possible dislocation density will be $\simeq 10^{14}$. However, in these cases little or no plastic flow can be expected. Even so, there is a limit to the possible dislocation density obtainable by static deformation, though, such ausforming methods induce precipitation and so provides more sites for dislocation multiplication. It is believed that explosive deformation as a means for substantially increasing dislocation densities needs to be explored more, especially in the case of ausformed steels.

It is known that the dislocation density can be considerably increased with explosive deformation, e.g. by explosively deforming nickel, cell sizes of half those obtained by static deformation are obtained (15). This would roughly double the dislocation density. As multiplication at precipitates increases the dislocation density by about a factor of 5, dislocation densities as high as those allowed for the theoretical strength may be attained. However, explosive deformation can induce twinning in FCC metals after a particular value of pressure (depending on the technique of shock loading) is attained. This value of pressure has been shown to depend on the stacking fault energy of the Cu-Al FCC alloys (26). In iron (34) explosive deformation has been shown to induce allotropic transformations at high pressures (170 kbar and higher). Thus, if the composition and pressure can be properly controlled so that the occurrence of twinning and other phase changes are avoided, shock loading may provide a means for further increasing the dislocation density and strength.

Precipitates also provide a mechanism for increasing the dislocation density, provided they remain unsheared during deformation. As shown by Kelly and Nicholson (28), whether a precipitate is deformable or not depends on γ, the surface energy of the precipitate. It can be shown that γ is directly dependent on the bond energy of the precipitating phase, and thus the higher the bond energy, the stronger the particle in resisting shearing (10). For higher strengths then, stronger particles of small sizes would be more beneficial (where the size and distribution is controlled through composition and degree of deformation), than particles which would deform easily. However, deformable particles may give greater ductility. Various alloying conditions should be investigated in order to obtain dispersoids such that the final product has desirable ductility at the highest strength levels. It may also be possible to introduce some such deformable particles beforehand and then introduce dislocations through explosive deformation. A combination of these various parameters should enable stronger and tougher materials to be made.

CONCLUSIONS

1. Precipitation is observed in all of the 30% ausformed steels in both austenitic and martensitic conditions. Precipitation is not observed in undeformed or 8% ausformed steels. It is shown that a critical amount of deformation is necessary to nucleate the precipitates. The growth rate of alloy carbides is very small, unless the temperature is high enough to redissolve the precipitates. The growth rate of Fe_3C is large, hence carbide formers are beneficial in stabilizing precipitates.
2. The benefit of precipitates to properties is by providing sites for dislocation multiplication and by pinning the dislocations.
3. Carbon in steels is necessary if ausforming is to improve properties. The beneficial effect of carbon is indirect in that it provides precipitates which, in turn, increase the dislocation density during ausforming. Solid solution strengthening due to carbon is small, provided it is mostly used up by precipitation of carbides. A high carbon content in solution is harmful to ductility, and increases the

amount of retained austenite.

4. The high strength of ausformed steels is primarily due to the very high dislocation density ($\sim 10^{13}/cm^2$). The total dislocation density includes contributions from deformation of austenite, multiplication at the precipitates, and from the invariant shear strain during the phase transformation.

5. Precipitates are also observed in ausformed Fe-28% Ni-0.3%C steel, but its strength is inferior as compared to other steels, due to the ease with which cementite can grow.

6. In conventional steels, transformation twinning during the martensitic reactions is favored primarily by the effect of solutes on the M_s temperature of the steel. The rise of M_s, due to deformation and depletion of solutes by precipitation, considerably decreases the extent of twinning in ausformed steels.

7. The absence of twinning and presence of a very high density of dislocations are favorable to ductility of ausformed steels.

8. Mechanical twinning was observed in austenites of some steels and is thought to be due to the effect of solutes on the stacking fault energy of austenite.

9. The selection of suitable carbide forming alloying elements and their amounts should depend on their diffusivity, their effects on stacking fault energy and M_s and M_f temperatures, besides considerations specific for a particular application.

10. To achieve still higher strengths, explosive deformation of ausformed steels as a means of increasing dislocation density may be used. For better ductility, at high strengths, explosively deformed dispersion

hardened materials containing deformable dispersoids or ausformed steels of proper composition so as to result in deformable precipitates may be beneficial.

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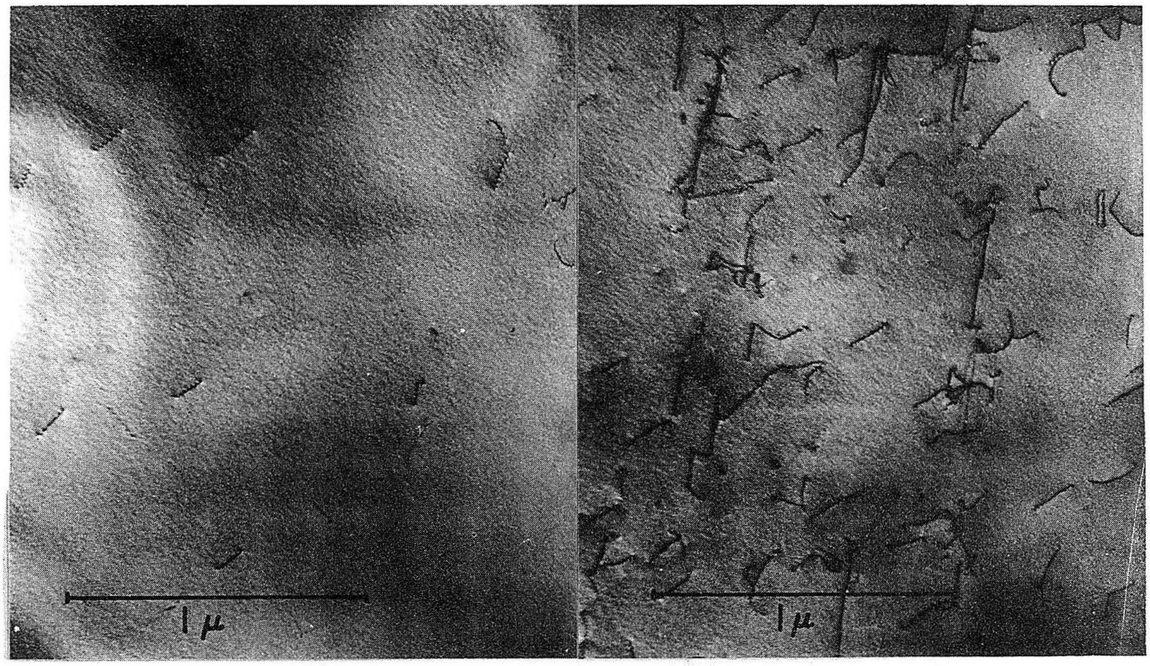


(a) (b)

ZN-4611

Fig. 1

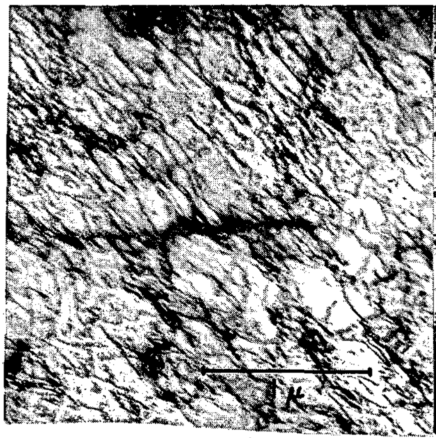


Fig. 1c

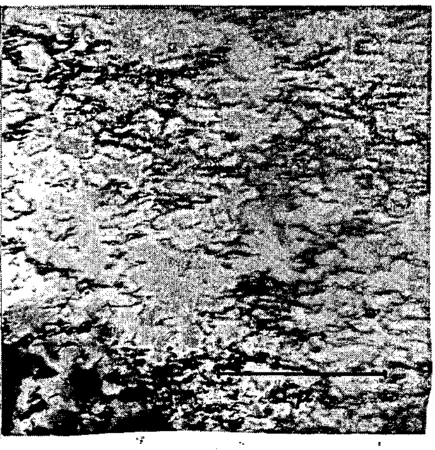
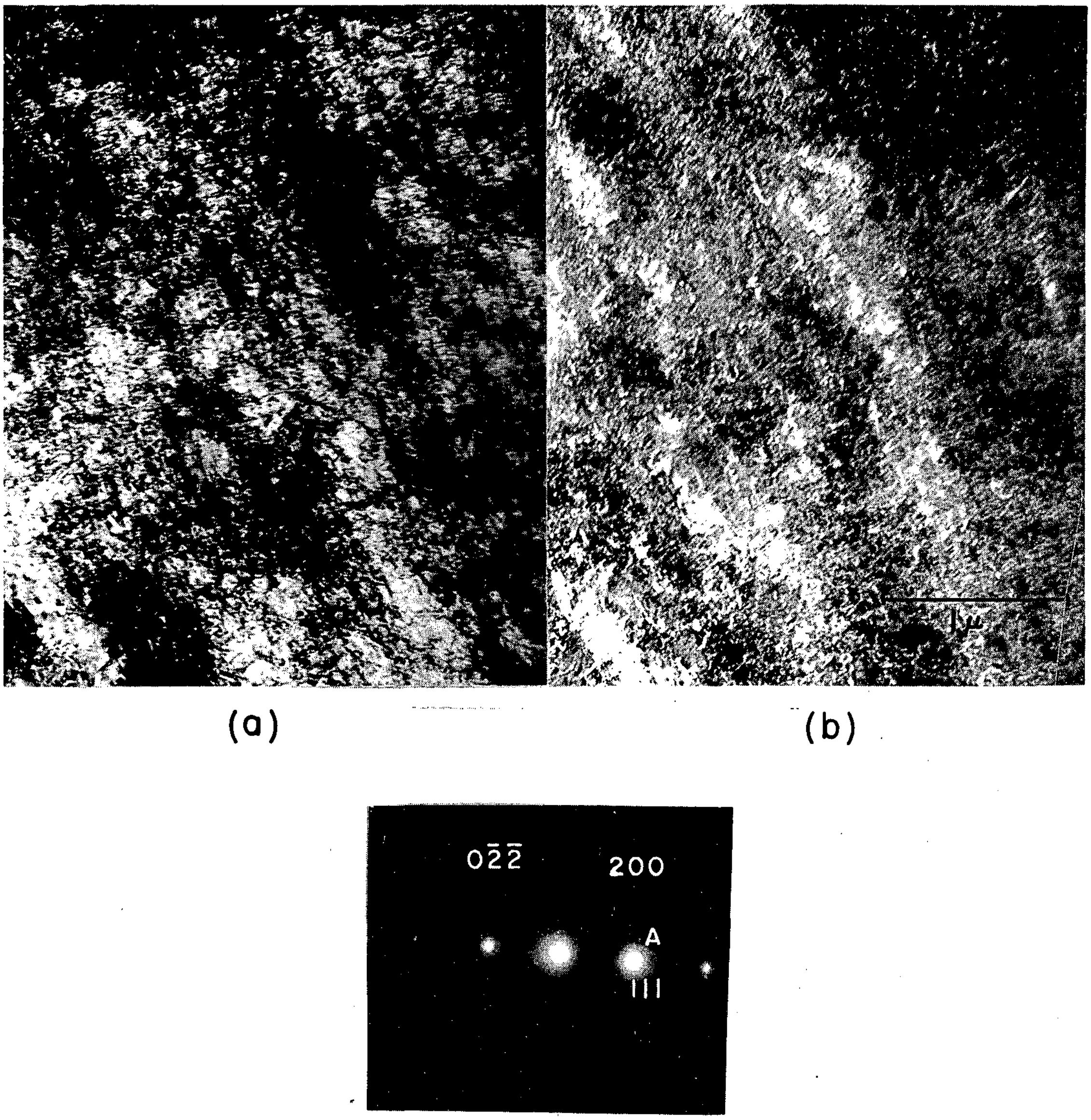


Fig. 1d

ZN-4613



(a) (b)

(c)

ZN-4615

Fig. 2

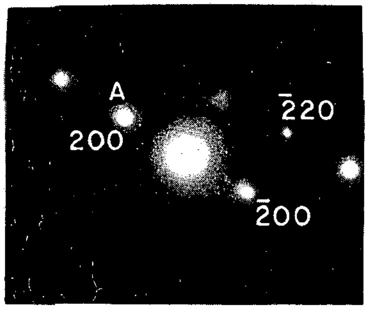
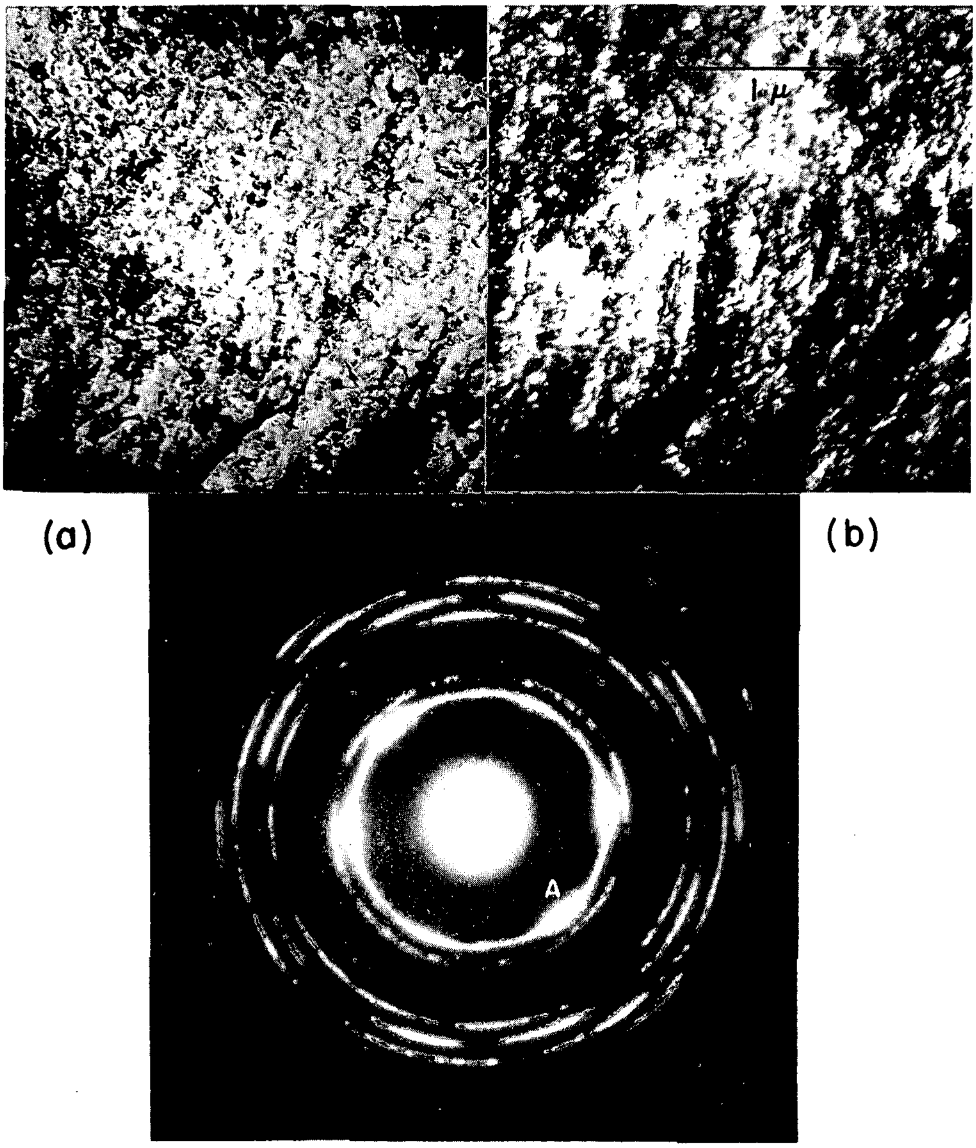


Fig. 3

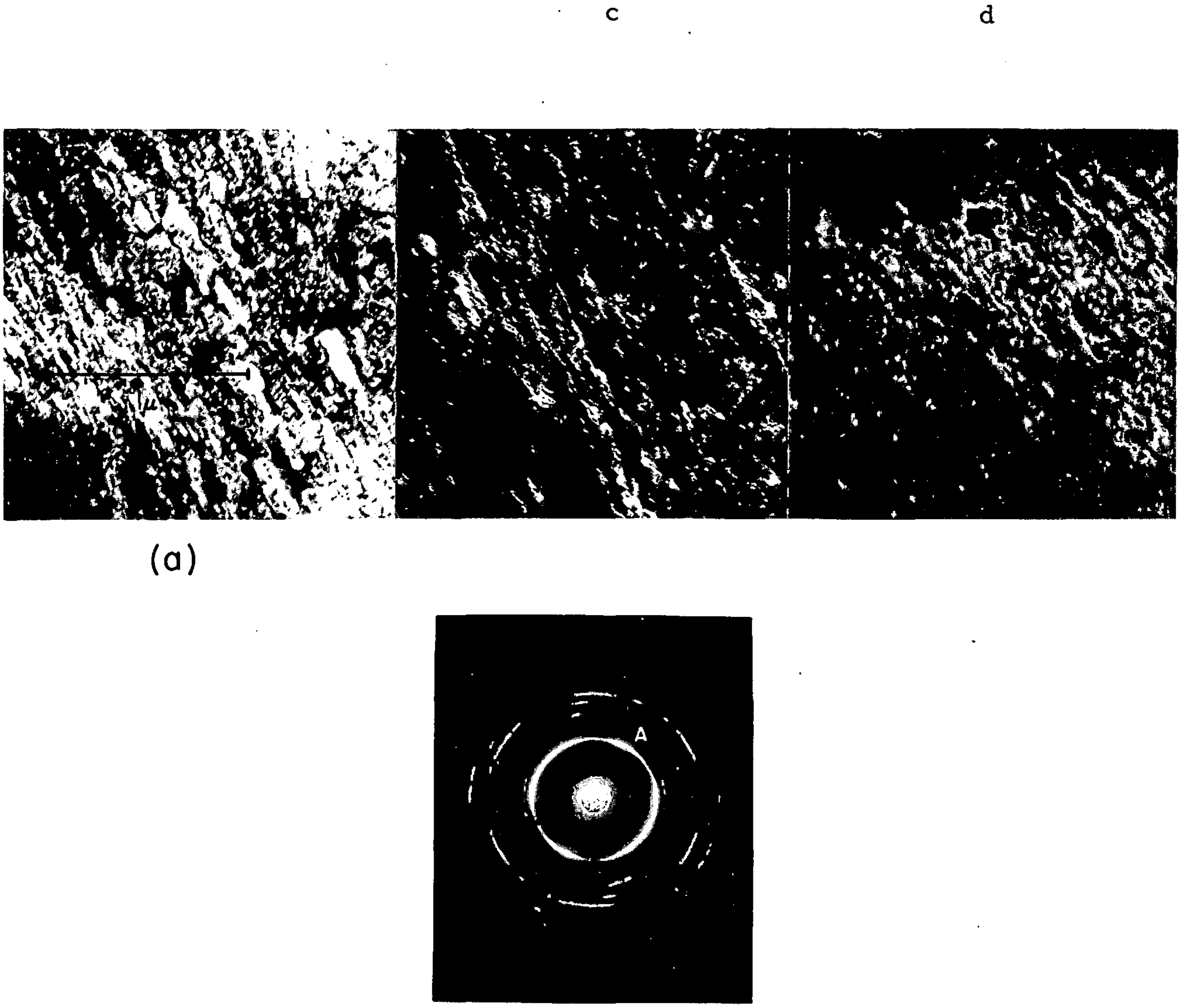


(a) (b)

(c)

ZN-4619

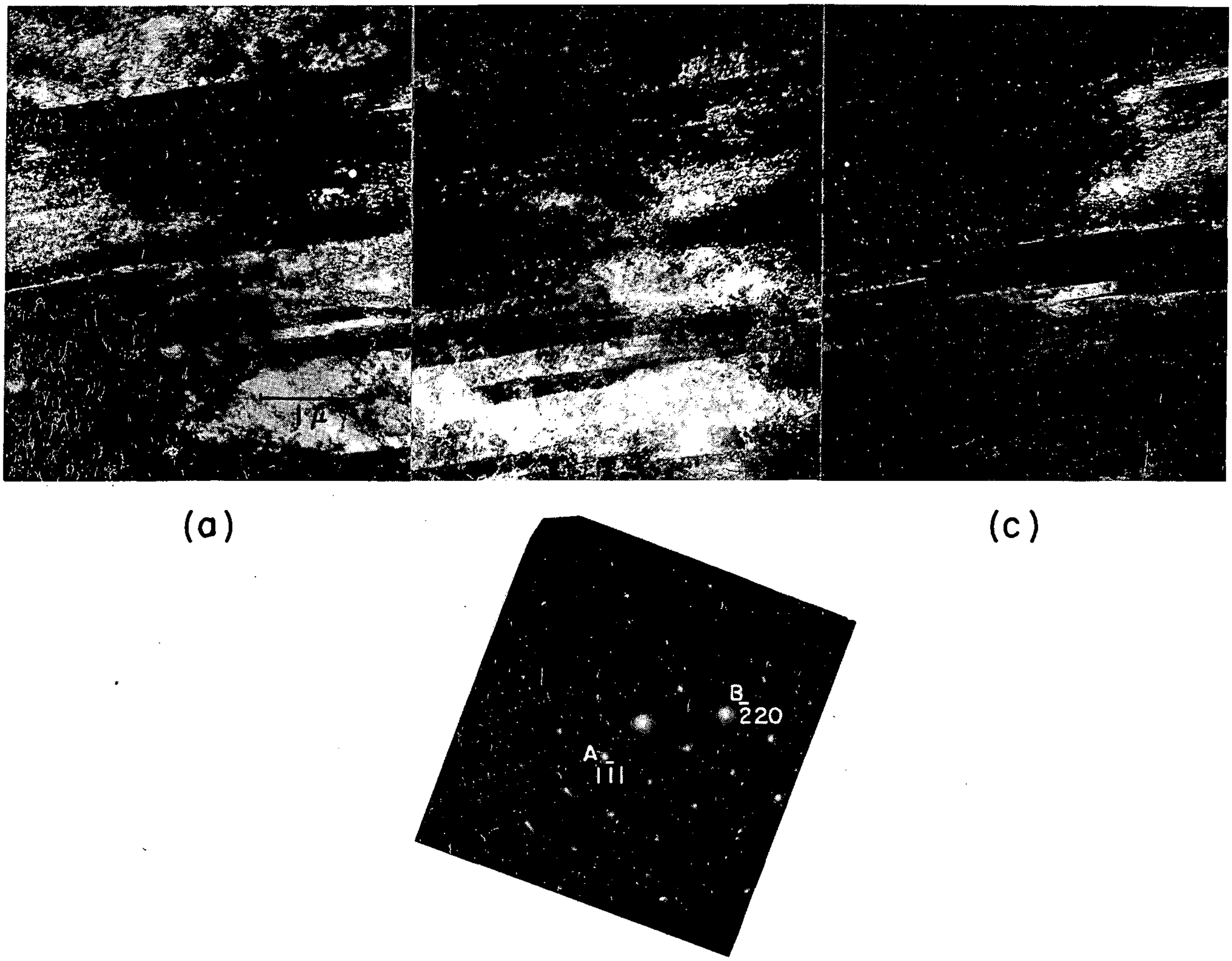
Fig. 4



ZN-4620

Fig. 5

d

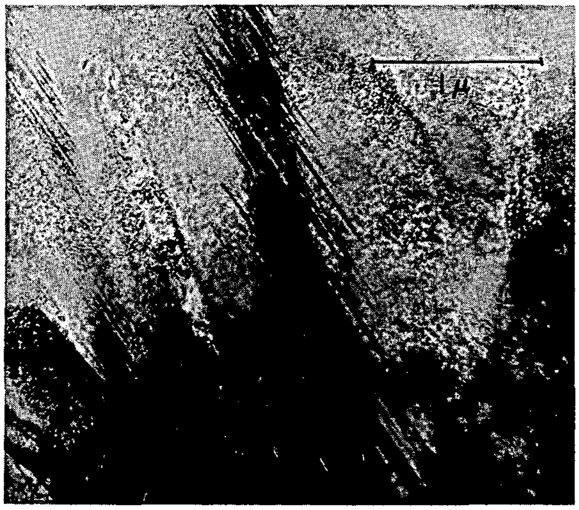


ZN-4621

Fig. 6

Fig. 7a

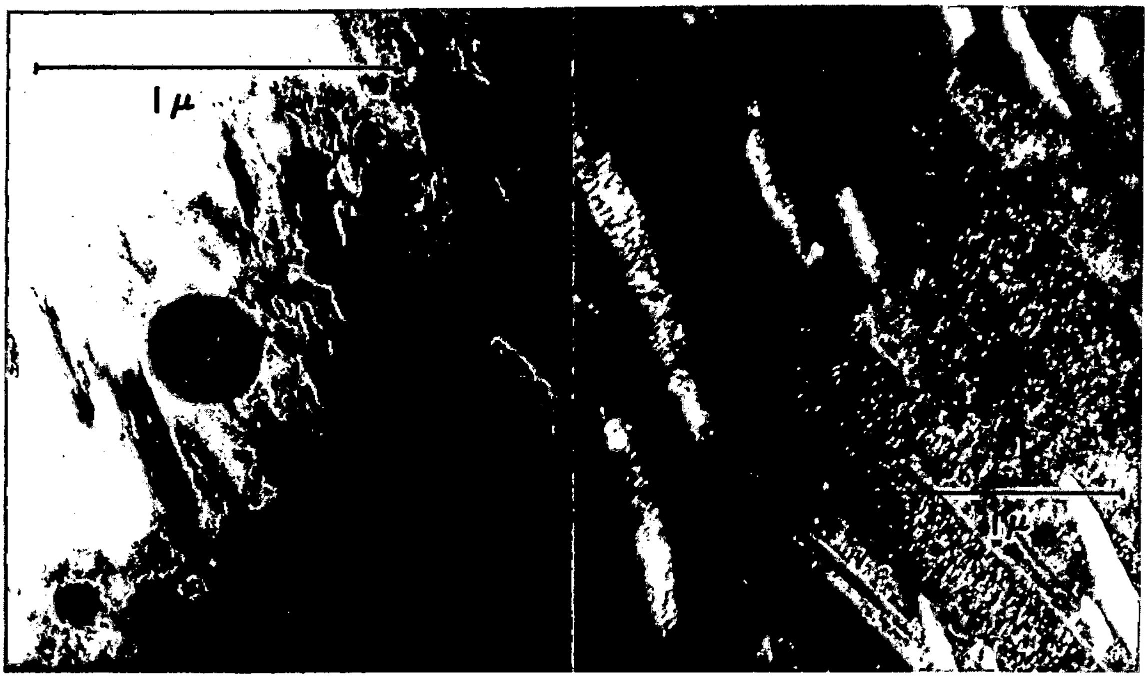
Fig. 7b



ZN-4622

Fig. 7c

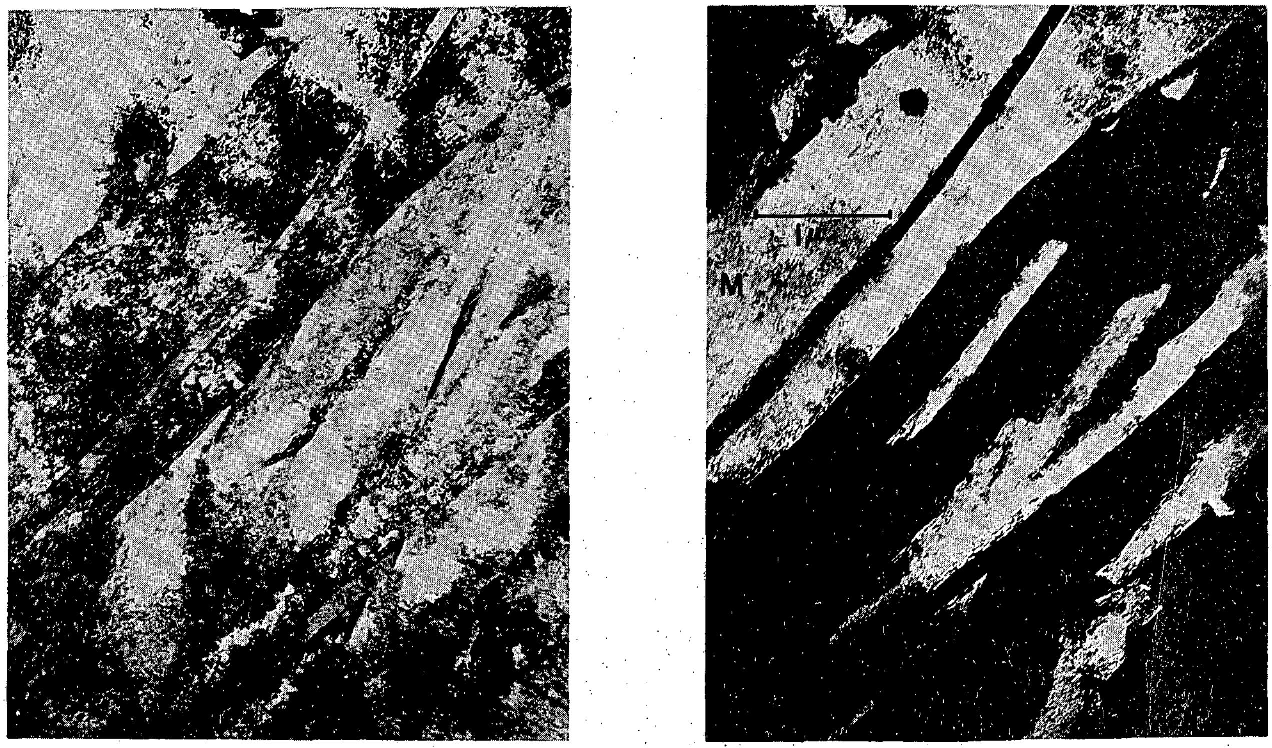
Fig. 7d-



(a) (b)

ZN-4628

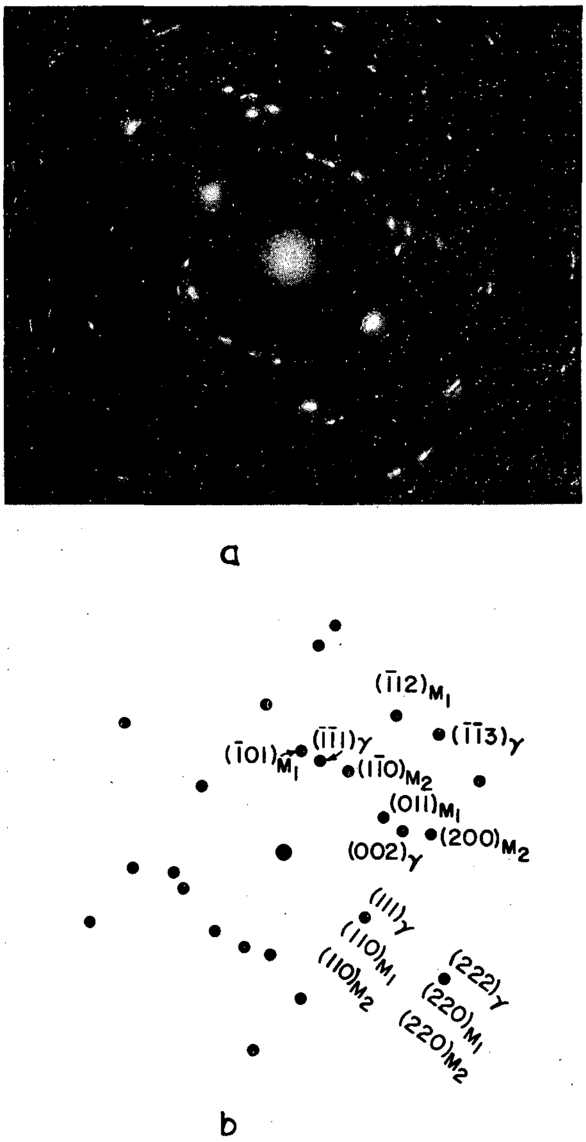
Fig. 8



(a) (b)

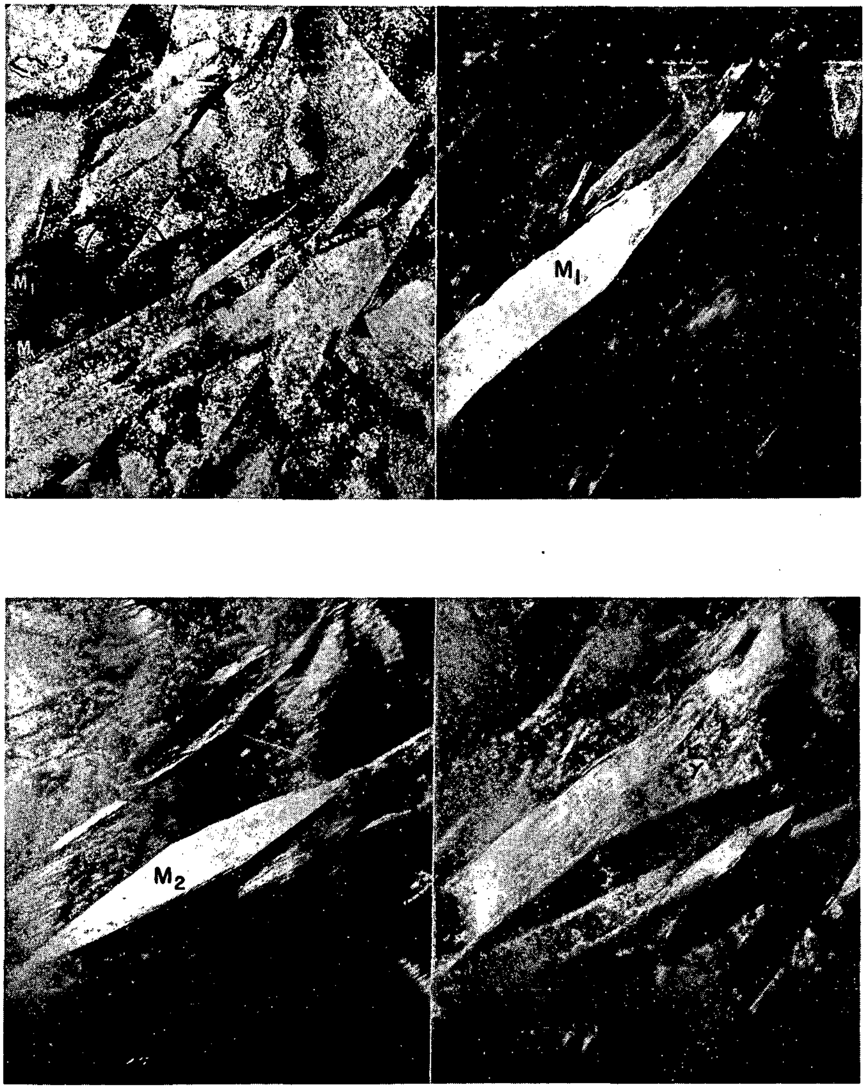
ZN-4629

Fig. 9



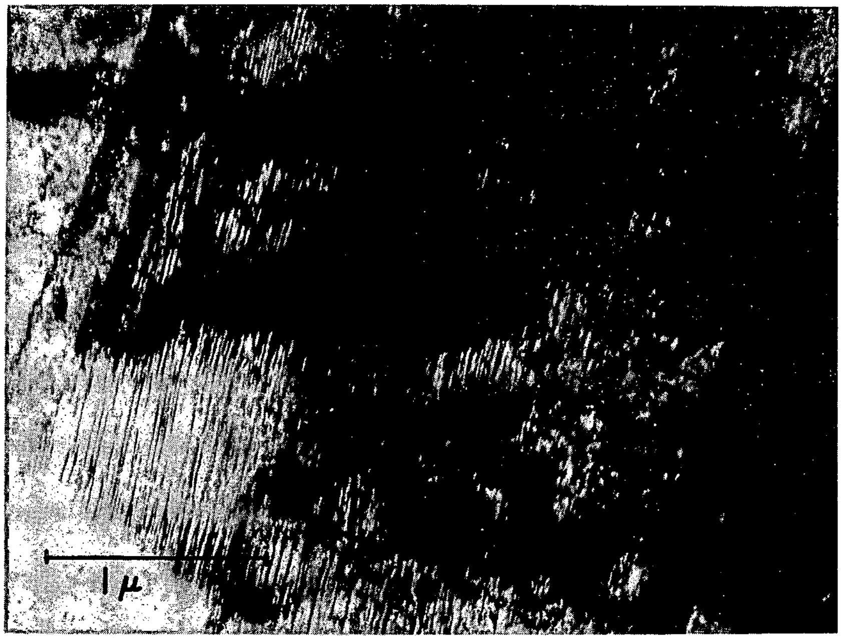
ZN-4632

Fig. 10



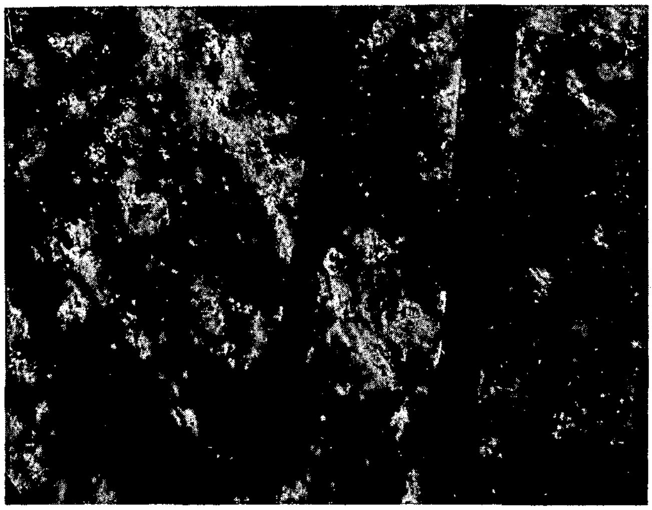
ZN-4633

Fig. 10 c, d, e f



(a)

Fig. 11



(b)

ZN-4637

Fig. 11

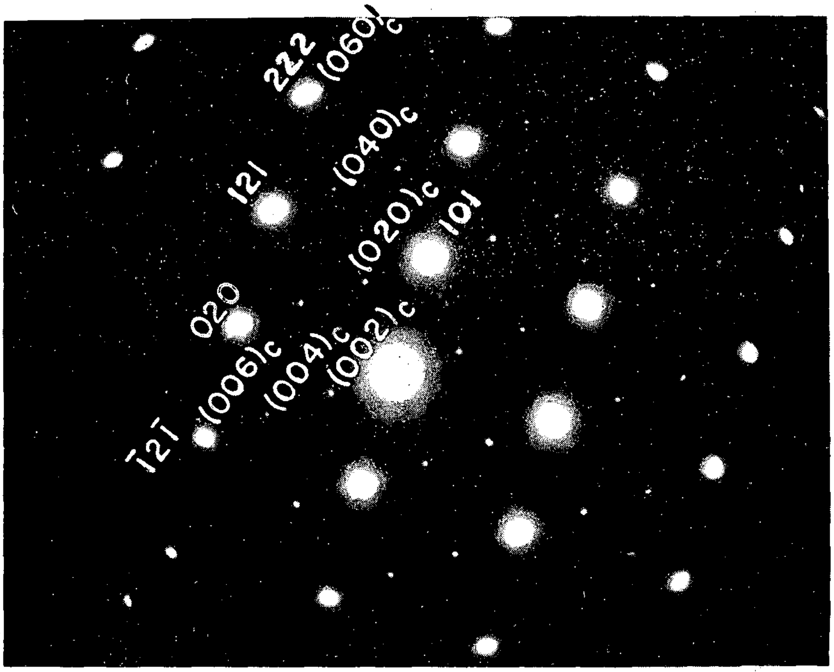
(a)

Fig. 12

(b)

ZN-4639

Fig. 12



ZN-4641

Fig. 13