

The thermal etching of silver

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[PLATES 9 TO 12]

The mechanism whereby grain boundaries are delineated and striations formed on polished surfaces of heated metal specimens has been examined. Experiments on electrolytically polished silver show that grooves form at grain boundaries at temperatures as low as 300° C and striations at 500° C in air. Striations only appear in the presence of oxygen and may be removed by heating in nitrogen.

A furnace for high-temperature photomicrography, suitable for specimen temperatures up to about 950° C, is described.

Previous theories are found inadequate to explain the effects observed in silver, and a theory which regards the surface etching as an approach to equilibrium by the reduction of surface free energy is suggested. Thus the equilibrium condition of the boundary is a groove whose shape is determined by the relative magnitudes of the free energy per unit area of the boundary and the surface energies of the crystalline faces meeting the boundary in the surface of the specimen. The striations are caused by the development of those crystalline planes having the lowest free energy; the relative surface energies of different planes being modified by the presence of oxygen. It is suggested that the chief means whereby the boundary grooves are formed is that of surface migration of ions: both surface migration of ions and evaporation of silver oxide molecules may be expected to play major parts in the formation of the striations.

1. INTRODUCTION

The nature and the properties of the material constituting the boundaries of the crystal grains in polycrystalline metals are of profound importance in the study of metals, yet there exists comparatively little detailed information concerning them. As part of a general investigation of the grain boundary, experiments were carried out to examine the nature of the etching effect known to occur frequently on polished surfaces of metals when they are heated. When conditions are such that this etching occurs, the grain boundaries are delineated and it was felt that an understanding of the mechanism of this phenomenon would provide valuable information concerning their nature. Under some conditions of heating, polished surfaces show, besides grain-boundary markings, striations which cross the different crystal grains in different directions. As, in the course of the experiments on the grain-boundary etching, the opportunity arose to observe this effect as well, it was examined and some additional experiments designed specifically to provide information concerning it were performed.

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The experiments were all carried out on silver and it was found that none of the explanations previously put forward for the thermal-etching process was completely satisfactory for the results obtained. A tentative explanation consistent with published results is suggested.

2. PREVIOUS OBSERVATIONS UPON THERMAL ETCHING*

At the outset it is necessary to distinguish clearly between the phenomena of thermal etching and those of 'thermal fatigue' recently described by Boas & Honeycombe (1946, 1947). There are distinct similarities between the appearance of specimens which have been subjected to 'thermal fatigue' and that of specimens thermally etched. In both cases the grain boundaries are delineated upon what was initially a polished surface, and striations develop which run across the grains themselves. Despite the similarity in appearance of the specimens, however, there is little doubt that the phenomena are different. The phenomena of thermal fatigue were produced in Boas & Honeycombe's experiments by subjecting specimens of the non-cubic metals, tin, zinc and cadmium to cycles of heating and cooling, and were not observed when specimens of lead, which is cubic, were similarly treated. Boas & Honeycombe explained their results by the fact that the non-cubic metals expand and contract anisotropically when heated and cooled and thus in a randomly orientated aggregate of crystal grains stresses are set up with change of temperature. These stresses are sufficient to cause slip in certain crystals and the striations observed are in fact slip lines. The stresses also cause changes in level between different grains and the grain boundaries are delineated. With increasing numbers of cycles of heating and cooling the striations become more numerous and if grain growth occurs, there are formed, in addition to the old grain-boundary outlines, new lines which coincide with the new grain boundaries. In this way a series of boundary networks is formed, one corresponding to each cycle. The phenomena observed appeared to be independent of the environment in which the cyclic heating took place.

Boas & Honeycombe give much additional evidence in support of their explanation and 'thermal fatigue' is undoubtedly the explanation of the delineation of the grain boundaries observed by Carpenter & Elam (1920) when they heated and cooled specimens of an antimony-tin alloy.

As distinct from 'thermal fatigue' the phenomena of thermal etching are observed in many cubic metals, they can be produced by maintaining the metal at an elevated temperature without any cyclic heating and cooling, and they are affected by the environment in which the metal is heated. The grain boundaries are delineated not by difference in level between adjacent grains but by grooves formed at the intersection of the boundary with the surface. The striations are corrugations or a stepped structure of the surface.

* [Note added in proof.] Previous observations upon thermal etching have recently been reviewed; Shuttleworth, R., July, 1948, *Metallurgia*. (In course of publication.)

During the past thirty years thermal etching phenomena have been observed by numerous workers. Networks of grooves were observed on iron heated in a vacuum by Rosenhain & Humfrey (1910) and on iron heated in hydrogen by Rawdon & Berglund (1928) who also observed striations. Grain-boundary networks on steels were observed by Kroll (1912), Humfrey (1912), Rawdon & Scott (1922) and Hemingway & Ensminger (1922). The phenomenon has been used (Day & Austin 1940; Miller & Day 1942) for the determination of austenitic grain size. Parker & Smoluchowski (1945) observed that molten silver spread along the boundary grooves on a molybdenum steel more rapidly than across the crystal faces. Where explanations of the phenomena were offered they were attributed to selective evaporation.

Striations were observed on the surfaces of cast specimens by Ewing & Rosenhain (1900) and Graf (1942).

Specific attention has, however, been directed by few workers towards the understanding of the phenomena. The formation of the boundary grooves was considered by Rosenhain & Ewen (1912), who heated polished specimens of copper, silver and zinc in a vacuum and found that grooves developed at grain boundaries but not at twin boundaries. They observed that when heated under otherwise identical conditions, specimens with small grain size evaporated more rapidly than those with large grain size. They interpreted their experiments by supposing that metallic grains are joined by a cement of amorphous metal which has a greater vapour pressure than the crystalline metal. On heating in vacuum the amorphous metal exposed at the boundaries evaporates more rapidly than the grains, thus producing the boundary grooves. They attributed the greater loss of weight from the small grained specimens to the fact that they exposed more grain boundary material than did the specimens of large grain size, and also as the grooves formed the effective area was increased.

They also suggested that the grooves at the boundaries could have been produced in part by the rearrangement of the mechanically polished surface layer to conform with the crystalline structure beneath.

Fonda (1923), working on the rate of evaporation of tungsten filaments at 2677° C, found that grooves developed at the grain boundaries both in inert atmospheres and in a vacuum. In a vacuum the rate of evaporation from filaments with small grain size was 1.4 times that from filaments whose grains were 4 to 100 times longer, and Fonda attributed the phenomena he observed to the greater volatility of the grain boundary material.

Cases of the formation of striations were examined by Johnson (1938) and Gwathmey & Benton (1940*a, b*, 1942) who explained their formation by the migration of ions or the rearrangement of atoms and by Leroux & Raub (1930) and Elam (1936) who ascribed the phenomena they observed to oxidation of the surface.

Johnson (1938) observed striations on tungsten filaments, the surfaces of which he examined in considerable detail, after they had been heated under various conditions. He found that the surface structure produced by the heating depended upon the nature of the atmosphere and the heating current. Thermal gradients in

the filaments modified the surface structure. Stepped structures which occurred with D.C. heating, and were also caused by temperature gradients, Johnson supposed were produced by the surface migration of positive tungsten ions in the electric and thermal fields, the rate of drift depending upon the crystallographic direction. A subsidiary experiment showed that thorium migrated over the surface of tungsten in an ionic form, the direction of migration being influenced by an applied electric field. Johnson also found that tantalum, molybdenum, platinum, iron and nickel filaments roughened when heated with d.c. Mrowca (1943) observed very similar results on tantalum ribbons; striations appeared with d.c. heating and when there were thermal gradients. He explained the striations in the same way as Johnson.

Gwathmey & Benton (1940*a*, *b*, 1942), examining the reaction of gases on the surface of copper, used a spherical single crystal of copper whose surface was obtained unoxidized in a strain-free condition by electrolytic polishing followed by annealing in hydrogen. They found that heating in a vacuum of 10^{-4} mm., or in hydrogen at atmospheric pressure, caused no change on the surface of the crystal, but if the sphere was heated in air at pressures and temperatures which produced only a thin oxide film, an oxide pattern was produced which indicated that different crystallographic planes are oxidized at different rates. A sphere heated to $1,000^{\circ}$ C at a pressure of 0.3 mm. showed, beside this differential oxidation, circular striations spreading out to 3 to 5 mm. diameter around the (110) and (111) poles of the crystal. The striations were caused by the development of {110} and {111} planes at these positions. When the sphere was heated to 580° C in hydrogen the oxide film disappeared and the striations were diminished.

From these experiments Gwathmey & Benton concluded that at temperatures below the melting point rearrangements of the surface atoms can occur to produce facets with simple crystallographic indices.

Leroux & Raub (1930) carried out careful weighing experiments upon specimens of silver heated to temperatures of 600 and 750° C in a stream of oxygen and in a stream of air, and observed that there was a loss of weight which they attributed to the formation of an oxide which they suggested was Ag_2O , and which was volatile at the temperatures of their experiments. Striations were formed on the surface of the specimens. When the specimens were heated under similar conditions in hydrogen there was no measurable loss in weight and no striations were formed. They concluded, therefore, that the rate of oxidation was different for different crystallographic planes of the silver and that the striations were due to the development of these planes. Graf (1942) correlated the striated structure to that observed when metals solidified from the molten state.

Elam (1936) heated a mechanically polished specimen of copper containing cuprous oxide, in a vacuum of about 0.5 mm., to a temperature between 900 and 950° C, and found that striations appeared; oxygen-free copper heated under similar conditions developed no striations. If, however, the surface of the oxygen-free copper was first oxidized and the specimen then heated in a vacuum to 900° C the oxide disappeared to leave a striated surface. There was a nett loss of weight

indicating evaporation of the oxide in a molecular form. It was found that the formation of striations was very sensitive to surface preparation, and even prolonged heating at 950° C did not remove the effects of the mechanical polish.

Elam found that if an etched face was polished and reheated, the striations reappeared in the same directions and that their spacing was the same. Separate specimens cut from the same single crystal also showed the same striations on corresponding faces. Where striations appeared on three faces of a single crystal they could not be identified as the intersection of a single plane with those three surfaces, although the directions of the lines on single faces were consistent with their being the intersection of {100} or {110} planes with that surface.

The mechanism suggested by Elam for the formation of the striations is that when the surface of copper is oxidized the rate of oxidation is greatest for the {100} and the {110} planes. When the specimen is then heated in a vacuum to a high temperature, the oxide evaporates leaving a striated surface. In the case of the copper containing cuprous oxide, the oxide decomposes on heating and the oxygen diffuses to the surface, which it oxidizes. The striations are then produced as in the case of the specimen whose surface was initially oxidized.

3. EXPERIMENTAL PROCEDURE

A number of experiments were performed to examine the thermal etching of high purity silver. Preliminary experiments indicated that the phenomena were very sensitive to surface preparation, and attention was concentrated upon finding a method of preparation which gave consistent, reproducible results. A method of electrolytic polishing was found most satisfactory and a series of experiments was carried out on specimens prepared in this way to examine the effects of temperature and various atmospheres on the etching process. To examine the surface of silver specimens when they were at elevated temperatures a furnace was designed to enable microscopy to be carried out at high temperatures.

(a) Selection of material

Silver was selected as the material for the first experiments on thermal-etching phenomena for a number of reasons. Since the grain boundaries are concerned in the etching, purity of the metal is of great importance, as quite a small average impurity content might, if concentrated at the grain boundary, have a large effect. Silver may be obtained in a condition of high purity. The silver used was supplied specially by Johnson, Matthey and Co. Ltd., who cast it in a vacuum and then cold forged and cold rolled it into 8 s.w.g. sheet. Analysis showed 0.00016 % iron, 0.00014 % manganese and faint traces of magnesium, calcium, silicon and lead.

In oxygen at atmospheric pressure silver oxide (Ag_2O) in bulk is unstable and decomposes above 200° C. This reaction is reversible, but below 200° C the rate of oxidation is small, becoming negligible below 100° C (Lewis 1906; Keyes & Hara 1922; Benton & Drake 1932, 1934).

As the crystal structure of silver is cubic its thermal expansion is isotropic and no stresses are set up when a polycrystalline specimen is heated or cooled provided there are no thermal gradients in the specimen.

(b) *The preparation of specimens*

Initial experiments were carried out using silver which had been ground on emery papers and then mechanically polished on velvet with a commercial metal polish. Because of the softness of the silver considerable difficulty was experienced; for reasonably reproducible results a tedious process of alternately polishing and chemically etching was needed and even after this process it was found (in agreement with the results of Elam (1936) for copper) that the effects of grinding were not removed by heating to a temperature near the melting point.

Finally a method of electrolytic polishing was found, which gave reproducible results and all specimens were prepared by this process. The process is described elsewhere (Shuttleworth, King & Chalmers 1947).

(c) *The effect of temperature on the etching*

To examine the effect of temperature on the etching of silver, specimens were heated in a fused silica tube open to the atmosphere. The tube was placed in an electric furnace already set at the required temperature. A thermocouple placed near to the specimen was used to indicate the specimen temperature and the furnace was controlled to maintain the temperature to within $\pm 1^\circ\text{C}$. The temperatures examined were 300, 500, 700, 850 and 940°C and figure 2, plate 9 ($\times 250$) shows the structures exhibited on examination when cool after 11 hours at these temperatures. Figure 3, plate 9 ($\times 1500$) shows the structures for 500, 850 and 940°C at a higher magnification.

Grooves have appeared at the grain boundaries and striations have occurred on the grains themselves. The striations change their direction at grain and twin boundaries. Extensive grain growth has occurred at the higher temperatures and the proportion of twinned crystals is higher at these temperatures. At 300°C no striations have appeared and the grain boundaries are incomplete. At 500°C the boundary grooves are complete and striations have begun to appear. The proportion of grains striated is seen to increase with temperature and above 850°C nearly all the grains are striated. At the higher temperatures the striations are more closely spaced and a second set of striations, inclined to the first, appear on some grains. The striations which form at the lower temperature are not as straight and regular as those formed at the higher temperature a few circular striations are shown in figure 3a ($\times 1500$). At the lower temperatures; the curvature caused by the boundary grooves appears to extend over an appreciable area of the grain surface; if the striations were the traces of specific crystallographic planes, they would be curved on a curved surface. Gwathmey & Benton (1940a, b) observed circular striations on spherical crystals of copper.

(d) The effect of atmosphere on the etching

Specimens were heated at 920° C in air, in oxygen, in pure nitrogen and in a vacuum of better than 10⁻⁴ mm. of mercury. The specimens were once more heated in a silica tube. The required atmosphere was established in the tube before it was placed in the furnace which was already at the required temperature. The specimen reached the required temperature in about 10 min. After the period of heating the tube was allowed to cool in air and the specimen cooled to 100° C in about 10 min. In all cases the atmosphere was maintained until the specimen cooled to room temperature.

Ordinary commercial oxygen was used and oxygen-free nitrogen. The nitrogen contained less than 10 vol./million of oxygen, less than 50 vol./million of hydrogen and less than 0.02 g./cu.m. of water vapour at 120 atm. pressure.

Typical photomicrographs of surfaces after these tests are shown in figure 4, plate 10 ($\times 250$).

In all cases extensive grain growth has occurred. In air (figure 4*a*) grain boundaries have formed and strong striations have appeared. Similar results are shown in figure 4*b* for specimens heated in oxygen, but in general the striations are more closely spaced and frequently a second set of striations appears inclined in direction to the first. In some cases a third set appears. Figure 5, plate 10 ($\times 2000$) shows the complicated structure developed in oxygen. In nitrogen, grooves appear at the grain boundaries and much less noticeably at twin boundaries; no striations appear. In a vacuum the grain boundaries show as grooves. No striations are produced, but the surface rapidly becomes rough. Figure 4*d* ($\times 250$) shows the surface after only 1½ hr. in a vacuum at 920° C, and is therefore not strictly comparable with the other photomicrographs. It may, however, be compared with figure 8*g*, plate 12 which shows the surface after heating in air for 1½ hr. at 920° C.

Some attempts were made at heating in hydrogen, but the results were unsatisfactory because the hydrogen was of doubtful purity. The results did, however, show no evidence of striations.

To verify that the boundary markings observed were in fact grooves as suggested by microscopic examination and not differences in level between adjacent grains, electron microscope replica photographs were obtained of a sample heated in nitrogen. The photographs confirmed that the markings were grooves below the level of both grains.

(e) The reversibility of striation etching

Because striations only appear in atmospheres containing oxygen, experiments were carried out to determine whether striations could be made to disappear by heating in nitrogen after heating in air (Shuttleworth, King & Chalmers 1946). Specimens were first heated in nitrogen until grain growth was only proceeding slowly, then in air for a sufficiently long period for striations to form, then in nitrogen for various lengths of time. Figure 6*a*, plate 11 ($\times 250$) shows the surface after 11 hr. in nitrogen at 920° C. Figure 6*b* shows the same surface after heating

for 1 hr. in air at the same temperature; striations have formed. Figures 6*c*, *d* and *e* show the surface after a further heating of 1, 3 and 11 hr. respectively in nitrogen; the striations have gradually disappeared. Figure 6*f* shows the effect of heating for a further period of 1 hr. in air. The striations have appeared in the same directions as before, but are more closely spaced.

During the preliminary anneal in nitrogen there was extensive grain growth and subsequently little boundary migration occurred. However, boundary migration restarted after figure 6*c* was taken and scars were seen to remain in the positions where the boundaries had halted. One scar appears on figure 6*d* and is indicated by the arrow. The scars gradually disappeared on further heating in nitrogen.

(f) *High-temperature microscopy*

In the previous experiments the specimens were all examined after cooling. In order to determine whether the boundary grooves and striations appeared whilst the silver was at the high temperature or whether they appeared during the processes of heating or cooling, specimens were examined continuously while they were maintained at high temperatures. The furnace constructed for this purpose is described in the appendix.

Figure 8, plate 12 shows a series of photomicrographs taken while a specimen was heated up to 920° C and maintained at that temperature. Figure 8*a* shows that after only 6 min., by which time the temperature had reached 575° C, the boundaries had appeared. Striations may be seen in figure 8*c* which shows the surface after 19 min. when the temperature had reached 850° C. The photomicrographs clearly demonstrate that both grain boundaries and striations are present at the high temperature and are not formed by the cooling process.

The technique provides a convenient means of observing grain growth continuously. Grain growth is seen to occur by the migration of the boundaries; the grooves move with the boundaries, leaving in general no scars at previous positions. Occasionally a network of scars is left and it is believed that the network coincides with a position of the boundaries where for some reason grain growth was temporarily halted.

When silver of commercial purity is heated in air, grain growth is retarded at the surface owing to oxidation of impurities at the grain boundaries, but Chaston (1945) has shown that in high-purity silver, grain growth proceeds at the same rate at the surface as in the centre of the material. Figure 8 should therefore be typical of what happens at the centre.

(g) *The direction of the striations*

As the striations appeared to be due to the development of specific crystallographic planes at the specimen surface, the following experiment was carried out to provide information concerning the crystallographic indices of those planes. A specimen was first heated in nitrogen at 920° C until grain growth was proceeding only slowly, and then heated in air at 920° C for $\frac{1}{2}$ hr. to produce striations. A selected field on the specimen was then photographed and the specimen heated

in nitrogen at 920° C until the striations had completely disappeared. The specimen was then compressed in a vice to produce a little plastic deformation and to show slip lines. The same field of the specimen was then photographed once more. Results are shown in figure 7, plate 11 ($\times 250$). Figure 7*a* shows the thermal etching striations. Figure 7*b* shows the slip lines. In some of the crystals there were more than one set of slip lines, but in all cases there was one set parallel to the striations previously produced by thermal etching: as slip occurs on the $\{111\}$ planes in silver and the slip lines are thus the intersections of $\{111\}$ planes with the surface, it is a reasonable conclusion that the faces of the steps causing the striated appearance are $\{111\}$ planes, since their intersection with the surface is in all cases parallel to a set of slip lines. This disagrees with the results of Graf (1942) who identified the planes as $\{100\}$ planes, but it is possible that there may be cases where the orientation of the surface of the specimen relative to crystal is such as to favour the development of $\{100\}$ planes.

(h) Summary of results

Briefly summarized, the results of the experiments may be stated as:

(i) Grain boundaries appear as grooves when silver is heated in air, oxygen, nitrogen, hydrogen and in a vacuum. They were observable in specimens heated in air at temperatures as low as 300° C.

(ii) Striations appear when oxygen is present in the atmosphere and may be caused to disappear by heating in nitrogen. The lowest temperature at which they were observed on heating in air was about 500° C. The directions of the striations were consistent with their being due to the development of $\{111\}$ faces.

(iii) Both striations and grain-boundary grooves are formed at the high temperature and are not produced by the cooling process.

(iv) When grain growth occurs the grooves move forward with the boundaries and there are not, in general, scars left at previous positions.

4. DISCUSSION

The rate of evaporation of silver in an inert gas at atmospheric pressure is but a few hundredths of that in a vacuum (Rosenhain & Ewen 1912). This is because most of the evaporating atoms are reflected after collision with the gas molecules and recondense on the surface. In effect, under these conditions silver exists in equilibrium with its vapour and an explanation of thermal etching will be sought in a consideration of the equilibrium configuration of the surface, i.e. that which has the lowest Gibbs Free Energy. Under such conditions where the nett loss of silver is negligible, any change from a polished to an etched surface occurs by the transfer of silver atoms from one part of the surface to another and the final equilibrium form will be independent of the mechanism of this transfer. In a vacuum, however, evaporation occurs without subsequent condensation and it may well be that the surface produced by this process bears no relation to the equilibrium surface.

(a) The formation of boundary grooves

A detailed picture of the grain boundary is not necessary for the interpretation of the grain-boundary grooves. The grain boundary must be a region of comparative atomic disorder; because of this the free energy of a polycrystalline metal is greater than that of a single crystal with the same dimensions. Formally this excess free energy may be regarded as a free energy per unit area of the crystal boundaries; this is analogous to the free energy per unit area attributed to the heterogeneous regions between different phases, in the thermodynamic description of multi-phase systems (see, for example, Guggenheim 1933).

When a metal is heated and no chemical action takes place, the only changes which can occur are rearrangements of the atoms to reduce the total free energy of the metal to a minimum. Assuming that the grains are strain free this free energy for a given specimen can be divided into three parts: (i) The free energy which the mass of the metal would possess if it were at the centre of a strain-free lattice. This is obviously constant. (ii) An additional free energy associated with the surface of the specimen. The value of the free energy per unit area associated with each element of surface may be expected to depend upon the crystallographic indices of that element of area. (iii) An additional free energy associated with the grain boundaries. The value of the free energy per unit area associated with each element of area of boundary may be expected to depend upon which crystallographic planes are in contact at this element of area, i.e. upon the relative orientation of the two crystal grains meeting at the boundary and the direction of the boundary. It is seen therefore that the approach to a minimum of free energy in a strain-free specimen must take place by the reduction of the surface and grain-boundary free energies.

Adam (1941) shows that in obtaining equilibrium conditions it is mathematically equivalent to regard a surface having a free energy per unit area as having a tensile force per unit length of the same numerical value and acting parallel to the surface. Equilibrium conditions for the grain boundaries can therefore be obtained by regarding them as the seat of surface-tension forces. At the intersection of a grain boundary with the surface, therefore, there are three tension forces acting at a line; the grain-boundary surface tension, and the surface tensions of the two crystalline faces meeting the boundary. The conditions for equilibrium therefore are given by figure 1. The plane of the figure is perpendicular to the line of intersection of the forces. T_A is the surface tension of the surface of grain A , T_B that of B , and T_{AB} the surface tension of the grain boundary. The condition for equilibrium is then $T_{AB}/\sin \gamma = T_A/\sin \beta = T_B/\sin \alpha$, and it is clear that a groove should form on the surface at the intersection of the boundary with it.

While the conditions so far considered specify the angles in the boundary grooves, their depths are controlled by the grain size, the equilibrium state being reached when each grain surface is a convex cap intersecting its neighbours at the equilibrium angles. The grooves which are observed in polished specimens represent an intermediate state in the approach to equilibrium.

No measurements have yet been made of the angle γ at the bottom of grooves, but the photomicrographs indicated that it may be small enough to mean that the free energy of the boundary is comparable with those of the crystal surfaces. While this in itself is surprising, it is possible that the free energies of the crystal surfaces have been reduced from those of clean surfaces by the presence of adsorbed gas. It is therefore suggested that quantitative measurements would have little significance except where made on perfectly clean surfaces. It is possible that grooves might not appear on such surfaces.

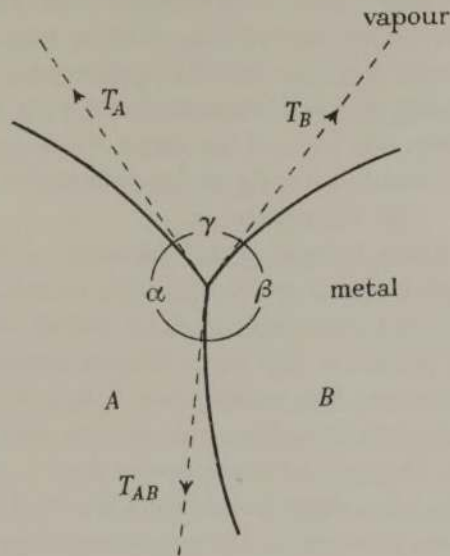


FIGURE 1

The consideration of the boundary as a seat of surface-tension forces should be significant in cases where grain growth (as distinct from recrystallization) occurs. The changes produced by the grain growth must reduce the free energy of the system, and the only manner in which this can be brought about is by reduction of the grain-boundary energy. The conditions for equilibrium at the intersection of the three grain boundaries are similar to those for the intersection of the boundary with the surface, i.e. the angles between the boundaries are governed by the relationship $T_{AB}/\sin \gamma = T_{BC}/\sin \alpha = T_{CA}/\sin \beta$, where T_{AB} is the surface tension of the boundary between grains A and B and γ is the angle made by grain C, etc. If the free energy per unit area of each boundary were a constant for that boundary and independent of its direction, the boundary area should for equilibrium be a minimum and the boundaries should be surfaces of zero curvature. A metastable state would then exist when the boundaries met at the correct angles and were surfaces of zero curvature.

Migration of the boundaries should occur in an endeavour to satisfy these conditions. However, this cannot be checked from the grain growth observed in these experiments as the surface of the specimen intersects the boundary network at an

arbitrary angle. Suitable information could be obtained by using specimens in which the recrystallized grain size was larger than the thickness of the sheet, so that the boundaries were perpendicular to the surface.

(b) *Possible mechanisms for the formation of boundary grooves*

When the silver is heated in the presence of an inert gas or in a vacuum the boundary grooves appear on the surface. Possible mechanisms for the transfer of silver from one portion of the surface to another are: slip, evaporation and condensation of silver in atomic form, surface mobility of silver atoms or ions. We shall try to estimate the relative importance of these possible mechanisms.

Slip is the normal process by which metallic crystals are plastically deformed, and effectively it is the slipping of whole atomic planes over each other in particular crystallographic directions. In view of the large forces necessary it is extremely doubtful whether the surface-tension forces are sufficient to cause any appreciable slip deformation even at high temperatures.

As suggested by Rosenhain & Ewen (1912), boundary grooves could be produced by the preferential evaporation of grain boundary metal, and the fact that they and also Fonda (1923) found that small grained metals showed a greater rate of evaporation in vacuum seems, at first sight, strong evidence for this. However, a rough calculation shows that this explanation is not adequate. To estimate the excess rate of evaporation of boundary material it will be supposed that the crystals are separated by a layer of super-cooled liquid. At a temperature T° K near the melting point T_M° K, integration of the Clausius-Clapeyron equation gives for the ratio of the vapour pressure of the super-cooled liquid to that of the solid

$$P_L/P_S = \exp \frac{F}{R} \left(\frac{1}{T} - \frac{1}{T_M} \right),$$

where F is the heat of fusion.

If the condensation coefficients of liquid and solid are the same, the rates of evaporation will be almost in the same ratio. Even at temperatures appreciably below the melting point this ratio is not much greater than unity; for silver at 900° C, for example, the ratio is 1.06. Crude as this calculation is it shows that the excess vapour pressure of the boundary material is not sufficient to explain the greater rate of evaporation when a small-grained metal is heated in a vacuum. Rosenhain & Ewen found that for a small-grained metal the loss of weight was 50% greater than for a large-grained metal. For a grain diameter of 10^{-2} cm. and a boundary of thickness 10^{-7} cm. the boundary would occupy but one fifty-thousandth of the surface area, necessitating a vapour-pressure ratio of about 2×10^4 to explain the results on these lines. The figure 10^{-7} cm. for the boundary thickness, while adequate for Kê's interpretation (1947) of the anelastic properties of aluminium, is probably too small, but it would need to be considerably increased before the increased evaporation of small-grained material could be explained.

Rosenhain & Ewen did not believe that the excess vapour pressure of the amorphous layer accounted for all the enhanced loss of weight, but thought that

some was due to evaporation from the walls of the grooves once they had formed. However, this cannot be; if we assume that the condensation coefficient of metallic atoms is unity, some of the atoms evaporating from one part of the groove condense on the opposite side. Direct application of Knudsen's Cosine Law shows that the nett evaporation from a groove is only equal to that which would occur from the plane surface occupying the neck of the groove. Nor does this small difference in the vapour pressures seem to be sufficient to explain the rapid formation of grooves which reach a depth of about 10^{-3} cm. in a few hours.

While it is maintained that Rosenhain & Ewen's and Fonda's observations of the enhanced loss of weight in small-grained material cannot be explained by the evaporation of an amorphous grain-boundary cement, the experimental fact cannot be gainsaid and further work to explain it is contemplated.

Surface mobility is probably a more important mechanism in the formation of the boundary grooves. Frenkel (1945) has shown that a necessary preliminary to evaporation is the presence of mobile atoms on the surface. Because the activation energy necessary for an atom to become mobile is less for surface migration than for evaporation followed by condensation, it is to be expected that the surface migration of atoms or ions will be a more important mechanism for the achievement of equilibrium than evaporation. Frenkel (1945) has developed a detailed theory for the change of shape caused by surface-tension forces which involves superimposing drift velocities in particular directions upon the random motion of atoms.

Andrade & Martindale (1935) have shown that surface migration occurs in silver on heating to temperatures as low as 280° C. They sputtered silver films 30 to 100 atoms thick on glass and on heating them in a vacuum of 10^{-2} mm. found that the film thickened in some places and flat crystals with {111} faces developed leaving the silver film thinner but still continuous on the remainder of the surface. In view of Johnson's discovery (1938) that the surface structure of tungsten filaments depends upon whether they are heated by A.C. or D.C. and Mrowca's (1943) similar observations on tantalum, it is probable that while surface migration is the most important mechanism for the formation of the boundary grooves it is the migration of positive ions not neutral atoms as considered by Frenkel (1945).

The mechanism of surface migration accounts for the fact that when the grain growth occurs the boundary grooves always coincide with the instantaneous positions of the boundaries and scars seldom remain in the old positions. After the grain boundary has moved away from a particular point of intersection with the surface the free energy condition for the existence of the groove no longer holds and the equilibrium condition for that particular portion of the surface is that it should be smooth or striated. The ions then migrate over the surface and fill in the groove. If an artificial groove is made by scratching the surface, the same effect occurs; when the metal is heated, the fine structure of the scratch disappears in about 20 min. at 850° C. The occasional appearance of scars corresponding to previous positions of the grain boundaries when grain growth occurs is explained by the fact that if for any reason the boundary halts for some time in one position

the groove will get deeper with time and when the boundary moves away from that position the grooves take longer to fill in. If the grooves were due to preferential evaporation of grain-boundary material, then during grain growth material would be lost more or less evenly over the surface of the growing grain and there would be a step rather than a groove at the grain boundary.

The complete reversibility of the processes by which the striations appear and disappear when the silver is alternately heated in oxygen and nitrogen suggests that the striations exist in equilibrium with an atmosphere containing oxygen and are not merely the result of a particular mechanism of evaporation or oxidation. It is supposed that the presence of the oxygen modifies the equilibrium configuration of the silver surface, so that a stepped structure in which specific crystallographic planes are developed has less energy than a smooth surface of less area but at arbitrary orientation. If this is so, the free energy per unit area of the specific planes developed must be significantly smaller in an environment of oxygen than that of other planes.

That, for an ionic crystal, the free energy per unit area of a crystal face depends on its crystallographic direction was shown by Lennard-Jones & Taylor (1925), who found by calculation that for rock salt the surface energy of a {110} face is almost four times the surface energy of a {100} face, so that in equilibrium the {100} face would be expected to develop preferentially. Lukirsky (1945) found that on heating a spherical crystal of rock salt it developed crystallographic facets and changed its shape to that of a polyhedron.

Since in inert atmospheres no striations appear, it may be assumed that any difference in the free energies per unit area of different crystallographic planes is too small to cause the formation of striations with the consequent increase of area. In oxygen, however, the relative values of free energies per unit area must be considerably modified. The possible interactions between the silver and the oxygen are: solution of oxygen in silver, the formation of an adsorbed monolayer on the surface of the silver, and the existence of silver oxide molecules in the vapour phase. Because the amount of oxygen dissolved in silver is small, increasing only to about 2 atomic per cent at the melting point (Steacie & Johnson, 1926), and because the partial pressure of silver oxide in the vapour phase will be small, it is probable that the most important effect is the preferential adsorption of oxygen on different faces. Direct experiments on the heterogeneous equilibrium of silver and oxygen are not sufficiently sensitive to show the presence of molecular oxide in the vapour phase; it must therefore be small compared with the equilibrium pressure of oxygen, but it is probably a number of times greater than the partial pressure of atomic silver vapour. Its existence may, however, be inferred from the enhanced evaporation of silver in the presence of oxygen, it being supposed that silver evaporates in the form of molecular oxide.

When silver is heated in air or oxygen at atmospheric pressure it will evaporate in the forms of atomic silver and molecular oxide. As for evaporation in the presence of an inert atmosphere it will be assumed that most of the evaporating atoms and

molecules are reflected and recondense on the surface so that the silver exists in equilibrium with its surroundings. Under these conditions, by the principle of detailed balancing, each process of evaporation will be balanced by the condensation of an equal amount of the same constituent.

In a consideration of the mechanisms whereby the striated equilibrium-surface configuration may be approached in an atmosphere of oxygen all three mechanisms—slip, atomic evaporation and condensation, and surface migration, which may contribute to the formation of boundary grooves, and in addition the evaporation and condensation of molecular silver oxide—must be considered. In so far as the evaporation of molecular silver oxide tends to expose certain crystallographic planes it may be interpreted as the preferential attack of those planes by the oxygen, but this is not the only mechanism as was suggested by Leroux & Raub. There must be redistribution of the silver by surface migration, evaporation and subsequent condensation of silver atoms and the condensation of oxide from the vapour phase. It is impossible to estimate the relative importance of the contributions of these mechanisms to the attainment of the final surface configuration, but that the transfer of material without the formation of the oxide is an important mechanism is clearly demonstrated by the fact that the striations disappear without appreciable loss of weight when the specimen is heated in nitrogen.

The authors wish to record their appreciation of the assistance of Professor F. Simon, F.R.S., Dr W. M. Jones and Mr A. F. Brown in the electron microscope examination of some silver surfaces and of Mr C. G. Earley in much of the microscopy. This work forms part of a general investigation carried on at the Royal Aircraft Establishment and the authors are indebted to the Ministry of Supply for permission to publish.

APPENDIX

A furnace for high-temperature microscopy

The requirements set in the design of a furnace for use in the microscopic examination of specimens at high temperatures were that it could be used with a microscope objective having a useful magnification up to 250; that fairly large areas of the specimen could be scanned by movement of the specimen relative to the objective; and that the specimens could be examined in various atmospheres and at temperatures up to the melting point of silver. Furnaces for high-temperature photomicrography have been described by Esser & Cornelius (1933) and by Swinden Howie & Chesters (1939), but neither meets all these requirements.

The limiting feature in the design of such a furnace is the working distance of the objective. For objectives with the necessary numerical aperture for the magnifications required, the distance between the hot specimen and the objective, which has to remain cool, is small and this necessitates very efficient insulation of the specimen and cooling of the objective. For the highest magnifications it was decided to use a 16 mm. achromatic objective with 0.28 numerical aperture and

a working distance of 7 mm.; this has a maximum useful magnification of about 250. In view of the short working distance it was decided to use gas or a vacuum for thermal insulation rather than a porous refractory, and reduce radiation losses by silver plating all hot surfaces. The furnace finally constructed is shown in figure 9. The base of the furnace, made of mild steel, stands on three adjustable legs on the

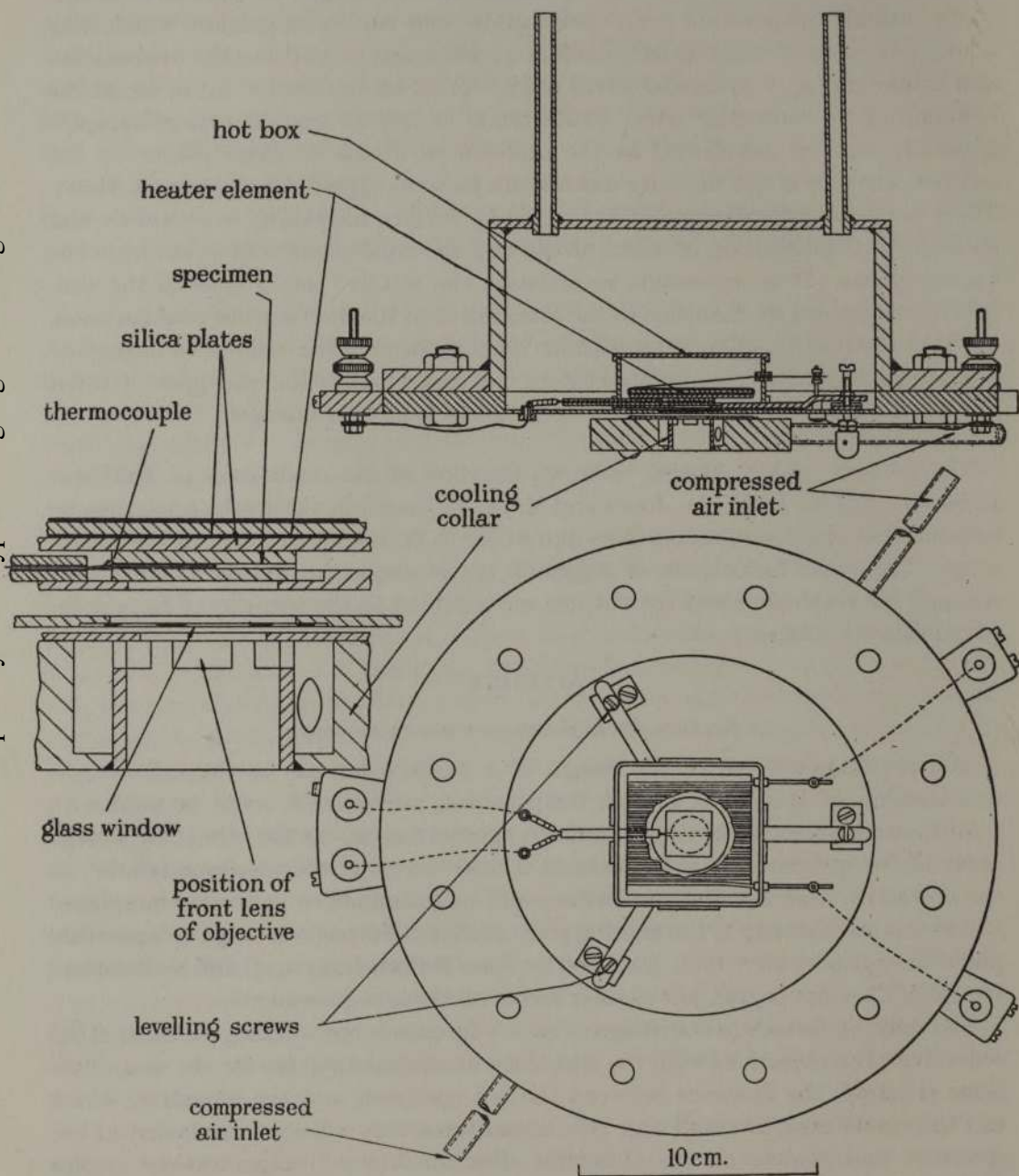


FIGURE 9. Furnace for high-temperature microscopy.

specimen support of a Vickers projection microscope. At the centre of the base is a glass window consisting of a microscope cover glass which is sealed in position by means of I.C.I. high-temperature optical cement. The specimen—a 2 cm. square piece of 8 s.w.g. silver—is supported above and about 4 mm. away from the window, on a stand made of heat-resisting steel. The specimen rests over a circular hole in the centre of the stand. The stand, which consists of a square plate with three radiating arms, is supported by adjustable screws at the ends of the arms; the screws have spherical ends and rest in grooves in the base of the furnace. Above the specimen is placed a sheet of silica $\frac{1}{16}$ in. thick and on this rests the heater which consists of nichrome tape (0.1×0.002 in.) wound on a similar silica sheet. Heater and specimen are enclosed in a box made of heat-resisting steel. The whole is enclosed by a cylindrical cap of mild steel which is provided with a flange and may be bolted to the base to form, with a synthetic rubber gasket, a gas-tight enclosure. Inlet and outlet tubes are supplied in the cap for the atmosphere required for the test. The specimen is drilled so that a thermocouple may be inserted at its centre, and the thermocouple leads pass out through the wall of the heat-resisting steel hot-box by means of alumina insulators, as do the heater wires. Both thermocouple leads and heater leads pass out of the furnace through silvered porcelain insulators which are soldered into the base. The thermocouples are waxed into the insulators and the heater current is carried in copper wires which are soldered to the insulators. All the portions of the hot-box are silvered to reduce radiation losses and the supporting arms and screws are thin to reduce conduction. The upper surface of the mild steel base is silver plated and polished to reflect radiant heat.

Below the mild-steel base is the cooling collar which rests on the microscope specimen support. The legs of the furnace base are adjusted so that there is a distance of about 1 mm. between the collar and the base. The microscope objective lies in the central space of the cooling collar with its front lens a little below the level of its top surface. Compressed air is supplied at an initial pressure of 10 lb./sq.in. through the two inlet tubes and allowed to expand into the annular space inside the collar. After expanding in this space it flows on to the surface of the lens and thence radially outwards between the collar and the furnace base, thus cooling both objective and glass window. Experiments using a dummy objective carrying a thermocouple showed that the temperature of the front lens did not rise more than two or three degrees above room temperature.

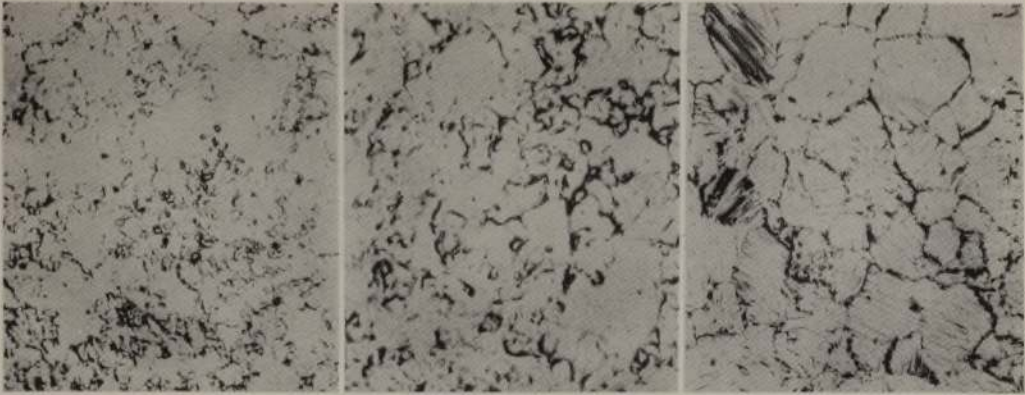
It has been found that a specimen temperature of 920° C can be maintained with a power consumption of 300 W. Because of the small heat capacity of the furnace it is not possible to regulate the temperature with a commercial controller. The current is therefore supplied from a constant-voltage transformer and this enables the temperature to be controlled by hand to within 2° C without too frequent attention. When setting up the furnace, the height of the base is first adjusted to give the required clearance between it and the collar, then with the objective front lens just below the top surface of the collar the specimen is levelled and its height adjusted by means of the screw supports of the hot-box. The specimen is set a little

below the correct height for focus in order to allow for expansion when the apparatus heats up. Afterwards, when the cap is on and the furnace running, focusing is achieved by means of the microscope fine adjustment which moves the objective.

Difficulty was experienced with a form of contamination which has not yet been fully explained. It was found that after a period of heating in the furnace striations gradually disappeared, the process spreading slowly over the surface. It was found by auxiliary tests that this could be caused by contamination of the surface by some component of the heat-resisting steel. Although this has been reduced by the silver plating on the steel, investigations still have to be limited to 3 hr. The thermocouple and heater wires also form possible sources of contamination. This effect is being investigated in detail.

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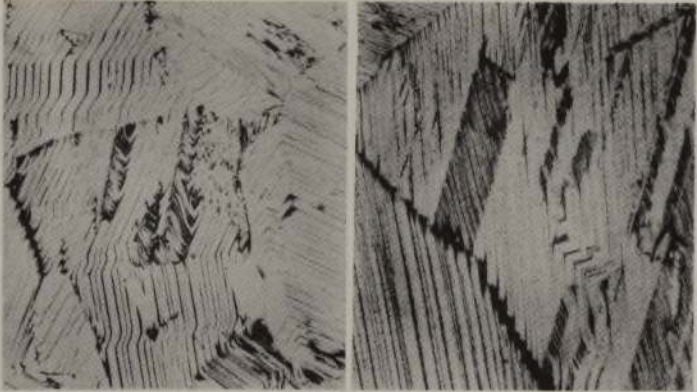
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a

b

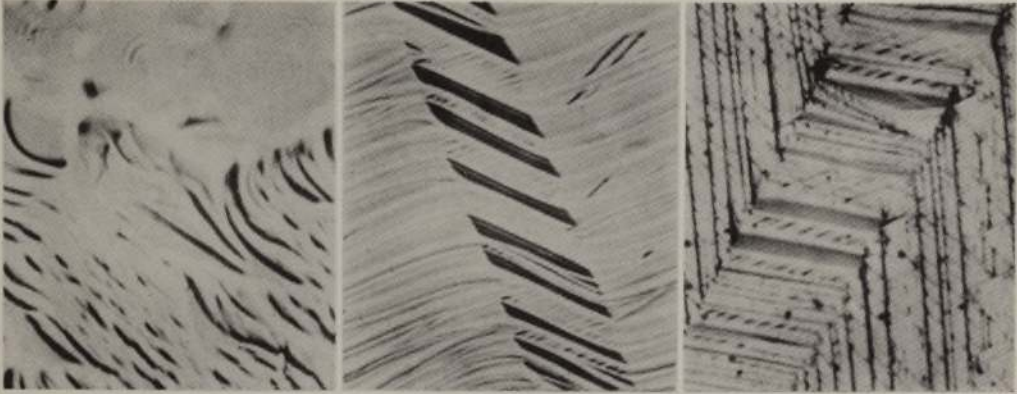
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FIGURE 2



a

b

FIGURE 3

(Facing p. 482)

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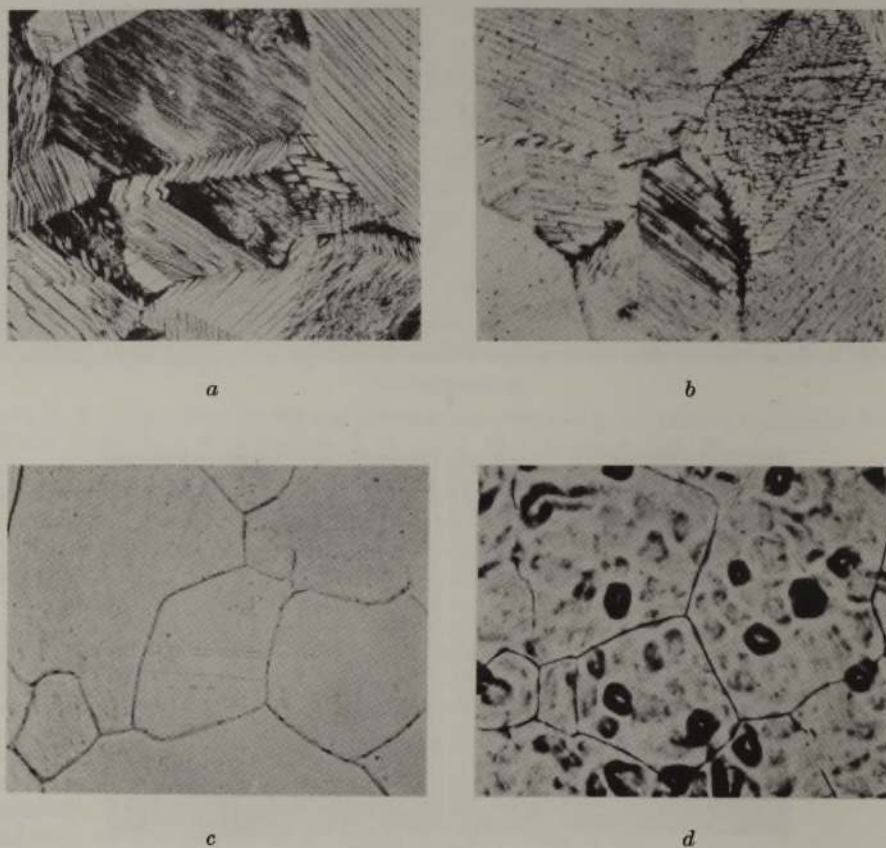


FIGURE 4

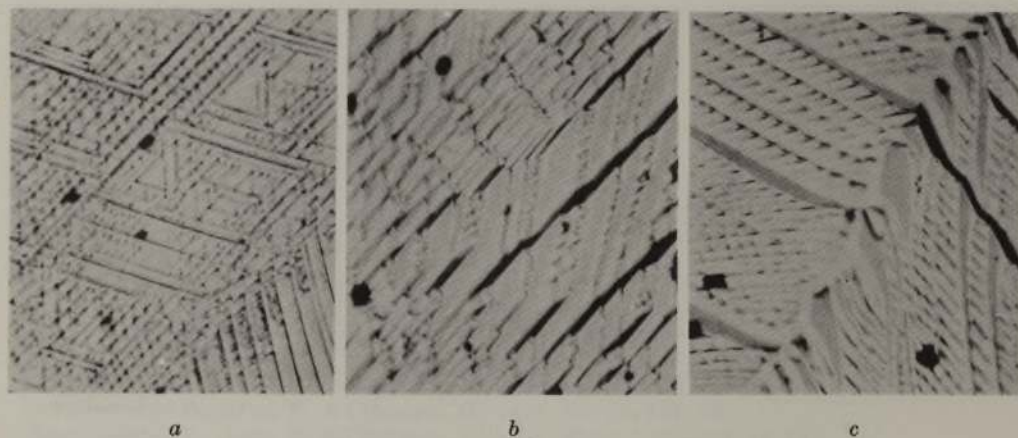


FIGURE 5

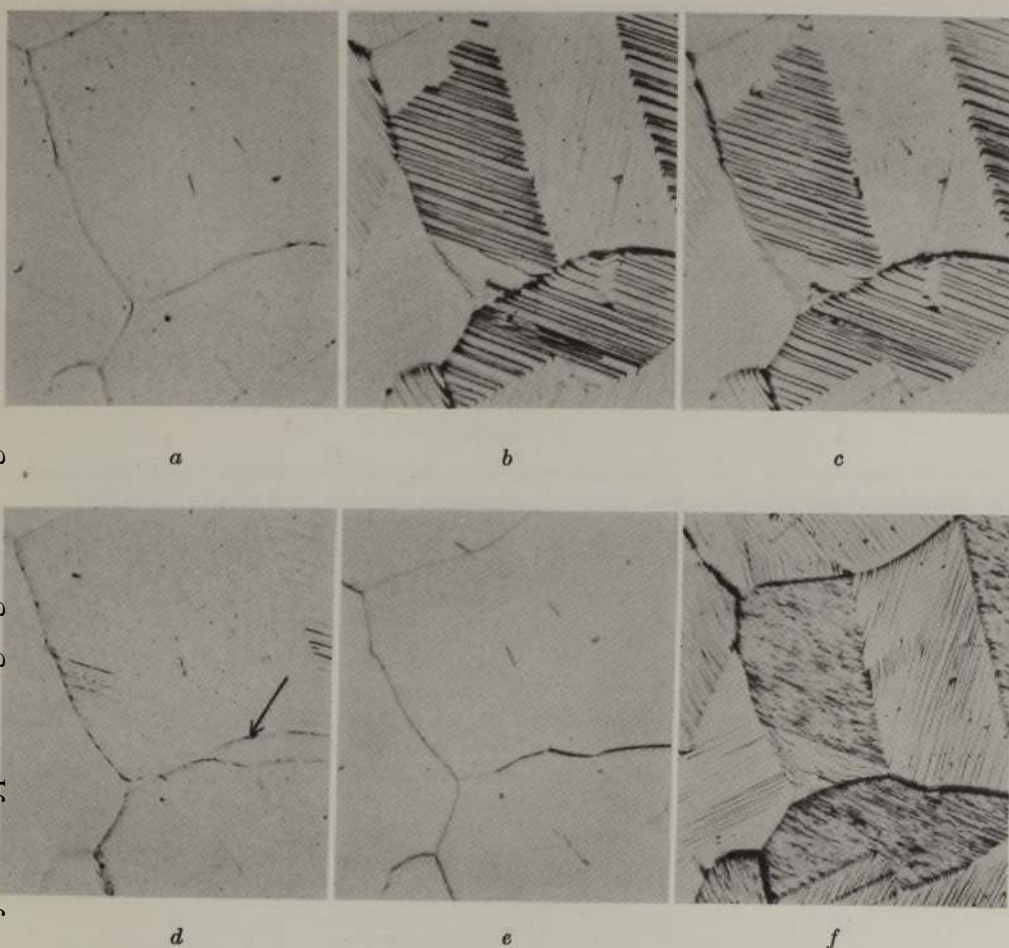


FIGURE 6

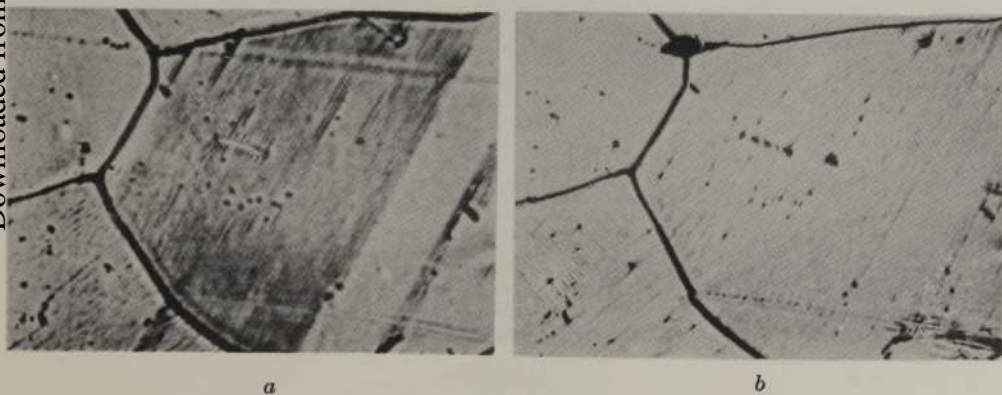
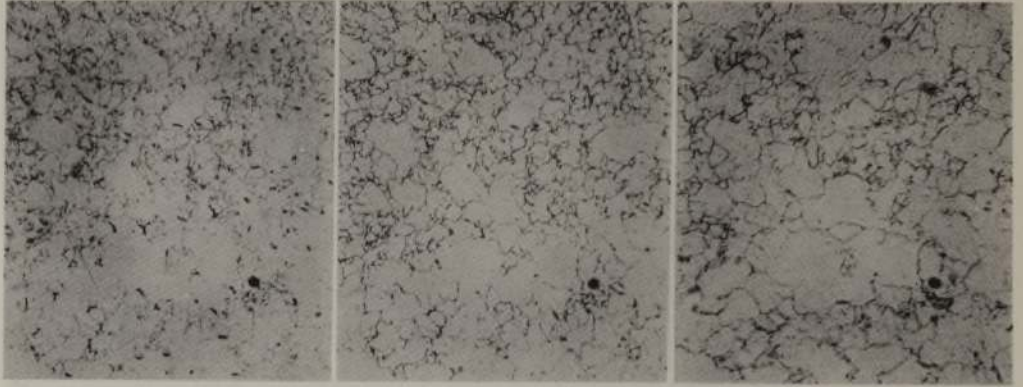


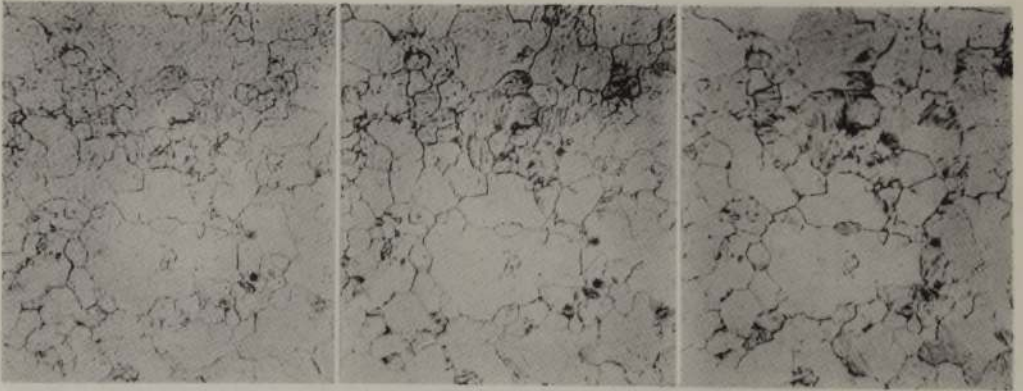
FIGURE 7



a

b

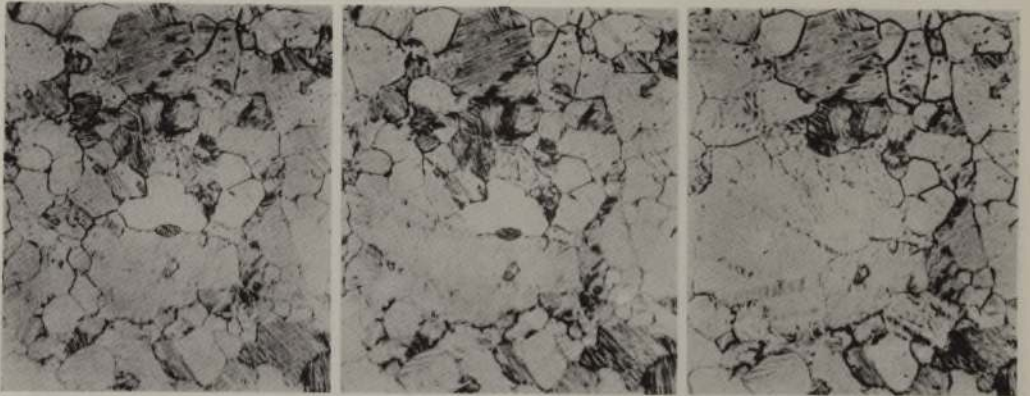
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FIGURE 8

DESCRIPTION OF PLATES 9 TO 12

PLATE 9

FIGURE 2. Silver heated in air for 11 hr. at different temperatures. (a) 300° C. (b) 500° C. (c) 700° C. (d) 850° C. (e) 940° C. ($\times 250$.)

FIGURE 3. Silver heated in air for 11 hr. at different temperatures. (a) 500° C. (b) 850° C. (c) 940° C. ($\times 1500$.)

PLATE 10

FIGURE 4. Silver heated in different atmospheres at 920° C. (a) 11 hr. in air. (b) 11 hr. in oxygen. (c) 11 hr. in nitrogen. (d) 1½ hr. in a vacuum. ($\times 250$.)

FIGURE 5. Some etch patterns obtained on silver heated in oxygen for 11 hr. at 920° C. ($\times 2000$.)

PLATE 11

FIGURE 6. The reversibility of striations. Silver heated at 920° C. (a) 11 hr. in nitrogen. (b) Same field after 1 hr. in air. (c) After a further 1 hr. in nitrogen. (d) After a further 2 hr. in nitrogen. (e) After a further 8 hr. in nitrogen. (f) After a further 1 hr. in air. ($\times 250$.)

FIGURE 7. The determination of the planes causing the striations. (a) Silver showing striations produced by heating in air. (b) Silver showing slip lines due to deformation after the etching striations had been removed by heating in nitrogen. ($\times 250$.)

PLATE 12

FIGURE 8. High-temperature microscopy. Photomicrographs of a silver specimen taken while the specimen temperature was raised at 920° C and maintained at that temperature in air. Same field throughout. ($\times 100$.) (a) After 6 min. temperature up to 575° C. (b) After 9 min. temperature up to 670° C. (c) After 19 min. temperature up to 850° C. (d) After 25 min. temperature up to 900° C. (e) After 40 min. temperature up to 917° C. (f) After 50 min. temperature up to 927° C. (g) After 60 min. temperature at 920° C. (h) After 70 min. temperature at 920° C. (i) After 90 min. temperature at 920° C.