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ATI No. **9033**

ROYAL AIRCRAFT ESTABLISHMENT

Farnborough, Hants.

THE "THERMAL ETCHING" OF SILVER

by

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Report No. Met.11

September, 1946.

ROYAL AIRCRAFT ESTABLISHMENT, FARNBOROUGH

The "Thermal Etching" of Silver

by

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R.A.E. Reference: Mat.N6/9726/5

SUMMARY

R

The mechanism whereby grain boundaries are delineated and striations formed on the polished surface of heated metal specimens has been examined. Experiments on electrolytically polished silver show that grain boundary grooves form 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 tensions of the crystalline faces meeting the boundary in the surface of the specimen. The striations are caused by the formation of these crystalline planes having the lowest free energy, the relative surface energies of different planes being modified by the presence of adsorbed oxygen. It is suggested that the chief means whereby the final structure is attained is that of surface migration of ions.

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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.

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

Numerous workers during the past thirty years have observed that under certain conditions, when a metal specimen is heated, polished surfaces develop an etched appearance, even though no chemical reaction is to be expected. The two etching phenomena which occur, the delineation of the grain boundaries and less frequently the appearance of striations on the crystal faces, have been explained in various ways, and the work of previous investigators may be classified for convenience according to which of these phenomena they considered and the theory put forward to explain it.

2.1 Observations on grain boundary delineation

Two main mechanisms have been postulated for processes resulting in the outlining of the grain boundaries; - (a) the preferential evaporation of the boundary material and (b) strains resulting from expansion and contraction.

2.1.1 Preferential evaporation of grain boundary material

The theory of preferential evaporation of grain boundary material was first introduced in 1912 by Rosenhain and Ewen¹, who heated polished specimens of copper, silver and zinc in a vacuum of 2×10^{-3} mm. of mercury and found that grooves developed at grain boundaries but not at twin boundaries. By weighing the specimens they measured the rates of evaporation from the surface, and observed that when heated under otherwise identical conditions, specimens with small grain size evaporated more rapidly than those with large grain size. Ratios of about 2.3, 1.4 and 1.2 for the rates of evaporation in the two cases were observed for zinc, copper and silver respectively. 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.

Fonda² 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 vacuum the rate of evaporation from filaments with small grain size was 1.4 times that from filaments whose grains were 4 - 100 times longer, and Fonda attributed the phenomena he observed to the greater volatility of the grain boundary material.

Thermal etching of the grain boundary has been observed in ferrous materials by a number of workers and since it shows the structure of the metal as it exists at high temperatures it has been used to study phase transformations. As early as 1909 Rosonhain and Humfrey³ found, on heating iron in a vacuum of 10^{-2} mm. of mercury, two separate networks of grooves. In the following year Kroll⁴ observed two networks on low and medium carbon steel when heated in either a vacuum or an inert gas. In 1912 Humfrey⁵ identified one of the two networks as the grain boundaries of the iron as it existed in the γ condition above 890°C; this network also showed twin boundaries. The other network which crossed the first at random, he identified as the outline of the boundaries of the α phase which existed below the transformation temperature. Rawdon and Scott⁶ found that the two sets of boundaries only occurred when specimens were heated above the $\alpha - \gamma$ transformation temperature, below this temperature only the α network was produced. They believed that the grooves were caused by preferential evaporation although they showed that evaporation from the crystal faces was small because slip lines on the surface remained after heating in vacuum. Homingway and Ensinger⁷ confirmed previous experimental work but suggested that the grooves were formed by evaporation followed by subsequent condensation.

Rawdon and Berglund⁸ heated electrolytic and open hearth iron in hydrogen at atmospheric pressure in the temperature range 750 - 800°C., and observed the formation of grain boundary grooves which they ascribed to preferential evaporation, and more recently Day and Austin⁹ have used the phenomenon as the basis of a routine method for the estimation of austenitic grain size in steels. The polished steel specimen is heated in hydrogen at atmospheric pressure and quenched in mercury; grooves coincident with the final grain boundaries appear. No scars are left at earlier position of the grain boundaries, and Day and Austin attribute this obliteration of scars to the wrinkling of the surface which occurs on quenching. When specimens are slowly cooled, however, scars often show. The formation of boundary grooves is explained by preferential evaporation and they suggest that in inert atmospheres at appropriate temperatures the method should be applicable to any metal or alloy. Miller and Day¹⁰ emphasize the necessity for oxygen-free hydrogen when examining steels containing aluminium; oxygen when present in very small quantities oxidises the aluminium in a thin surface layer and grain growth in this layer is inhibited.

Parker and Smoluchowski¹¹ found boundary grooves on heating in hydrogen to 1200°C, a steel containing 6% molybdenum, in which therefore transformation did not occur. They found that molten silver spread more rapidly along these grooves under capillary forces than across the crystal faces.

2.12 The delineation of the boundary due to strain

The suggestion that grain boundaries may be outlined as a result of stresses caused by the anisotropic expansion of the individual grains has recently been put forward by Boas and Honeycombe¹² to explain both the markings observed in their own experiments and those reported earlier by Carpenter and Elam¹³. The latter observed on examining an antimony-tin alloy, containing 1.5% antimony, after heating to between 150°C. and 200°C., that the grain boundaries were marked by lines which they stated were really differences in level between adjacent crystals. They did not explain the markings, but identified them with the boundaries shown by chemical etching. If grain growth occurred while the specimen was heated the new grain boundaries were indicated by the markings when the specimen was examined after cooling. Subsequent heating did not obliterate these markings, but where further grain growth occurred a new set of markings corresponding to the new grain boundaries were seen in addition to the old markings, on examining the cooled specimen once more. From this, Carpenter and Elam concluded that the markings were only produced upon cooling, when the grain growth was arrested. The grain boundary outlines were observed on specimens which had been heated in air, in hydrogen, and in vacuo.

Boas and Honeycombe observed boundary markings in specimens of tin, zinc and cadmium which had been subjected to cycles of heating and cooling. The specimens were electrolytically polished and heated between 30°C. and 150°C. in air at atmospheric pressure. Some specimens were examined continuously during the temperature cycle and others only after cooling. The results appeared consistent with Carpenter and Elam's observation that the boundary markings were produced on cooling. Similar experiments on lead resulted in no boundary markings. This together with observations on striations and X-ray investigation of strains, which will be referred to in para. 2.22 led Boas and Honeycombe to suggest that in the case of the non cubic metals tin, zinc, and cadmium, since the expansion is anisotropic, stresses are set up in a randomly orientated aggregate when it is heated and cooled, and that these stresses caused the differences in level at the grain boundaries which they observed. In the case of lead which is cubic the expansion is uniform and no stresses are set up.

An earlier suggestion that anisotropic expansion could cause boundary markings was made by Ewon¹⁴ to explain the phenomena observed in steels. He suggested that preferential evaporation was insufficient to account for the double network observed and that the network corresponding to the α grains was due to the anisotropic expansion of the ferrite crystals while that for the γ grains was caused by the volume changes occurring in the ferrite-austenite transformation. As it is now known that anisotropic expansion does not occur in the ferrite crystals the suggestion must be discounted in this case.

Grain boundary grooves have been observed by Johnson¹⁵ on tungsten and appear on photomicrographs published by Elam¹⁶ but these workers do not offer explanations of the phenomenon.

2.2 Observations on the formation of striations

Five mechanisms have been suggested for the appearance of striations on the faces of crystals: evaporation, migration of surface ions, strain causing slip lines, preferential oxidation, and the formation of a new component.

2.21 Evaporation

Rosenhain and Ewen¹ published a photomicrograph of silver which showed marked striations after heating in air. No explanation of the phenomenon was offered in their paper but in the discussion it appeared that they regarded it as being due to selective evaporation.

Rawdon and Berglund⁸, in their experiments on electrolytic and open hearth iron heated in hydrogen at atmospheric pressure, observed striations on large numbers of grains and attributed the effect to "slight volatilization."

2.22 Migration of surface ions

More careful attention was paid to the phenomenon of striations by Johnson¹⁵, who observed it in 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. The filaments were heated by the passage of current through them; the structure resulting from D.C. heating was different from that produced by A.C. heating and that produced by A.C. was independent of the frequency. Johnson concluded from this that A.C. heating was equivalent to heating from an external source.

Filaments heated by A.C. in a vacuum developed only grain boundary grooves, except where thermal gradients near the supports caused a stepped structure. When heated by A.C. in lamp gas (Argon 86% Nitrogen 14% at 60 cm. pressure) the filaments developed facets which X-ray examination showed to have simple crystallographic indices. Near the supports the facets were superimposed on the stepped structure caused by thermal gradients.

Filaments heated by D.C. in a vacuum developed a stepped structure orientated with respect to the direction of the current, and those heated in lamp gas showed facets similar to those of the A.C. heated filaments as well as the stepped structure. Except for minor differences, filaments heated in nitrogen and in argon showed a similar structure to that developed in lamp gas.

Because the loss of weight due to evaporation was not sufficient to account for the change in shape of the filaments heated in gas, Johnson concluded that the facets developed by evaporation of surface atoms and their reflection back on to the surface by the gas atoms. The stepped structure which occurred with D.C. heating and that caused by temperature gradients, Johnson supposed were caused 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 remained smooth on heating with A.C. but roughened when heated with D.C.

Gwathmey and Benton,¹⁷⁻¹⁹ 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°C. at a pressure of 0.5 mm. showed beside this differential oxidation, circular striations spreading out to 3-5 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.

A mixture (3 : 1 by volume) of hydrogen and oxygen was passed over another spherical copper crystal and the temperature gradually increased. Oxidation occurred up to a temperature of 260°C. but at higher temperatures the oxide film was reduced. At 360°C. rough and smooth areas appeared on the surface and simultaneously the catalytic reaction became appreciable. On microscopic examination it was seen that the facets had developed parallel to the (111) and (110) planes.

From these experiments Gwathmey and Benton concluded that at temperatures below the melting point rearrangements of the surface atoms can occur to produce facets with simple crystallographic indices. These facets are probably the active centres at which catalysis is concentrated.

2.23 Striations due to strain

Boas and Honeycombe¹², in their experiments on the heating of specimens through cycles of temperature change, observed the formation of striations on the grains of polycrystalline samples of tin, zinc and cadmium, but not upon those of lead specimens. The striations occurred to different extents in each metal; in zinc after 200 cycles almost every grain was striated; in cadmium after 200 cycles most grains were striated and in tin few grains showed striations. Using cadmium they found that the proportion of grains that were striated and the number and intensity of the striations increased with the number of cycles but was independent of the duration of the cycle. By examining the specimen continuously they found that the striations increased during both the cooling and the heating portions of the cycle. A single crystal of cadmium showed few striations when subjected to temperature cycles.

Lead photographs indicated that internal strain accumulated in the metal with increasing numbers of cycles. This was confirmed by heating cadmium specimens after different numbers of cycles to 250°C. when recrystallization occurred. The resulting grain size varied with the number of thermal cycles in the manner to be expected if plastic deformation had accumulated with each cycle. Boas and Honeycombe attributed the appearance of the striations to the same mechanism as they did the appearance of the grain boundaries (Sec. 2.12); the expansion of the grains of tin, zinc and cadmium is anisotropic and stresses are caused in the randomly orientated aggregate of crystals on heating and cooling. The striations are the slip lines resulting from the deformation caused by these stresses.

2.24 Preferential oxidation

Blum¹⁶ heated a mechanically polished specimen of copper containing cuprous oxide, in a vacuum of about 0.5 mm. to a temperature between 900°C. 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. 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 polish.

Using single crystals she 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 intersections 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 oxidised the rate of oxidation is greatest for the (100) and the (111) planes. When the specimen is then heated in 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 oxidises. The striations are then produced as in the case of the specimen whose surface was initially oxidised.

2.25 The formation of a new component

Day and Austin⁹, who observed 'wrinkles' on the surface of steels heated in hydrogen and quenched in mercury, attributed them to the formation of a thin surface layer of martensite or some similar product by the quenching. They did not appear on slowly cooled specimens.

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 were 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.

3.1 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.

The reaction of silver with oxygen is reversible²⁰⁻²³ and no oxidation of silver occurs at temperatures above 200°C even in oxygen at atmospheric pressure. Below 200°C oxidation is slow and it becomes negligible below 100°C.

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 as long as there are no thermal gradients in the specimen.

3.2 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 Elam¹⁶ 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 cell used is shown in Fig. 1 and the process is described in detail in Appendix I.

3.3 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°C , 500°C , 700°C , 850°C and 940°C and Fig. 3 ($\times 250$) shows the structures exhibited on examination when cool after 11 hours at these temperatures. Fig. 4 ($\times 1500$) shows these structures (excluding that for 300°C) at a higher magnification. The structure of the hard-rolled silver before heating is shown in Fig. 11.

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 temperatures are not as straight and regular as those formed at the higher temperatures; a few circular striations are shown in Fig. 4a ($\times 1500$). 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 and Benton¹⁷ observed circular striations on spherical crystals of copper.

3.4 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 mins. After the period of heating the tube was allowed to cool in air and the specimen cooled to 100°C in about 10 mins., and room temperature in about 20 mins. 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 gr/cu. metre of water vapour at 120 atmospheres pressure.

Typical photomicrographs of surfaces after these tests are shown in Fig.5 ($\times 250$).

In all cases extensive grain growth has occurred. In air (Fig.5a) grain boundaries have formed and strong striations have appeared. Similar results are shown in Fig.5b 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. Fig.6 ($\times 2000$) shows the complicated structure developed in oxygen and may be compared with Fig.7 ($\times 2000$) which shows the structure after heating in air. In nitrogen, grooves appear at the grain boundaries and to a lesser extent at twin boundaries; no striations appear. In vacuum the grain boundaries show as grooves. No striations are produced but the surface rapidly becomes rough. Fig.5 ($\times 250$) shows the surface after only 1/2 hours in vacuum at 920°C, and is therefore not strictly comparable with the other photomicrographs. It may however be compared with Fig.12f which shows the surface after heating in air for 1/2 hours 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 boundaries 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. Electron microscope photographs of a specimen heated in oxygen were also obtained. Fig.9 ($\times 2500$) shows the complexity of the surface structure.

3.5 The reversibility of striation etching

Because striations only appeared 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. 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. Fig.10a ($\times 250$) shows the surface after 11 hrs. in nitrogen at 920°C, Fig.10b ($\times 250$) shows the same surface after heating for 1 hr. in air at the same temperature; striations have formed. Figs.10 (c, d and e) ($\times 250$) show the surface after a further heating of 1, 3 and 11 hours respectively in nitrogen; the striations have gradually disappeared. Fig.10f ($\times 250$) 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 extensive grain growth occurred and subsequently little boundary migration occurred. However between Figs. 10c and 10d boundary migration restarted and scars are seen to remain in the positions where the boundaries halted. The scars gradually disappeared on further heating in nitrogen.

3.6 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 and cooling, specimens were examined continuously while they were maintained at high temperatures. The furnace constructed for this purpose is shown in Fig. 2 and described in Appendix II.

Fig. 12 shows a series of photomicrographs taken while a specimen was heated up to 920°C and maintained at that temperature. Fig. 12b shows that after only 6 mins. by which time the temperature had reached 575°C the boundaries had appeared. Striations may be seen in Fig. 12d which shows the surface after 19 mins. 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 Chaston²⁴ has shown that in high purity silver, grain growth proceeds at the same rate at the surface as in the centre of the material. Fig. 12 should therefore be typical of what happens at the centre.

3.7 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 vacuo. 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 in heating in air was about 500°C.
- (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 results of the experimental work on silver may conveniently be discussed, initially, in relation to the theories put forward by earlier investigators, outlined in Section 2.

4.1 Discussion of previously suggested theories

4.11 Preferential evaporation

Rosenhain and Ewen¹ outlined the first detailed theory of the structure of the grain boundary in metals when discussing the results of their experiments on the rate of evaporation of silver in a vacuum. They suggested that the grains in a pure metal are joined together by a layer of "amorphous cement". The atoms of this amorphous cement are identical with those of the rest of the metal but they are in a state of disorder as in a supercooled liquid or a Boilby polished layer. Implicitly they considered this cement as a distinct thermodynamic phase, with specific mechanical and thermal properties; in particular it was regarded as possessing a definite vapour pressure greater than that of the crystalline material. They observed that specimens of small grain size evaporated about 50% more rapidly than specimens of large grain size and explained this by the fact that the small grained specimens exposed more grain boundary material than the large grained specimens; this boundary material evaporated more rapidly than the crystalline material of the grains. In addition when the boundary material evaporated it left grooves and additional evaporation took place from the walls of the grooves.

The fact that the different rates of evaporation could be explained in this way was taken as strong evidence that this picture of the grain boundary was correct and that the grain boundary grooves were produced by preferential evaporation. As was pointed out by Desch, however, in the discussion of Rosenhain and Ewen's paper, this theory was inadequate to account for the magnitude of the difference in rates of evaporation. The theory has been considered in detail from the standpoint of thermodynamics and the kinetic theory of gases in Appendix III, which shows that considered as a separate phase the grain boundary material must have a vapour pressure less than that of a supercooled liquid and even that of a supercooled liquid is far too small to account for the different rates of evaporation observed experimentally. In addition, it is shown that the formation of grooves, does not enhance the increased rate of evaporation by the evaporation from the walls of the grooves.

Since after all the theory of preferential evaporation is inadequate to explain the differences observed in rates of evaporation, these cannot be regarded as evidence that the grain boundary grooves are formed by preferential evaporation. The more recent work of Fonda² on tungsten has confirmed that small grained specimens evaporate more rapidly than those composed of large grains but no adequate explanation has yet been put forward. This experimental fact is regarded as significant and further work on the problem is contemplated.

Neither Rosenhain and Ewen, nor Rawdon and Berglund³ offered evidence in support of their suggestion that the striations they observed in silver and in iron respectively were caused by evaporation. The importance of evaporation as a possible mechanism for the formation of striations is discussed in Section 4.3.

4.12 Strain as the cause of the etching structure

The marked similarity which exists between the surface structures observed by Boas and Honeycombe¹² on zinc and cadmium and those shown by silver heated in oxygen suggests at first that the phenomenon is due to the same cause in both cases. A comparison of Fig. 3c ($\times 250$) which shows the surface structure of silver heated in air for 11 hours at 700°C, with Fig. 3c ($\times 100$), of Boas and Honeycombe's paper, showing zinc after 100 thermal cycles between 30°C and 150°C, brings out many points of similarity; the grain boundaries are outlined and the striations resemble one another in the two photomicrographs. Boas and Honeycombe's explanation of the striations as slip lines due to the stresses caused by the anisotropic expansion of the grains and the boundary delamination as steps caused by the same mechanism cannot apply in the case of silver. Silver, being cubic, expands isotropically so no stresses are caused; the striations increase in number with time when the temperature remains constant and they may be removed by heating in nitrogen. The striations in cadmium however were observed by Boas and Honeycombe to occur when the specimen was cooling.

Once again in silver the grains are outlined by grooves which move forward with the grain boundaries when migration occurs whereas both Boas and Honeycombe and Carpenter and Elam¹³ observed that in their specimens of non-cubic metals the grain boundaries were outlined by steps which did not migrate with the boundaries and that new steps appeared on cooling.

In view of these considerations it is probable that despite the similarity in appearance of the surface structures, the thermal etching of silver is produced by a different mechanism from that causing the features observed in tin, cadmium and zinc subjected to cycles of temperature change.

4.13 Preferential oxidation

Great similarity exists between the photomicrographs of silver heated in the presence of oxygen and those published by Elam¹⁶, for copper containing cuprous oxide heated in vacuum. The resemblance is so marked that it is difficult to believe that the structure are not produced by the same mechanism. The results are similar too in that Elam observes that striations only occur in copper when oxygen is present. Her explanation of the phenomenon however, as being due to the decomposition of cuprous oxide in the mass of the copper, diffusion of the oxygen through the copper to the surface, preferential oxidation in certain crystallographic directions at the surface followed by evaporation of the oxide to leave a bright striated surface, cannot apply in the case of silver, because silver does not form an oxide at the temperature of the experiments.

4.14 Other previous theories

The suggestion put forward by Day and Austin⁹ to explain the wrinkles on the surface of steels heated in hydrogen, that a thin surface layer of a new component was formed cannot have any significance when high purity silver is considered. The significance of the suggestion in relation to steels is somewhat doubtful as Day and Austin observed striations in hydrogen purified iron, in which martensite is not formed.

The suggestion of Gwathmey and Benton¹⁷ that the striations they observe on copper are due to the rearrangement of the surface atoms which occurs only in the presence of oxygen, a phenomenon which they carefully distinguish from preferential oxidation; and that of Johnson that the steps on tungsten filaments are due to migration of surface ions

under the action of potential and thermal gradients is in close accord with the tentative picture put forward by the authors and will be discussed with that theory in Section 4.5.

4.2 Suggested reasons for the thermal etching of silver

4.21 Grain 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 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 we can attribute a certain free energy to per unit area to 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 Guggenheim²⁵).

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:- (a) The free energy which the mass of the metal would possess if it was at the centre of a strain free lattice. This is obviously constant (b) The additional free energy introduced by the removal of the specimen from the centre of the lattice. This is defined as the free energy of the surface. (c) The additional free energy introduced by dividing the mass into crystal grains of random orientations. This is defined as the free energy of the grain boundaries. 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.

Adam²⁶ 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. It seems probable that the free energy per unit area of the surface between two grains will depend upon their mutual orientations.

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 Fig.13. The

plane of the figure is perpendicular to the line of intersection of the forces. T_A is the surface tension of surface of grain A, T_B that of B, and T_{AB} the equivalent surface tension of the grain boundary. The condition for equilibrium is then

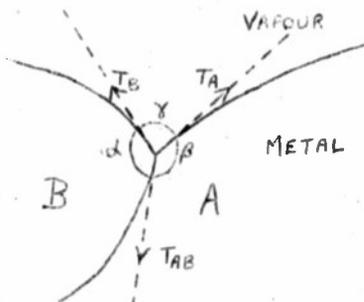
$$T_{AB}/\sin \gamma = T_A/\sin \alpha = T_B/\sin \beta.$$


Fig.13

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. If the free energy per unit area of the grain surface were independent of crystallographic direction, the equilibrium state would be reached when each grain surface was a spherical 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 that of a clean surface 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 too that grooves might not appear on such surfaces.

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 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 between grains A and B and γ is the angle made by grain C etc. The area of the boundaries should be a minimum and therefore they should be plane. A metastable state would then exist when the boundaries met at the correct angles and were plane.

Migration of the boundaries will occur so as to endeavour to satisfy these conditions. In general both these conditions cannot be satisfied simultaneously, a metastable state is not reached, and the metal should approach, more and more slowly, a single crystal. Harker and Parker²⁷ using a different approach and taking $\alpha = \beta = \gamma = 2\pi/3$ showed that metastable equilibrium is possible in general. This is the result which would be obtained in the above analysis if the free energy per unit area of a grain boundary were independent of the orientations of the crystals meeting at that boundary. This is unlikely and it would be expected that usually the angles would not be equal to $2\pi/3$.

In general when recrystallization is complete the grain boundaries are not plane and meet at arbitrary angles. It would be anticipated on this theory of grain growth that the boundaries would then advance so as to increase their radii of curvature and make the angles of intersection satisfy the equations for equilibrium. The grain boundaries shown in the series of photomicrographs of Fig. 12, do not all appear to behave in this way; some boundaries advance so as to decrease their radii of curvature. However these photomicrographs represent only a section of a three dimensional grain boundary system and the curvature shown is not necessarily the actual curvature of the boundary. The angular condition for equilibrium is appropriate only when the plane of section is perpendicular to the line of intersection of the boundaries.

It is felt that this subject could best be investigated by means of thin silver foil, suitably strained and then annealed at low temperature so that when recrystallization is complete the grain size is large compared with the thickness of the foil. The boundaries will then be

and it is clear that a groove should form on the surface at the intersection of the boundary with it.

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It is felt that this subject could best be investigated by means of thin silver foil, suitably strained and then annealed at low temperature so that when recrystallization is complete the grain size is large compared with the thickness of the foil. The boundaries will then be

normal to the sheet surface and when on heating to a higher temperature grain growth occurs the changes in the boundary can be quantitatively determined.

4.22 Striations

Only if the free energy per unit area is independent of the crystallographic surface will a grain surface in equilibrium be that of the minimum area consistent with boundary conditions. If different crystallographic surfaces have different surface energies the condition for minimum free energy will not be same as that for minimum surface. Lennard-Jones and Taylor²⁸ found by calculation that for rock salt the surface energy of a (110) face is almost four times as great as that of a (100) face, so that in equilibrium the (100) face will be preferentially developed. Lukirsky²⁹ found that on heating a spherical crystal of rock salt, it developed crystallographic facets and changed its shape to that of a polyhedron.

When silver is heated in nitrogen the condition for equilibrium seems to be that of the minimum surface area consistent with the boundary conditions. However when the silver is heated in the presence of oxygen striations appear on the grain surfaces and these increase the surface area. That this represents an equilibrium state or at least an approach to equilibrium is shown by the fact that the formation of the striations is reversible and they appear and disappear when the atmosphere is changed between nitrogen and oxygen. Whatever the exact mechanism may be, it seems that the presence of oxygen modifies the surface energy of crystallographic planes so that they have different energies.

Another effect that may be important is one investigated theoretically by Frenkel³⁰. He shows that at non zero temperatures the condition for equilibrium of a crystal face is not that it is plane, but that it should be covered by a series of steps of one atom deep; steps up or down being equally probable. This is because at non zero temperatures the equilibrium condition is that the free energy and not the internal energy must be a minimum; so, analogous with the molecular velocities and non minimum kinetic energy of a gas, we have for a crystal face not the minimum potential energy of a smooth surface but a natural roughness of the surface whose degree depends upon the temperature. It is possible that a run of steps in one direction might produce a visible roughness, but it is not clear how it would be induced only in the presence of oxygen.

Since the conditions of the experiments recorded in this report are such as to preclude the formation of oxide the oxygen must affect the silver by forming either a solid solution or an adsorbed layer. Steacie and Johnson³¹ have found that at 800°C and 800 mm. pressure, silver dissolves 0.0325 atomic % of oxygen; they made no measurements at higher temperatures but suggest that the amount of oxygen dissolved in solid silver just below the melting point is the same as that dissolved in liquid silver, i.e. 1.87 atomic %. There appears to be no information on the adsorption of oxygen on silver at temperatures in this region, but Bente and Drake³² have found that at 188°C activated adsorption occurs, the adsorption isotherm becoming flat at a pressure of 200 mm. Over the range of temperatures of the experiments on silver it is plausible to suppose that activated adsorption occurs and that this leaves different faces with different free energies; as shown above this would explain why the equilibrium state of a crystal surface is not smooth but striated.

4.3 The mechanism by which the surface structures form

So far only the form which the metal surface takes up has been considered, the various mechanisms by which it changes from a polished surface to a grooved and striated surface have not been examined.

From general thermodynamical considerations it can be said that the final equilibrium structure will be independent of the mechanism by which it is formed.

In principle the polished surface can change to its equilibrium form by means of at least four different mechanisms:- slip, viscous flow, evaporation, and surface migration of ions. All these might contribute to the final result and it is desirable to decide which are the more important and whether their relative importance changes with temperature.

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.

Viscous flow, although common in amorphous bodies, has only recently been invoked as a mechanism for the deformation of metals. Viscous flow in amorphous bodies occurs by the diffusion of a small number of holes, mainly in the direction of shearing stress. Frenkel³² has shown that in crystalline metals vacant lattice sites occur whose number increases exponentially with temperature, and as the result of the diffusion of these through the lattice, metals can be expected to display a viscous flow with a velocity gradient proportional to the shearing stress. The theory has the virtue that small forces acting for a long time can produce appreciable deformation, but the viscosity is very temperature sensitive, and though it might be important in the deformation of the silver surface at 900°C, in view of the mechanical properties of silver it is probably negligible at 300°C at which temperature the boundary grooves begin to appear.

Frenkel³⁰ has given a detailed theory of the mechanisms of evaporation and surface migration. As already mentioned, he shows that at non zero temperatures the equilibrium form of a crystal surface is not flat but covered by steps one atom deep. He suggests that on the surface of these steps there are mobile metallic atoms which behave as a two dimensional gas, and that on the edges of the steps there are mobile atoms which behave as a one dimensional gas. Evaporation proceeds in three stages; an atom leaves its lattice point at the edge of a step and joins the one dimensional gas on that edge; at a later stage the atom moves from the one dimensional gas to the two dimensional gas on the surface of the step; lastly, evaporation into the vapour phase occurs from among the mobile surface atoms. This mechanism is a consequence of the principle of detailed balancing and it is seen that the existence of mobile surface atoms is a necessary preliminary to evaporation.

Without going too deeply into the process it is conceivable that evaporation from a non equilibrium surface will occur more rapidly in some places than in others and this mechanism above could in time bring about the equilibrium surface, the effect of an inert gas or of the metallic vapour phase would be to reflect back some of the evaporated atoms so that they condensed on the surface in random positions thus allowing the equilibrium form at the surface to be obtained with a smaller nett evaporation of metal than in vacuum.

Since, however, evaporation from a surface is preceded by the existence of mobile atoms on the surface it appears that an equilibrium surface configuration would be obtained more readily by movement of these atoms in the surface than by evaporation for which additional energy is required. Frenkel³⁰ develops a detailed theory for the change in shape caused by surface tension forces, which involves superimposing

upon the random surface movements of the atoms, drift velocities in particular directions.

In view of Johnson's discovery¹⁵ that the surface structure of tungsten filaments depends upon whether they are heated by A.C. or D.C. it is probable that though surface migration is the most important mechanism which enables a surface to reach the equilibrium condition, it is the migration of +ve ions, not neutral atoms as suggested by Frenkel. Andrade³³ has shown that silver shows surface migration on heating to temperatures as low as 280°C. He sputtered silver films 30 - 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 on the remainder of the glass thinner but still continuous. Turner³⁴ had previously found that silver foil 2×10^{-5} cm. thick became transparent on heating in air to 240°C but not on heating in coal gas to 510°C, this was also presumably caused by surface migration which left very thin areas in the silver film.

The mechanism of surface migration explains why, when 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 position of the surface is that it should be smooth or striated; the surface ions then migrate back 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 twenty minutes at 850°C and in five or six hours the scratch becomes much shallower. 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 groove takes longer to fill in.

5 Conclusions

The etching effects on silver represent an approach to equilibrium governed by the reduction of the free energy of the surface and of the grain boundaries near the surface. The presence of specific gases modify the surface free energy and different structures are formed. It is believed that both the boundary grooves and the striations are produced mainly by the surface migration of ions, though other mechanisms may play a small part.

Acknowledgements

The authors are indebted to Professor F. Simon, F.R.S. and Messrs W.M. Jones and A.F. Brown of the Clarendon Laboratory, Oxford, for the electron microscope replica photographs of etched silver specimens.

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Appendices I - III
Drgs. Mat. 2033 and 2053
Negs. 8 pages photos.

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Appendix IThe Electrolytic Polishing of Silver.

The apparatus used in the electrolytic polishing of silver specimens is shown in Fig.1. The electrolyte is contained in a perspex box of square section. At the bottom of the cell is fitted a silver cathode to which connection is made by silver wire sealed into the perspex base. The specimen - a 2 cm. square of 8 S.W.G. sheet is supported in the electrolyte by means of a rubber "sucker" attached to a string which passes through a supporting tube and carries a counterpoise weight. In this way the specimen is held against the end of the supporting tube and its position and orientation can be adjusted by movement of the tube. The position of the specimen is set to reference marks on the perspex cell. Electrical connection to the specimen is made by means of a silver wire which fits into a hole drilled in the corner of the specimen. The electrolyte found most satisfactory is similar to that used by Gibbertson and Fortner¹ (Ag CN. 35 gm./l. KCN. 30 gm./l. K₂CO₃ 38 gm./l).

The potential difference is applied to the cell by means of a potentiometer. The variation of current with voltage is rapid at low voltages but decreases very much as the voltage is increased; the current only changes from 10 ma/cm.² to 12 ma/cm.² when the voltage is raised from 1.0 to 1.8 volts. For any given cell the optimum values of current and voltage must be found by trial; in the cell described the best results are obtained with voltages around 1.5 volts. This voltage is just below that necessary to produce the spontaneous fluctuations of current referred to by Gibbertson and Fortner.

To avoid surface distortion, specimens are not mechanically polished prior to electrolytic treatment; the as-rolled surface is used. Specimens are degreased in benzol washed with alcohol and dried. The specimen is carefully set to the reference marks on the cell. When the potential is applied, the current which is initially about 120 ma. falls rapidly to about 40 ma. A dark grey film first forms on the surface of the specimen and then quite rapidly the colour changes to a straw colour. Shortly afterwards the surface darkens along a number of irregular lines which divide the surface into areas about 1 mm. in diameter. These areas rapidly darken until the surface is uniform and the whole film gradually darkens until at the end of 10 minutes it is a grey green. At this stage, without switching off the current, the specimen is removed quickly from the electrolyte. If the current is switched off before the specimen is removed silver is redeposited on the surface. The film is removed by gently passing the specimen over the surface of a piece of wet velvet. Microscopic examination shows that the surface is now smoother but that traces of any scratches that were originally on the surface still remain. The specimen is electrolytically polished for a further ten minutes and this time washed and dried in alcohol. The surface is now bright and though it has slight undulations these do not show in microscopy. The crystal boundaries are not outlined but if the critical conditions are departed from pits or hills may occur. A typical polished surface is shown in fig.12(a) (x 150).

It is essential that the polishing be done in two stages and the deposited film removed between the stages. Polishing is only possible when the specimen is horizontal and the under surface is being dissolved; voltage-current relations are quite different if the voltage is applied to the cell in the reverse direction.

When the lower piece of silver is the anode; the current is only $1/3$ rd at 0.6 V and $1/6$ th at 1.8 V. of that when the anode is uppermost, and the specimen is etched not polished.

The mass of silver electrolytically dissolved is approximately that calculated assuming all the current is carried by silver ions, so that a thickness of about 10^{-3} cm. is removed in twenty minutes. If the voltage is below the critical value etching results, if above an insoluble oxide and/or cyanide film forms on the surface.

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APPENDIX IIA 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 $\times 250$; 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 and Cornelius¹ and by Swinden, Howie and Chesters², 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 $\times 250$. In view of the short working distance it was decided to use gas or a vacuum for thermal insulation rather than a porous refractory, (the conductivities are in the ratio of about 1:100) and reduce radiation losses by silver plating all hot surfaces. The furnace finally constructed is shown in Fig. 2. The base of the furnace, made of mild steel, stands on three adjustable legs on the 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 1/10 ins. thick and on this rests the heater which consists of nichrome tape (0.1" \times 0.002") 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.

To prevent the condensation of the silver on the glass windows and the consequent obscuring of the object, a shutter was placed between specimen and window and only removed when the specimen was examined and photographed.

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.ins. 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 watts. 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 by means of a constant voltage transformer and this enables the current to be controlled by hand to within 2 degrees 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 focussing is achieved by means of the 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 hours. The thermocouple and heater wires also form possible sources of contamination. This effect is being investigated in detail.

REFERENCES

- 1 Swinden, Howie and Chesters. Trans. Brit. Ceram Soc. 38 245 (1939).
- 2 Esser and Cornelius. Metals and Alloys 4 119. (1933).

APPENDIX IIIThe Evaporation of the Grain Boundary

Rosenhain and Ewen postulated the existence of an amorphous layer at the grain boundary to explain the results of their experiments on the relative rates of evaporation of large and small grained specimens. To this layer was attributed the properties of a separate phase; in particular it was regarded as possessing a vapour pressure in excess of that of the crystalline material. Additional support for the amorphous layer hypothesis was given by the fact that at temperatures above the recrystallisation temperature and under suitable conditions of stress and time, metals fracture in an intercrystalline fashion as compared with fracture at lower temperatures which is transcrystalline. The time to fracture increases with decreasing stress, as is also typical of super-cooled liquids with which an amorphous material may be compared.

In order to gain some idea of the properties to be expected in the hypothetical amorphous layer it is convenient to extend this comparison with a super cooled liquid. The viscosity of a liquid is a function of its disorder, and decreases with increasing temperature. The viscosities¹ of a number of liquid metals have been extrapolated below their melting points and the temperature at which the viscosity becomes twice that at the melting point determined in each case. In Table I ΔT shows the amount by which this temperature is below the melting point. It is seen to be of the order of 200°C. and even so far below the melting point the viscosity of the super cooled liquid metal is less than that of castor oil at room temperature (220×10^{-2} poise). It is clear from the comparatively large loads and times necessary to rupture metals in an intercrystalline fashion that the disorder of the grain boundary material must therefore be less than that of the super-cooled liquid.

TABLE A

Metal	M.P. °C	ΔT (Z = 2Z M.P.)	Z in Poise
Bi	544	300°C.	3.6×10^{-2}
Gd	594	400°C.	3.0×10^{-2}
Hg	234	60°C.	4×10^{-2}
Pb	602	300°C.	6×10^{-2}
Sb	903	300°C.	3×10^{-2}
Sn	505	200°C.	4.2×10^{-2}

The vapour pressure of the grain boundary material will therefore be less than that of the super-cooled liquid which may be approximately computed.

The difference between the specific heat of the solid and that of the liquid at any temperature may be written

$$\Delta C_p = \alpha + \beta T + \gamma T^3.$$

Considering the Gibbs Free Energy $G = E + pV - TS$, the excess of the free energy of the super cooled liquid over that of the solid may be written

$$\Delta G = \Delta H_0 - \alpha T \ln T - \frac{1}{2} \beta T^2 - \frac{1}{7} \gamma T^3 + \Delta T \quad (\text{Ref. 2}) \quad (1)$$

Where ΔH_0 = Change of Enthalpy at the melting point (latent heat of fusion)

T = Temperature

I = Constant of integration.

If as an approximation ΔC_p is regarded as constant. Equation 1 reduces to

$$\Delta G = \Delta H_0 - \Delta C_p T \ln T + IT.$$

And substitution of known values in this equation enables I to be determined.

For silver³ $\Delta H_0 = 11,700$ joules/gm. atom. Melting point = $1234^\circ T$

$$\Delta C_p = -2.9 \text{ joules/gm. atom/}^\circ\text{C.}$$

At the melting point $\Delta G = 0$ and thus I may be evaluated

$$0 = 11,700 + 2.9 \times 1234 \times 2.303 \log 1234 + 1234I.$$

$$I = -30.13 \text{ joules/gm. atom/}^\circ\text{C.}$$

Therefore $\Delta G = 11,700 + 6.68 T \log T - 30.13T$ (2)

Assume that at a temperature T the vapour pressure of the solid is p_1 and that of the super-cooled liquid is p_2 . Then the solid will be in equilibrium with the vapour at a pressure p_1 and consequently have the same free energy as the vapour at that temperature and pressure. Similarly the super-cooled liquid will have the same free energy as the vapour at pressure p_2 .

Because the vapour obeys the law of perfect gases its free energy may be written in the form

$$G = G_0(T) + RT \ln p. \quad (\text{Ref. 4}) \quad (3)$$

Where $G_0(T)$ depends only on the temperature and p is the vapour pressure.

Hence the free energy of the solid may be written

$$G_s = G_0(T) + RT \ln p_1 \quad (4)$$

and that of the super-cooled liquid

$$G_l = G_0(T) + RT \ln p_2 \quad (5)$$

The difference in free energy is then

$$\Delta G = RT \ln (p_2/p_1)$$

Hence from equation (2)

$$RT \ln(p_2/p_1) = 11,700 + 6.68 T \log T - 30.13 T \quad (6)$$

Using this equation values of p_2/p_1 have been calculated for various temperatures and are given in Table II. Since the value of ΔC_p has been assumed constant at its value at the melting point the inaccuracy of the table increases for the lower temperatures.

TABLE B

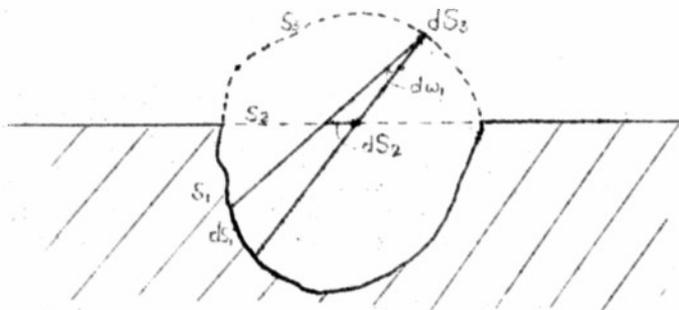
t_C	t_T	P_2/P_1
961	1234	1.000
950	1223	1.007
900	1173	1.042
850	1123	1.081
800	1073	1.130
750	1023	1.186
700	973	1.250
650	923	1.330
600	873	1.420

It is seen that the vapour pressure of the super-cooled liquid is not much greater than that of the crystalline phase, at temperatures at which appreciable vaporisation occurs. Since the vapour pressure of the amorphous phase, if it existed, would be less than that of the super-cooled liquid then assuming rates of evaporation proportional to the vapour pressures, grooves would only appear at the boundaries after considerable total evaporation had occurred, and the effect would be less pronounced at temperatures near the melting points.

It is clear that the excess vapour pressure attributed to the amorphous layer at the grain boundary is insufficient to explain the increased rate of evaporation (about 50%) observed by Rosenhain and Ewen and later by Fonda in small grained specimens compared with large grained specimens. On the assumption of a grain diameter of 10^{-2} cms. and a boundary thickness of even 5×10^{-6} cm. the boundary occupies only one thousandth of the surface area. An increased rate of evaporation corresponding to the highest value of P_2/P_1 in Table II over this area would account for only an insignificant amount of the observed differences.

Rosenhain and Ewen did not believe that the excess vapour pressure of the amorphous layer accounted for all the observed differences and suggested that the loss of weight due to the boundary was enhanced by evaporation from the walls of the grooves when once they formed.

On the assumption that atoms leave a solid surface at a rate proportional to the equilibrium vapour pressure and in random directions according to Knudsen's cosine law it may be shown that the evaporation from a groove in an isotropic medium is the same as that from a flat surface of the dimensions of the neck of the groove.



Consider a hollow in an isotropic material. Atoms are evaporating from the walls of the hollow. On Langmuir's hypothesis that all like atoms that hit a metallic surface condense, there will be no reflection at the walls. Because of the high vacuum and low vapour pressure of the metal, atomic collisions in small hollows may be neglected (mean free path of silver vapour at 800°C. ~ 20 cm.5).

Consider the surface of the hollow S_1 and the two imaginary surfaces S_2 in the plane of the surface of the surrounding metal and S_3 any arbitrary surface drawn to enclose the opening of the hollow.

The number of atoms leaving an element of surface dS_1 to pass through the element dS_3 of surface S_3 is by Knudsen's Cosine Law

$$dn_1 = \frac{n\bar{c}}{4\pi} \cos \phi_1 dS_1 dw_3 \quad (7)$$

Where n is the number atoms per unit volume under equilibrium conditions

ϕ is the angle between the normal to dS_1 and the line joining dS_1 to dS_3 .

and dw_3 is the solid angle subtended by dS_3 at dS_1 .

Equation (7) may be written

$$dn_1 = \frac{n\bar{c}}{4\pi} dA_1 \cdot \frac{dA_3}{r_1^2} \quad (8)$$

Where dA_1 and dA_3 are the projected areas of dS_1 and dS_3 perpendicular to the line joining them, and r_1 the distance between them.

Now consider the area dS_2 outlined in S_2 by the solid angle dw_1 . If there was no hollow, the evaporation from this element of surface through the small area dS_3 would be

$$dn_2 = \frac{n\bar{c}}{4\pi} dA_2 \cdot \frac{dA_3}{r_2^2} \quad (9)$$

Where r_2 is the distance between dS_2 and dS_3 and dA_2 is the projected area once more.

From (8) and (9)

$$dn_1/dn_2 = dA_1 r_2^2 / dA_2 r_1^2 = 1 \quad (10)$$

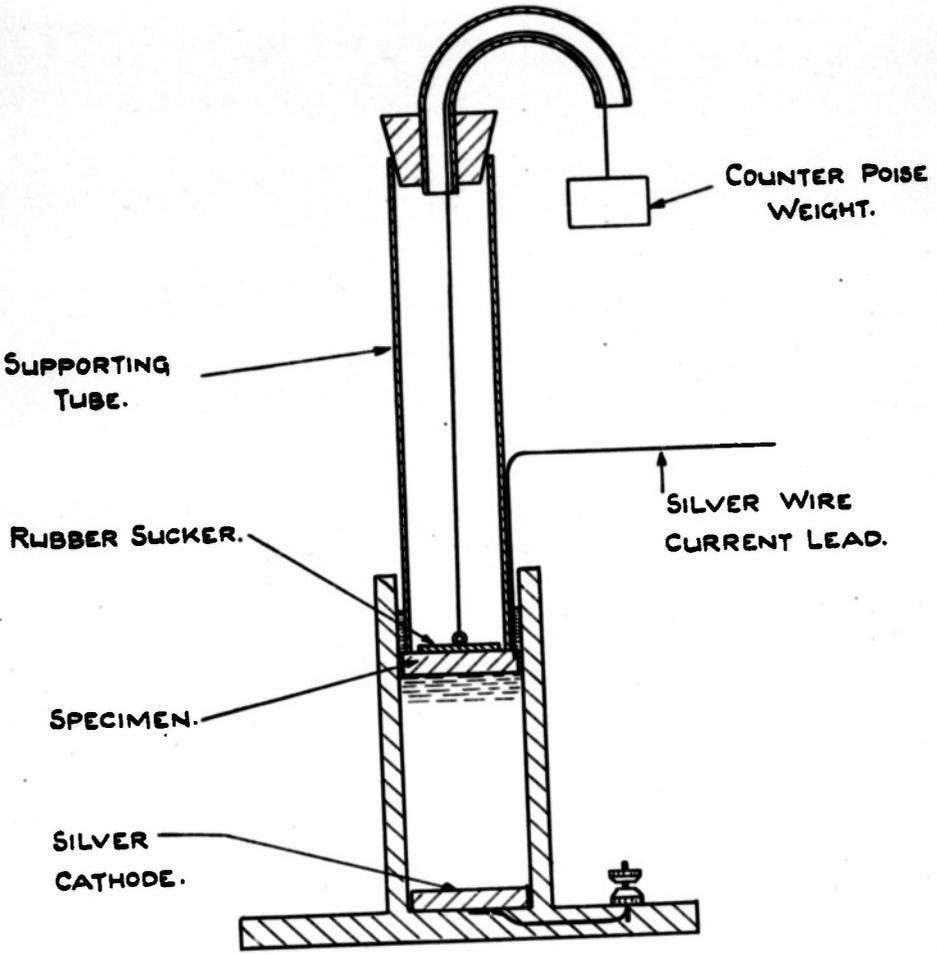
$$\text{since } dA_1/r_1^2 = dA_2/r_2^2 = dw_1.$$

Hence the number of atoms passing through dS_3 from any element of the surface of the hollow is the same as that which would pass through it from a corresponding element on the surface if the metal was solid. Thus the total number of atoms passing through dS_3 from the entire surface S_1 is the same as that which would pass through dS_3 from the area of surface S_2 covering the hole. Thus the total evaporation from the hollow i.e. the number of atoms passing through the surface S_3 is no greater than that from a flat surface.

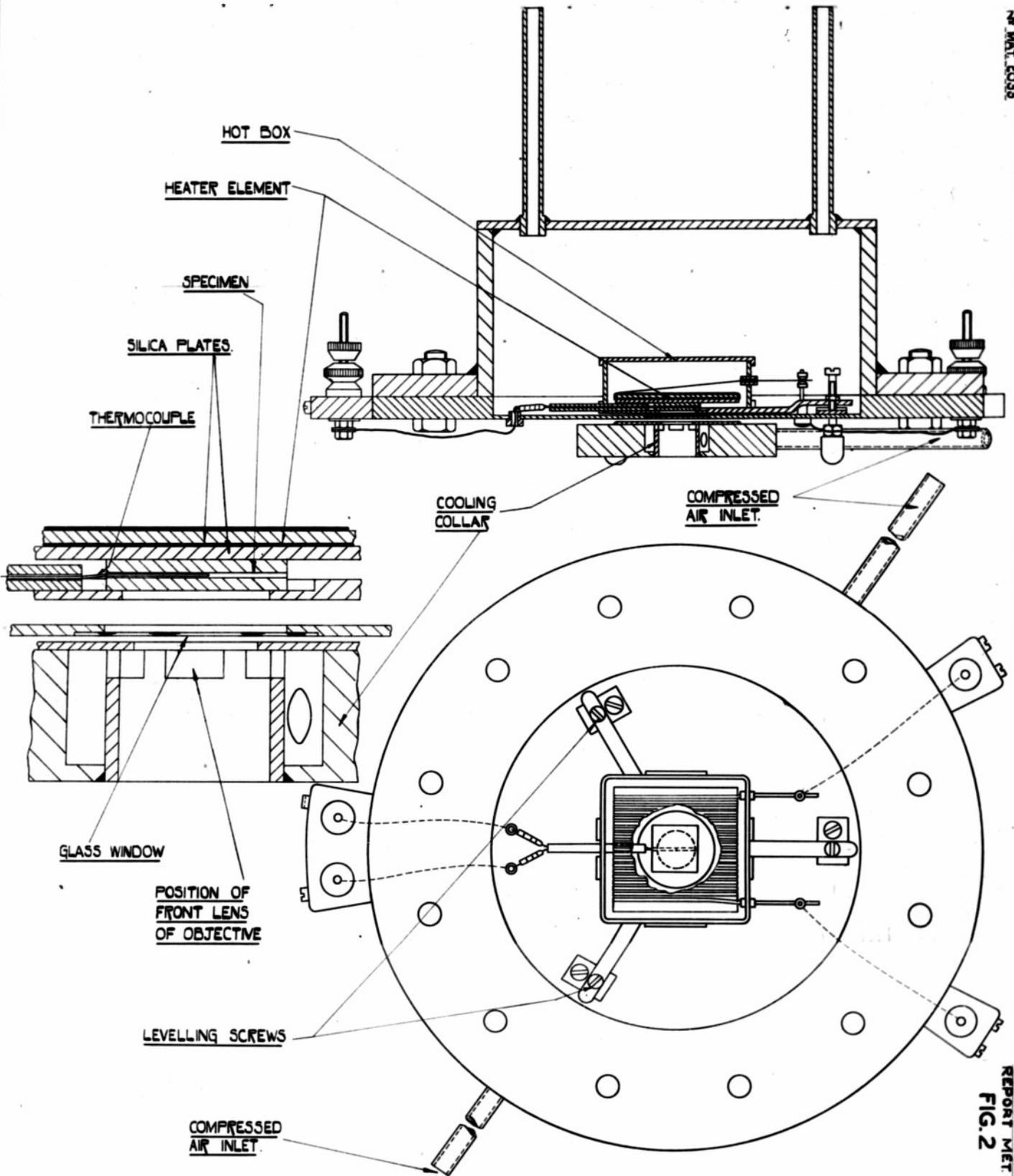
While therefore the formation of grooves increases the area of the metal it does not increase the nett rate of evaporation.

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- 1 International Critical Tables 5:7.
- 2 Steiner. Introduction to Chemical Thermodynamics p.307 (7).
- 3 International Critical Tables 2:458; 5:94.
- 4 Guggenheim. Modern Thermodynamics (Methuen) p.46(213).
- 5 Ditchburn and Gilmore. Review of Modern Physics 13 321 (1941).

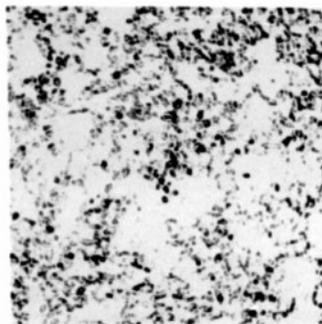


CELL FOR ELECTROLYTIC
POLISHING.

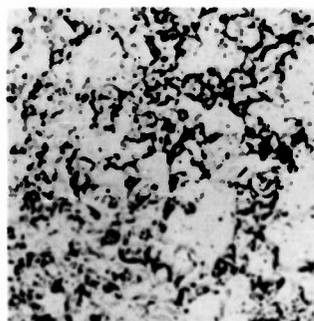


FURNACE FOR HIGH TEMPERATURE MICROSCOPY.

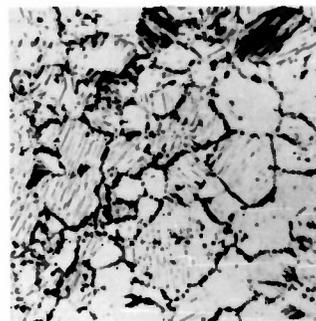
FIG.3.



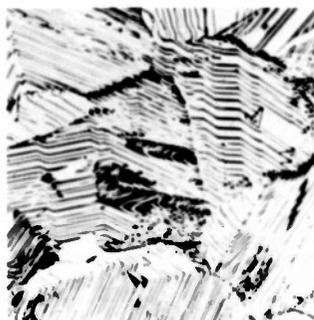
(a) 300° C.



(b) 500° C.



(c) 700° C.



(d) 850° C.



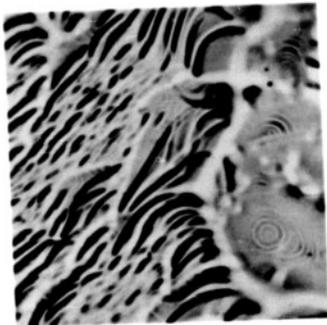
(e) 940° C.

RAE NEG NO 72667 47

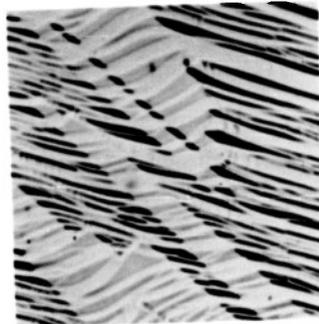
FIG.3. THE EFFECT OF TEMPERATURE ON THE ETCHING
(SILVER HEATED IN AIR FOR 11 HRS. (X 250))

32-

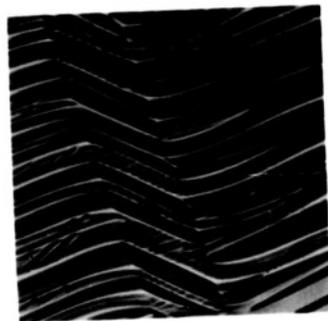
FIG. 4



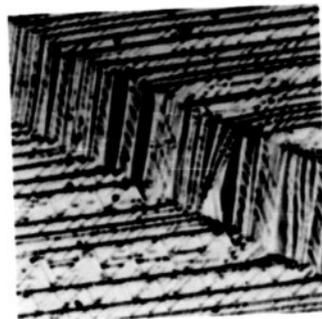
(a) 500° C.



(b) 700° C.



(c) 850° C.



(d) 940° C.

FIG.4. THE EFFECT OF TEMPERATURE ON THE ETCHING
(SILVER HEATED IN AIR 11 HRS. (X 1500))

RAE NEG. NO 72466 97

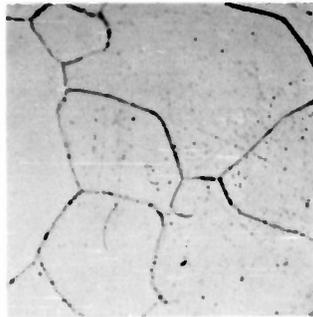
FIG.5



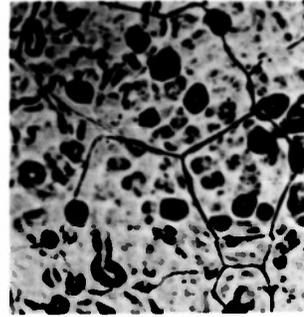
(a) AIR 11HRS.920°C.



(b) OXYGEN. 11HRS.920°C.



(c) NITROGEN. 11HRS.920°C



(d) VACUUM. 1½HRS.920°C.

FIG.5 THE EFFECT OF ATMOSPHERE ON THE ETCHING
(SILVER (X250))

RAE NEG NO 72669 77

FIG 6 & 7

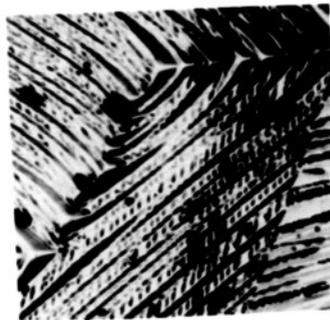
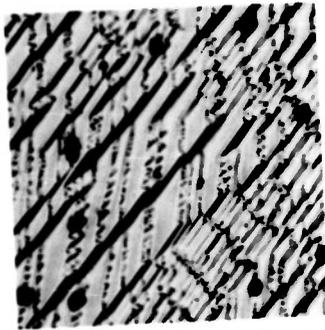
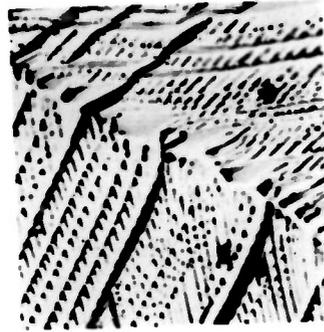
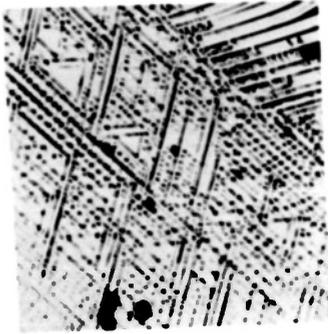


FIG. 6. SILVER HEATED IN OXYGEN
11 HRS. 920° C (X 2,000)



FIG. 7. SILVER HEATED IN AIR
11 HRS. 920° C (X 2,000)

RAE NEG NO 72470-7

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FIG.8 &9

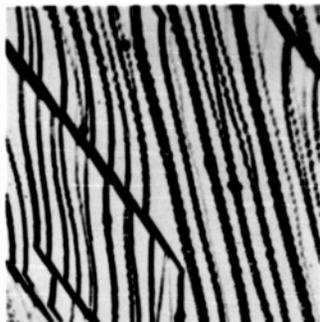


FIG.8. SILVER HEATED IN OXYGEN
17 HRS. 917° C. (X 1,500)

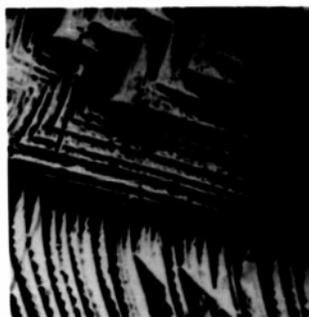
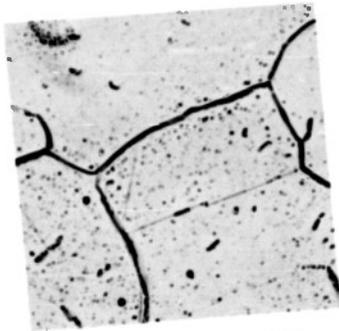


FIG.9. ELECTRON MICROSCOPE REPLICA PHOTOGRAPH
OF SILVER HEATED IN OXYGEN 17 HRS. 917° C. (X 2,500)

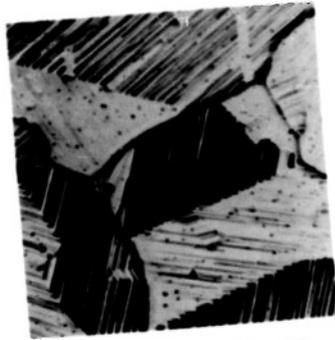
RAE NEG NO 78677-41

35-

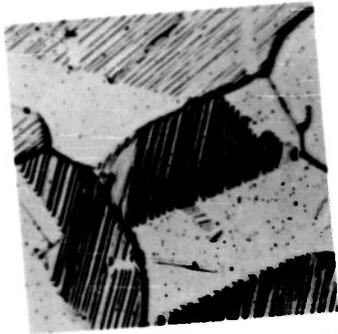
FIG.10.



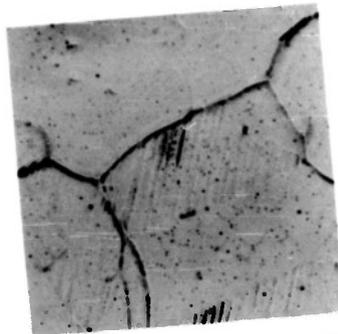
(a) NITROGEN 2 HRS.



(b) (a) AFTER 1 HR. AIR



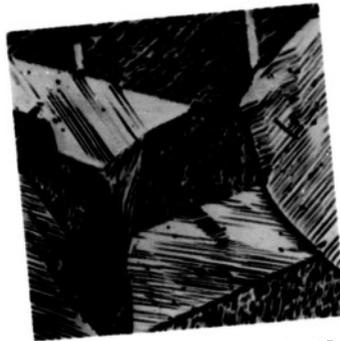
(c) (b) AFTER 1 HR. IN NITROGEN



(d) (c) AFTER 2 HRS. IN NITROGEN



(e) (d) AFTER 8 HRS. IN NITROGEN



(f) (e) AFTER 1 HR. IN AIR

RAE NEG NO 72678 (7)

FIG.10. THE REVERSIBILITY OF STRIATIONS 920° C. (X 250)

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FIG.11 & 12. (a-d)

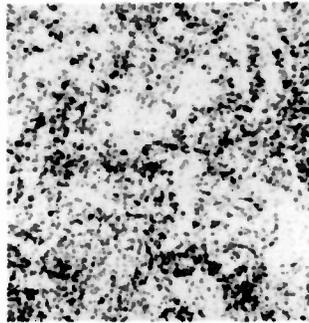
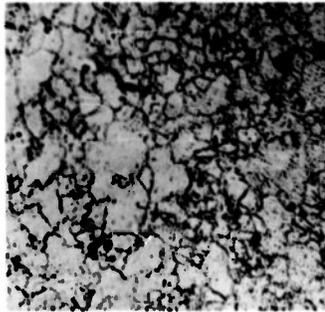
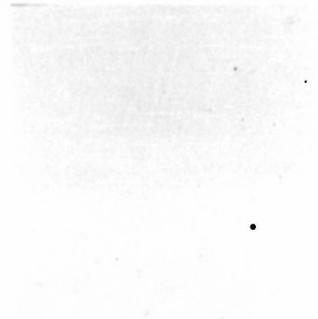
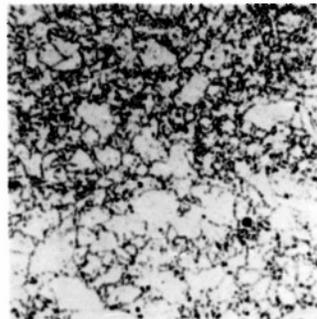


FIG.11. HARD ROLLED SILVER ELECTROLYTICALLY ETCHED
(SILVER (X 100))



(a) ELECTROLYTICALLY POLISHED SURFACE (b) 6 MINS. TEMP. UP TO 575° C.



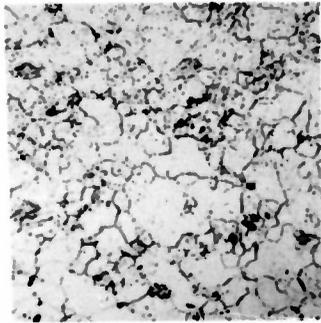
(c) 9 MINS. TEMP. UP TO 670° C. (d) 19 MINS. TEMP. UP TO 850° C.

FIG.12. (a-d) HIGH TEMPERATURE PHOTOMICROGRAPHY
(SILVER (X 100))

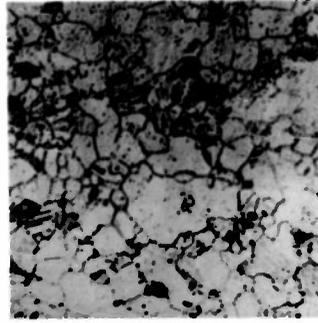
RAE NEG NO. 72079 47

37-

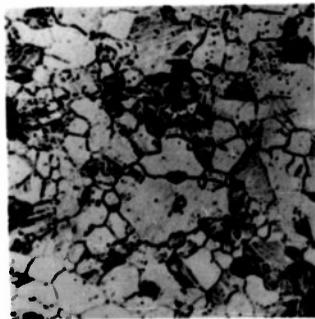
FIG.12. (e-i)



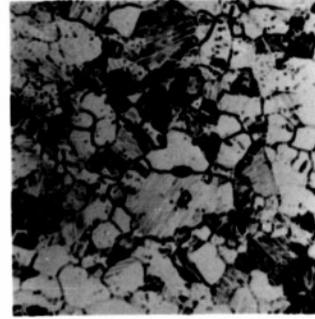
(e) 25 MINS. TEMP. UP TO 900° C.



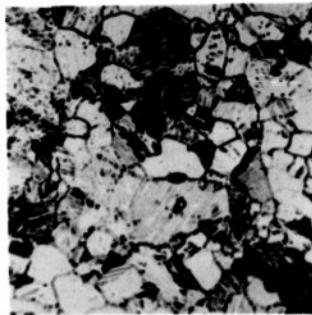
(f) 40 MINS. TEMP. UP TO 917° C.



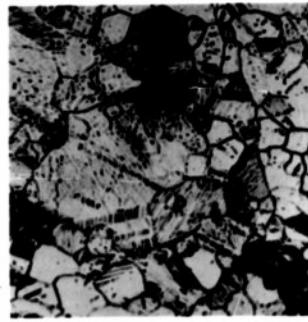
(g) 50 MINS. TEMP. UP TO 927° C.



(h) 60 MINS. TEMP. AT 920° C.



(i) 70 MINS. TEMP. AT 920° C.



(j) 92 MINS. TEMP. AT 920° C.

RAE NEG NO 72474-47

FIG.12. (e-i) HIGH TEMPERATURE PHOTOMICROGRAPHY
(SILVER (X 100))

38-

REEL - C

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A.T.I.

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RESTRICTED

TITLE: The Thermal Etching of Silver

ATI- 9033

AUTHOR(S) : Shuttleworth, R.; King, R.; Chalmers, B.
 ORIG. AGENCY : Royal Aircraft Establishment, Farnborough, Hants
 PUBLISHED BY : (Same)

REVISION

(None)

ORIG. AGENCY NO.

MET-11

PUBLISHING AGENCY NO.

(Same)

DATE	DOC. CLASS.	COUNTRY	LANGUAGE	PAGES	ILLUSTRATIONS
Sept '46	Restr.	Gt. Brit.	English	38	photos, tables, drwgs

ABSTRACT:

Experiments on electrolytically polished silver show that grain boundary grooves form at temperatures as low as 300°C and striations at 500°C in air. Striations only appear in presence of oxygen and are removed by heating in nitrogen. Furnace for high temperature photomicrography is described. Theory is suggested in which equilibrium condition of boundary is groove whose shape is determined by relative magnitudes of free energy per unit area of boundary and surface tensions of crystalline faces meeting boundary in surface of specimen. Striations are caused by formation of those crystalline planes having lowest free energy.

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SUBJECT HEADINGS: Metals, Nonferrous - Surface treatment (61262)

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ATI- 9033

TITLE: The Thermal Etching of Silver

REVISION
(None)

AUTHOR(S) : Shuttleworth, R.; King, R.; Chalmers, B.
ORIG. AGENCY : Royal Aircraft Establishment, Farnborough, Hants
PUBLISHED BY : (Same)

ORIG. AGENCY NO.
MET-11
PUBLISHING AGENCY NO.
(Same)

DATE	DOC. CLASS.	COUNTRY	LANGUAGE	PAGES	ILLUSTRATIONS
Sept '48	Restr.	Gt. Brit.	English	38	photos, tables, drwgs

ABSTRACT:

Experiments on electrolytically polished silver show that grain boundary grooves form at temperatures as low as 300°C and striations at 500°C in air. Striations only appear in presence of oxygen and are removed by heating in nitrogen. Furnace for high temperature photomicrography is described. Theory is suggested in which equilibrium condition of boundary is groove whose shape is determined by relative magnitudes of free energy per unit area of boundary and surface tensions of crystalline faces meeting boundary in surface of specimen. Striations are caused by formation of those crystalline planes having lowest free energy.

EO 10501 5 Nov 53

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DIVISION: Materials (8) 56 11
SECTION: Misc. Non-Ferrous Metals and Alloys (12) 3-3 7

SUBJECT HEADINGS: Metals, Nonferrous - Surface treatment (61262)

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AD#: ADA800697

Date of Search: 15 Oct 2009

Record Summary: AVIA 6/13110

Title: Thermal etching of silver

Availability Open Document, Open Description, Normal Closure before FOI Act: 30 years

Former reference (Department): MET 11

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