Field Emission Microscopy of an Allotropic Transformation: α–β Titanium

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The field emission microscope has been applied to a study of the allotropic transformation in single microcrystals of titanium. Patterns with symmetry characteristic of the high and low temperature phases are presented. Techniques for analyzing the patterns are outlined. Data derived from the pattern analyses give an orientation relation between patterns of the two phases that is consistent with the Burgers relation. The field emission microscope thus constitutes a new method for direct observation of phase changes. At the same time, it offers to the study of allotropic transformations the advantages of high resolution and great magnification that are not available with conventional methods.

INTRODUCTION

THE field emission microscope is uniquely suited to the study of fundamental physical properties of solid materials.[1,2] Its high resolving power, 20 A, and great magnification, 10^6, permit single microcrystal samples less than 10^{-4} cm in diameter to be examined. Its patterns can be used to determine crystal orientation. It is sensitive to surface contaminants in concentrations equivalent to very small fractions of a monomolecular layer.[3] It offers relatively contaminant-free environment: total pressures of chemically active residual gases usually are less than 10^{-11} mm Hg and often as low as 10^{-14} mm Hg.[4] The entire temperature range from the sample melting point down to liquid helium temperatures is readily available for study.[5]

Application of the field emission microscope to a wide variety of problems and materials has been made.[1] Investigations include surface adsorption, desorption, diffusion, and catalysis; crystal structure and growth; and electron emission properties as influenced by crystal plane and contaminant. Materials include W, Mo, Ta, Nb, Pt, V, Ni, Fe, Cu, and Re.[6]

A problem that has not been studied with the field emission microscope is the direct observation of an allotropic transformation. Another type of emission microscopy that uses thermal electrons has had success in detecting phase transformation effects on grain growth in zirconium sheet.[7] However, magnified images of only 100 or so are possible. Observations are limited to a temperature range in which the sample gives thermionic emission. And the orientation of the crystals must be obtained from auxiliary experiments. Other less direct but more widely used techniques for observing phase changes, such as x-ray and electron diffraction, cannot offer the potentially high spatial resolution and magnification of the field emission microscope.[8]

The possibility of studying allotropic transformations in microcrystals with the field emission microscope was explored in the present work. The results show how the field emission microscope can be used to observe phase transformations in crystals of titanium; how a unique orientation relation between the two phases can be demonstrated and how the crystal can be studied in its intermediate forms as it changes phase.[9] A subsequent paper will discuss the crystallographic aspects of these observations in more detail.

EXPERIMENTAL APPARATUS

The field emission microscope used in these experiments is shown schematically in Fig. 1. It is a five-inch

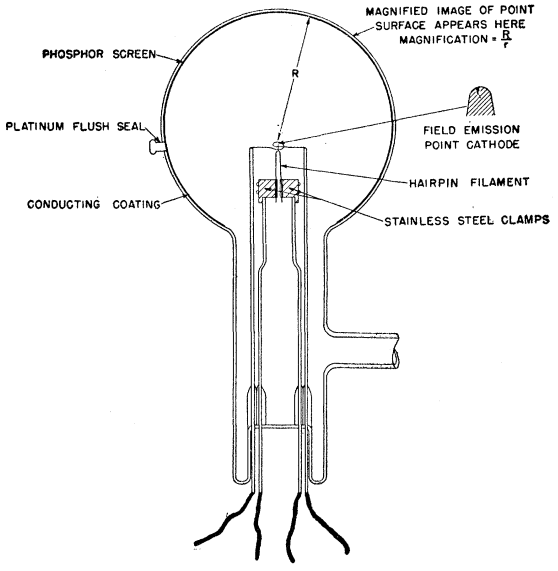


FIG. 1. Experimental field emission microscope in which the effect of phase transformations on the field emission patterns from titanium microcrystals is observed.

[1] E. W. Müller, Ergeb. exakt. Naturwiss. **27**, 290 (1953).
[2] F. Ashworth, Advances in Electronics **3**, 1 (1951).
[3] E. W. Müller, Naturwiss. **37**, 333 (1950).
[4] J. A. Becker, Bell System Tech. J. **30**, 907 (1951).
[5] R. Gomer and J. K. Hulm, J. Am. Chem. Soc. **75**, 4114 (1953).
[6] G. Barnes, Phys. Rev. **97**, 1579 (1955).
[7] W. G. Burgers, *Handbuch der Metallphysik* (Akademische Verlagsgesellschaft, Leipzig, 1935), Vol. III, p. 280.
[8] C. S. Barrett, *Phase Transformations in Solids* (John Wiley and Sons, Inc., New York, 1951), p. 343.
[9] Preliminary discussion of this work has been given. See E. G. Brock and J. E. Taylor, Phys. Rev. **98**, 1169(A) (1955); E. G. Brock, Phys. Rev. **99**, 1651(A) (1955).

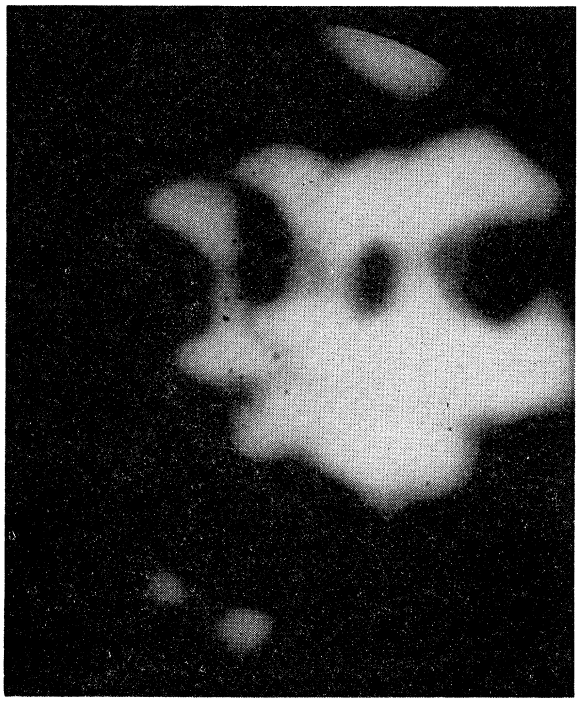


FIG. 2. Typical field emission pattern from titanium crystal that has not been heated above its transformation temperature. Pattern shows no long-range symmetry.

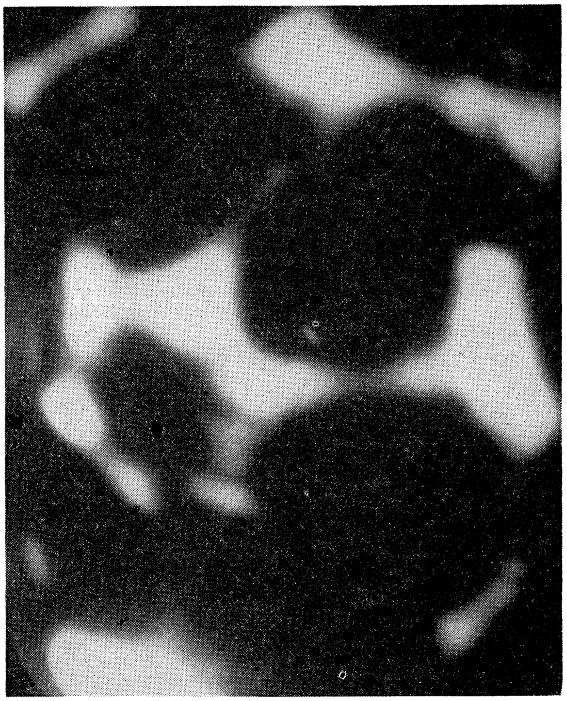


FIG. 3. Field emission pattern from titanium crystal that has been heated above its transformation temperature. Long-range hexagonal symmetry is discernible but imperfect.

diameter spherical Pyrex vacuum tube with a four-lead press. The inner wall of the sphere has a conducting coating which was deposited by the interaction of fuming tin chloride vapor with the glass surface at 500°C. Electrical contact to the outside is made through a platinum flush seal. Willemite phosphor was dusted onto the conducting surface to give a uniform translucent screen. It was held in place with a sprayed binder consisting of 5 drops of phosphoric acid in 75 cc of methyl alcohol and 25 cc of water.

The titanium field emission cathode was mounted on a hairpin filament of 0.010-in. diameter tungsten wire. The hairpin assembly was fastened to the 0.080-in. diameter nickel leads by a pair of stainless steel clamps. This arrangement afforded easy removal and replacement of titanium cathodes. It also permitted the mounting of the cathodes in a modified specimen holder for examination in a Philips Metalix electron microscope between observations in the field emission microscope. The tungsten hairpin supplied heat by conduction to the titanium crystal for both degassing and for phase transformation observations.

The temperature of the crystal was estimated from the temperature-resistance tables of Jones and Langmuir,[10] corrected for lead losses.[11]

Centered about the titanium crystal and mounted on two other nickel leads was a one-turn $\frac{1}{2}$-in. diameter spiral of 0.015-in. diameter tungsten wire. This spiral had two uses. During processing the wire supplied thermal electrons for electron bombardment degassing of the phosphor screens. During operation, the wire could be run at cathode or anode potential or at some intermediate value, so that magnification of the field emission pattern for constant electric field could be varied.

Titanium field emission cathodes were fabricated from an arc-melted ingot of commercially pure sponge titanium.[12] Small bars about 0.060-in. on a side were first cut from the ingot. These were turned uniformly round in a jeweler's lathe and then reduced to 0.010-in. diameter wires by chemical etching in 1 part concentrated hydrofluoric acid and 3 parts concentrated nitric acid by volume. The wires were spot welded to the apex of the tungsten hairpin loop in an atmosphere of helium. After clamping the hairpin filament to the stem leads, the titanium wire was sharpened to form a field emission cathode point of the order of 10^{-5}-cm diameter. This was done by electrochemical etching at 2 to 3 volts ac applied between the titanium wire and a platinum wire in the same reagents used for the chemical etching.

Standard high vacuum procedure[13] was followed in preparing the vacuum tubes for field emission observa-

[10] H. A. Jones and I. Langmuir, Gen. Elec. Rev. **30**, 310 (1927).
[11] Langmuir, MacLane, and Blodgett, Phys. Rev. **35**, 478 (1930).

[12] The titanium was generously supplied by J. B. Newkirk from samples on which measurements reported in reference 17 were made.
[13] S. Dushman, *Scientific Foundations of Vacuum Technique* (John Wiley and Sons, Inc., New York, 1949).

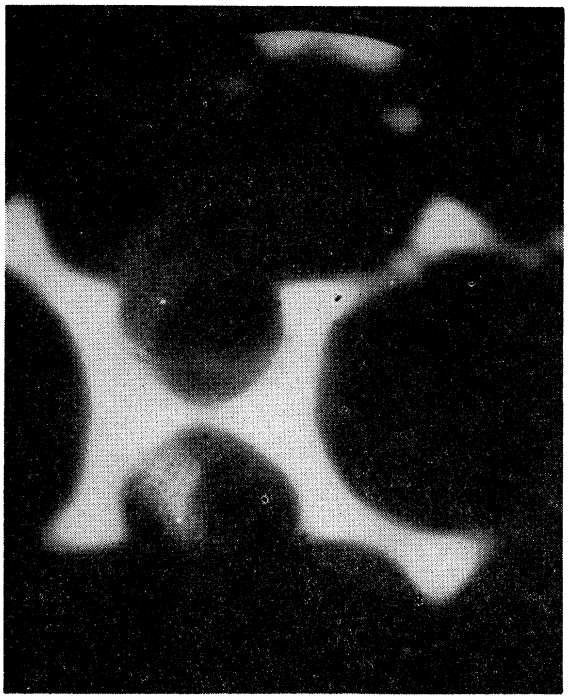


FIG. 4. High-temperature field emission pattern from titanium showing cubic symmetry.

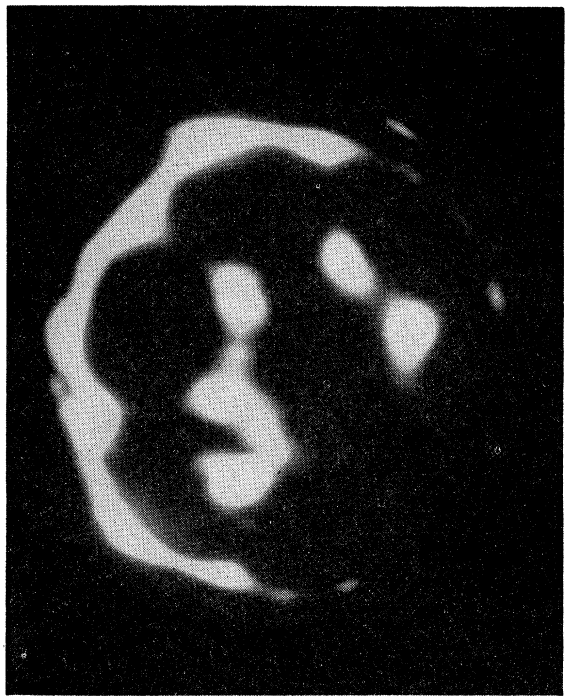


FIG. 5. Low-temperature field emission pattern from a titanium crystal that has been cooled in the presence of an electric field.

tions. The glass parts were baked at 425°C for several hours initially, and rebaked following degassing of all metal parts except for the tungsten filament and titanium cathode. When the residual pressure in the vacuum system had been reduced to 5×10^{-9} mm Hg or less, the hairpin filament was heated gradually to near but not above the transformation temperature of the titanium crystal mounted on it. The pressure was not permitted to exceed 5×10^{-9} mm Hg during this heating process or at any later time when the titanium crystal was hot. Field emission currents were then drawn from the crystal, and most field emission observations were conducted at pressures below 10^{-10} mm Hg on the continuously pumped system.

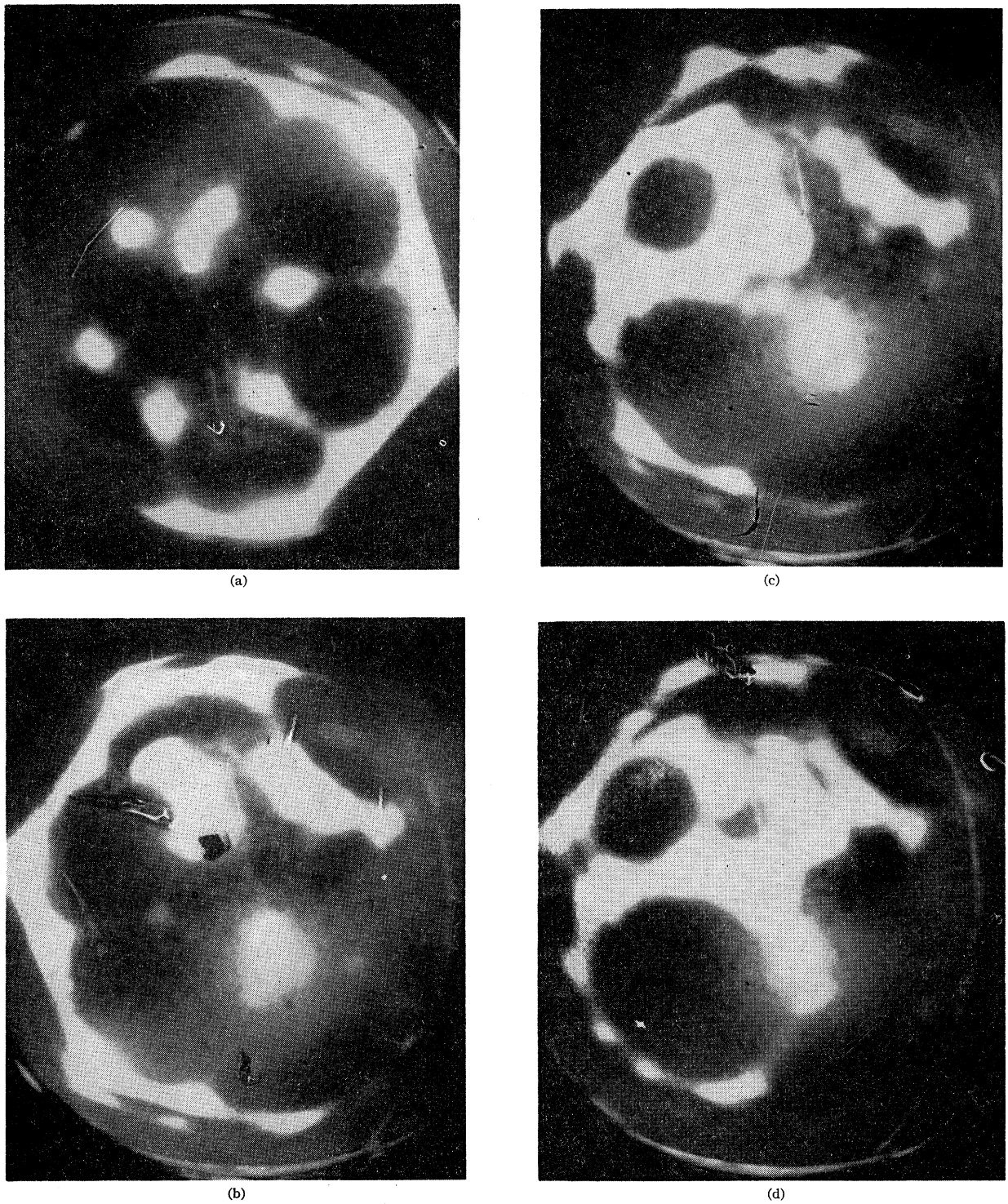
OBSERVATIONS

Field emission patterns from titanium crystals which have not been heated above the transformation temperature usually show some short-range symmetry. Figure 2 is a pattern typical of this early stage of treatment. However, prolonged heating below 850°C for as long as 200 hours in vacuum less than 1×10^{-9} mm Hg produces no improvement in symmetry. Only after a brief heat treatment at 1200°C or above do room-temperature patterns show improved symmetry. Even then the symmetry is imperfect (see Fig. 3).

If the electric field is applied when the crystal is at a temperature above 900°C, a pattern with long range cubic symmetry is observed, Fig. 4. A slow cooling of the crystal through its transformation temperature with the electric field applied often yields patterns such as Fig. 5, where one or more large areas having hexagonal symmetry are discernible. Further annealing, near the transformation temperature in an electric field, improves the symmetry of the pattern.

The hexagonal field emission pattern of Fig. 6(a) was obtained by following these procedures. The photograph of the field emission pattern was taken when the titanium crystal was just below the transformation temperature. Light from the hot supporting filament accounts for the asymmetrically located extra spot near the center of the pattern. The crystal axis coincides very nearly with the (00·1) pole. This is deduced from the fact that the center of sixfold symmetry is near the center of the pattern. Poles of other principal crystallographic planes may be obtained by comparison with an orthographic projection of these poles for the hexagonal-close-packed structure (see Fig. 7).

Upon heating this crystal to a higher temperature, part of the field emission pattern transforms by expansion and contraction of high current density emitting areas. Figures 6(b), 6(c), and 6(d) show a succession of these changes. Finally, at sufficiently high temperatures, patterns like that of Fig. 6(e) appear. This pattern has cubic instead of hexagonal symmetry. Comparison with an orthographic projection of the poles for a body-centered-cubic lattice establishes that the center of the pattern is a {110} pole (see Fig. 8). The other poles of this pattern may be found from their symmetry relations.



(a) (c)

(b) (d)

FIG. 6. Series of patterns for a titanium crystal that was heated through its transformation temperature with electric field applied. (a) Hexagonal pattern from crystal at temperature below 800°C. (b), (c), and (d) Patterns from crystal heated to successively higher temperatures. (e—on opposite page) Cubic pattern from crystal at termperature *circa* 1000°C.

ANALYSIS OF THE FIELD EMISSION PATTERNS

The poles of the field emission patterns were identified with the help of orthographic projections of the poles of the major crystallographic planes of titanium, Figs. 7 and 8. In the case of the hexagonal projection a ratio $c/a=1.587$[14] was used. It was found that the orthographic projection approximated more closely the field electron projection than the stereographic projection. This is so because the electrons, although emitted in a direction normal to the crystal, are accelerated subsequently in the forward direction by the electric field. However, the orthographic projection does not fit the patterns sufficiently well to be used to measure angular distances directly on the patterns.

A field emission pattern is analyzed by projecting its photographic negative with an enlarger onto a sheet of plain paper and drawing the boundaries of the high-intensity-emission areas. The size of the enlarged image is chosen to match the orthographic projections as closely as possible. Lines of symmetry, which correspond to zone lines in the crystal, are then sketched on the reproductions of the patterns. By using these zone lines and the orthographic projections the poles of Figs. 6(a) and 6(e) were located on their corresponding reproductions, Figs. 9 and 10.

Since each point on a field emission cathode surface corresponds uniquely to a point on its field emission pattern, the field emission patterns of Figs. 6(a) and 6(e), for example, may be used to map the poles of one phase onto the poles of the second phase. To make such a map, the crystal and the camera must remain fixed relative to the field emission vacuum tube. Frequently, however, transforming titanium crystals have been observed to move through large angles. In the case of the patterns of Figs. 6(a) and 6(e), the outline of the vacuum tube exactly matched when the two photographic negatives were placed one on top of the other, showing that the camera did not change position. Also, the boundaries of the field emission patterns matched when the two negatives were placed one on top of the other, showing that the crystal did not move.

To obtain the orientation relation between the two crystal phases from the field emission patterns, the tracings of the patterns, Figs. 9 and 10, with poles and zone lines drawn in, may be superimposed; or, the angular separations of the various poles may be estimated from the two reproductions and plotted on a single orthographic projection. This has been done in Fig. 11.

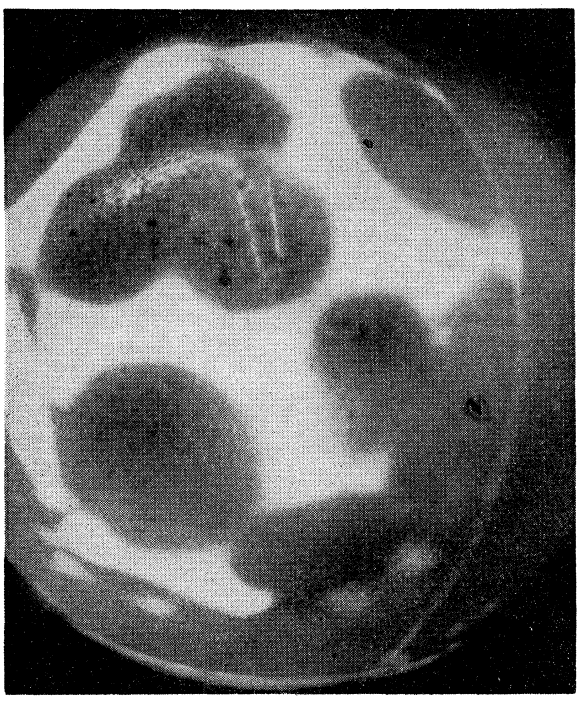


FIG. 6(e). Figs. 6(a)-(d) on opposite page.

[14] H. T. Clark, J. Metals **185**, 588 (1949).

DISCUSSION

Results of the analysis of the titanium field emission patterns are interpretable in terms of the crystal properties of titanium. Titanium is a hexagonal-close-packed metal at room temperature. This alpha phase changes to a body-centered-cubic beta phase at 882°C.[15] Crystallographically, titanium is similar to zirconium. Generally, the relative orientation of the two crystal forms has been assumed to be the same as reported for zirconium.[16] Recent x-ray diffraction analyses of single-crystal hexagonal grains descended from a parent cubic crystal[17–19] have demonstrated that titanium obeys the zirconium orientation relation, namely:

- a $\{00\cdot1\}_\alpha$ hexagonal plane parallel to a $\{110\}_\beta$ cubic plane
- a $\langle11\cdot0\rangle_\alpha$ hexagonal direction parallel to a $\{111\}_\beta$ cubic direction.

Accordingly, a transformation scheme proposed originally by Burgers[16] for zirconium may apply to titanium.

This transformation scheme is illustrated by Fig. 12. In the upper left is a unit cell of the high-temperature body-centered-cubic beta form of titanium. The horizontal plane is a {110} plane. Four more unit cells may be combined to give a body-centered-tetragonal cell outlined with heavy lines. This cell is bounded laterally by {211} planes and on the ends by {110} planes. As the titanium crystal cools, the atoms move to new locations. The rearrangement process can be represented as a shear between {211} planes in a ⟨111⟩ direction. When

[15] C. J. Smithells, *Metals Reference Handbook* (Interscience Publishers, Inc., New York, 1949).
[16] W. G. Burgers, Physica **1**, 561 (1933–34).
[17] J. B. Newkirk, Acta Met. **1**, 370 (1953).
[18] Williams, Cahn, and Barrett, Acta Met. **2**, 117 (1954).
[19] C. J. McHargue, Acta Cryst. **6**, 529 (1953).

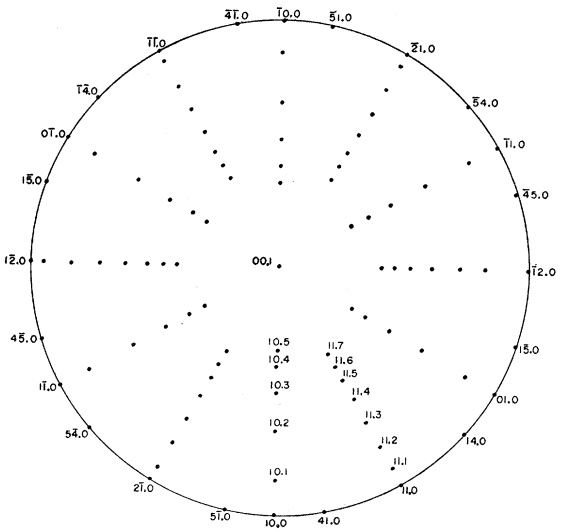


FIG. 7. (00·1) orthographic projection of poles of some major crystallographic planes of the hexagonal-close-packed phase in titanium. $c/a=1.587$.

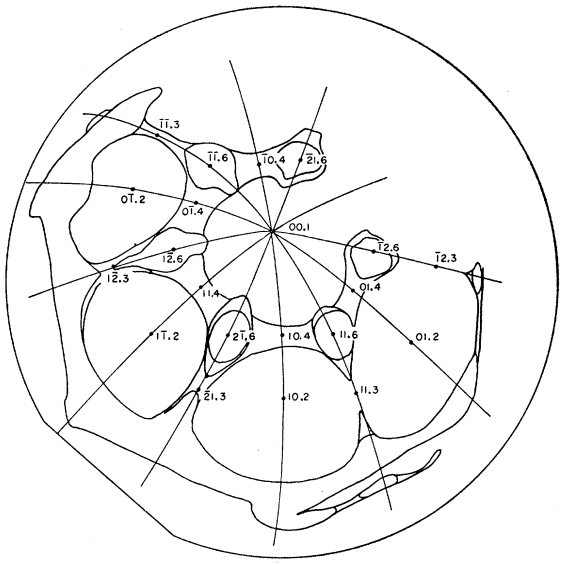


FIG. 9. Location of major crystallographic planes and zones of Fig. 6(a).

the transformation is complete, a unit hexagonal-close-packed alpha cell of the low-temperature phase of titanium results. Two modes of shear are illustrated in Fig. 12. The six-sided lattice cylinder in the lower left may be formed from three of these unit cells. If the crystal structure of titanium determines the symmetry of its field emission patterns, then the patterns from a transforming crystal should be consistent with the Burgers transformation scheme.

A discussion of field emission patterns, however, must recognize the influence of crystal structure and also the effects of surface contaminants and surface morphology on the appearance of the patterns. The generally accepted criterion for a clean metal field emission pattern is that the emission current density should vary gradually with crystal direction. The titanium patterns reported here do not have this characteristic.

Possibly the titanium surface was contaminated. Contaminated surfaces of other metal emitters frequently give patterns with sharply defined light and dark areas. The gas contaminants in the present experiments were those that constitute the residual pressure of 10^{-9} mm Hg or less in the field emission tube. Ion-

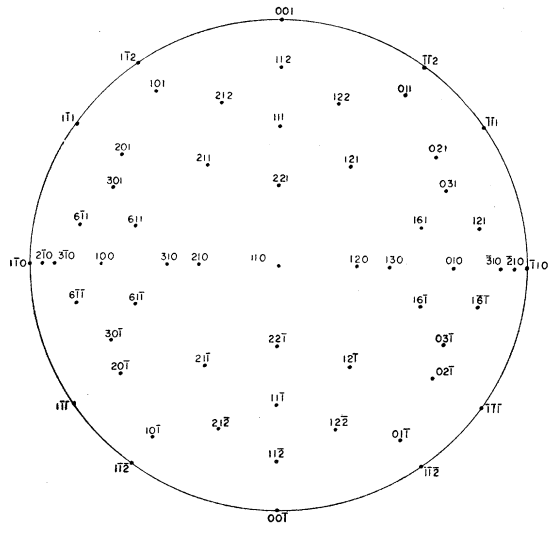


FIG. 8. (110) orthographic projection of poles of some major crystallographic planes of the body-centered-cubic phase in titanium.

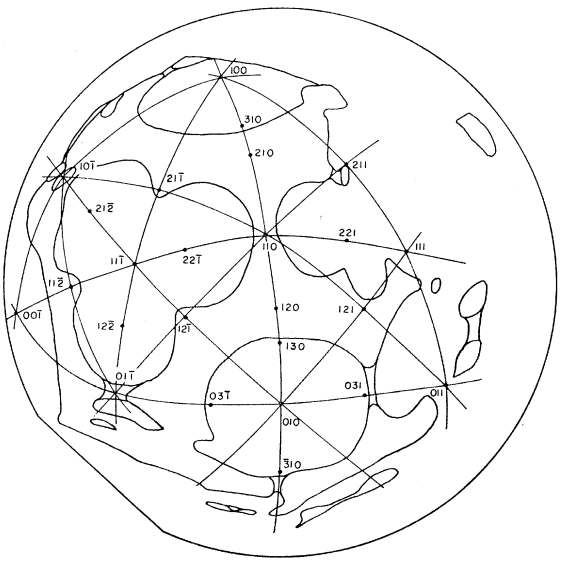


FIG. 10. Location of major crystallographic planes and zones of Fig. 6(e).

resonance mass spectrometer[20] measurements showed that N_2 was the main constituent. At the temperatures where the field emission patterns were photographed, nitrogen diffuses into the metal lattice.[21] Volume sorption together with the low partial pressures of contaminants make a contaminated titanium surface unlikely.[22]

An alternate possibility is that the titanium surface was not smooth but faceted. Tungsten field emission cathodes, when heated in the presence of an electric field to a temperature sufficient for surface migration to occur, give patterns which are attributed to the formation of edges and facets on the cathode. The intersecting boundaries of such facets are regions of smaller radii of curvature than the radius of the emitter tip. The resulting local field enhancement causes increased emission current density from those regions. In the limit, an emitter surface bounded by a few well-developed flat crystal planes would give a field emission pattern consisting of areas of low current density outlined sharply with boundaries of high current density. Since the titanium cathodes were heated while field emission current was being drawn, it is quite likely that they developed facets. Thus, facets could account for the abrupt variation of current density over the field emission pattern. They could account also for the hexagonal-shaped border which persists from the low temperature to the high temperature patterns [see Figs. 6(a) and 6(e)].

The assignment of poles to the high-temperature pattern of Fig. 6(e) or Fig. 10 could be made unambiguously. The symmetry was sufficient to determine the crystal orientation. However, the low-temperature pattern, Fig. 6(a) or Fig. 9, cannot be identified so easily. By using the argument that low-index planes generally are planes of low electron emission,[23] two sets of lines can be found each of which passes through centers of large nonemitting regions on the pattern. Their common point of intersection, of course, is a (00·1) pole. One set corresponds to the trigonal axes in the basal plane and the other set is rotated from it by 30° about the (00·1) pole. A choice between the two sets arrived at by correlating low emission planes with low index planes cannot be made conclusively. One set does meet the requirements of Burgers' orientation relation. This set was chosen as a basis for the assignment of poles to the hexagonal pattern.

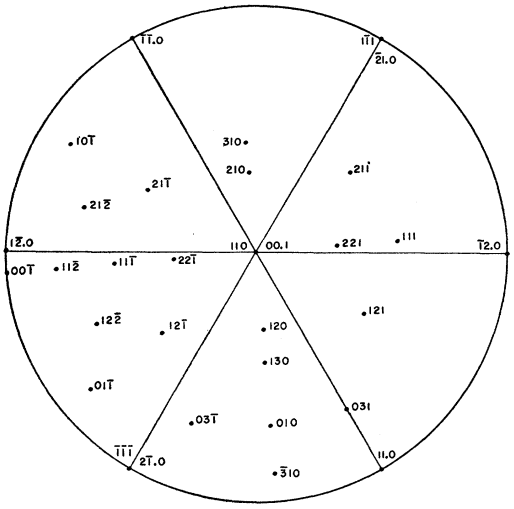


FIG. 11. Composite plot of the poles of the major crystallographic planes of the body-centered-cubic pattern identified in Fig. 10 with the trigonal axes found for the hexagonal-close-packed pattern of Fig. 9. The Burgers orientation relation is obeyed.

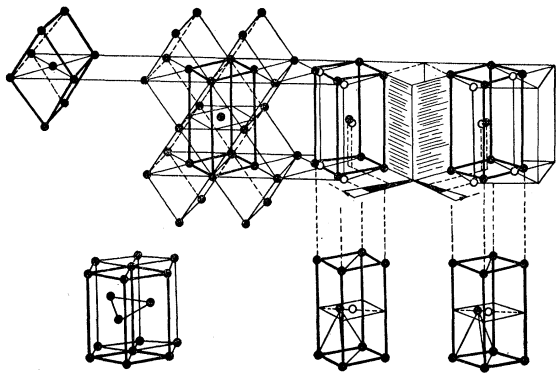


FIG. 12. Burgers' transformation scheme for titanium produces the required orientation relation between high-temperature body-centered-cubic beta phase and low-temperature hexagonal-close-packed alpha phase.

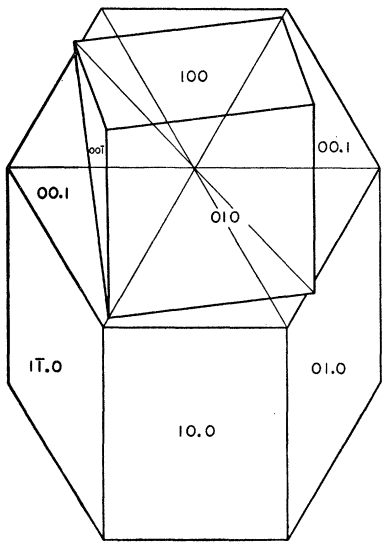


FIG. 13. Illustration of the orientation relation shown in Fig. 11 between the cubic and hexagonal phases of the titanium crystal that gave the series of field emission patterns Figs. 6(a) through 6(e).

[20] D. Alpert and R. S. Buritz, J. Appl. Phys. **25**, 202 (1954).
[21] E. A. Gulbransen and K. Andrew, J. Metals **185**, 741 (1949).
[22] See reference 1, p. 310.
[23] M. K. Wilkinson, J. Appl. Phys. **24**, 1203 (1953).

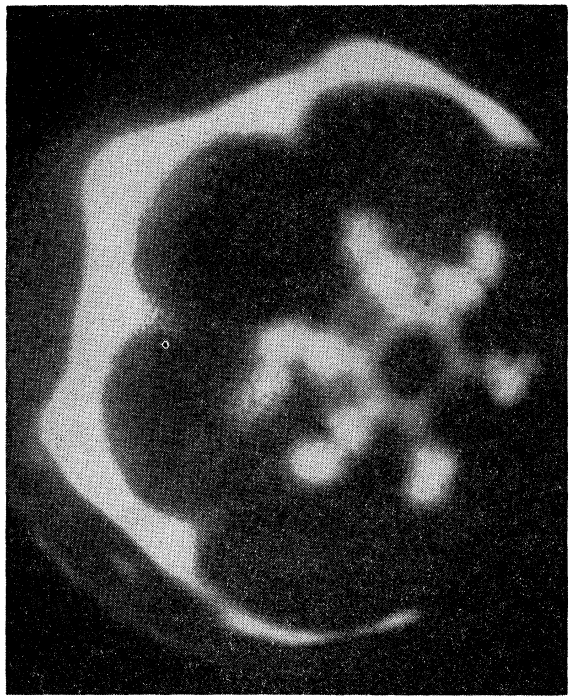


FIG. 14. Field emission pattern from crystal that gave the patterns in Figs. 6(a) through 6(e) taken after crystal was returned from high temperature to room temperature. The original orientation and single crystal are preserved.

Within the accuracy to which the poles could be assigned, the analysis of the patterns shows that the $(00\cdot1)_\alpha$ pole became a $\{110\}_\beta$ pole when the crystal transformed. Furthermore, the positions of the 110 and 100 zone lines in the beta phase relative to the hexagonal axes in the alpha phase are such as to make a $\langle 11\cdot0\rangle_\alpha$ direction lie parallel to a $\langle 111\rangle_\beta$ direction. The relative orientation of the two phases was as shown in Fig. 13. These relationships meet the requirements of the Burgers orientation relation.

The remaining patterns shown in Figs. 6(b) through 6(d) can be interpreted as intermediate stages in the transformation process. At present, the effect of surface morphology on the patterns cannot be separated from the effect of transforming crystal structure. Possibly the patterns are a direct measure of the rate of transformation of the crystal. On the other hand, because of the influence of the electric field, the changes in the patterns may measure only the rate of change in physical shape of the surface. These latter changes could lag considerably the actual transformation of the bulk crystal. That the surface morphology can assume ultimately a symmetry consistent with the symmetry of the underlying crystal may be concluded from the initial and final patterns of this sequence, Figs. 6(a) and 6(e).

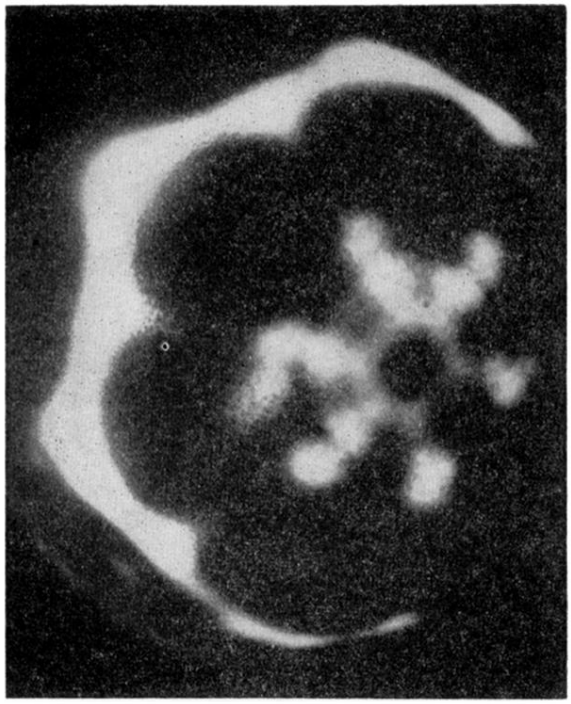
It is interesting to note that these patterns show one alpha crystal of titanium can transform to one beta crystal. Subsequently, the crystal was returned to room temperature, and the pattern in Fig. 14 was photographed. This pattern has the identical orientation of the initial hexagonal pattern. The transformation sequence illustrated by Figs. 6(a), 6(e), and 14 demonstrates that a crystal need not break up into several crystals when it changes phase. Furthermore, it shows that a crystal may return to its original orientation after changing phase, even though other orientations are allowed by the orientation relation.[17,18]

CONCLUSIONS

Phase transformations in single microcrystals can be observed with the field emission microscope. Field emission patterns from titanium crystals in both the low temperature alpha and the high temperature beta phase have been obtained. A comparison of patterns from one crystal which at different times had been in both phases demonstrates the existence of a definite orientation relation between the two phases of titanium. This relation agrees with the Burgers relation. In the intepretation of these field emission patterns, possible effects of surface morphology and surface contaminants must be considered. With these precautions, the study of phase transformations in solids appears to be a feasible extension of field emission microscopy.

ACKNOWLEDGMENTS

The author would like to acknowledge several valuable discussions held with Dr. D. Turnbull, Dr. J. B. Newkirk, and Dr. J. E. Taylor. The work was initiated with Dr. J. E. Taylor.



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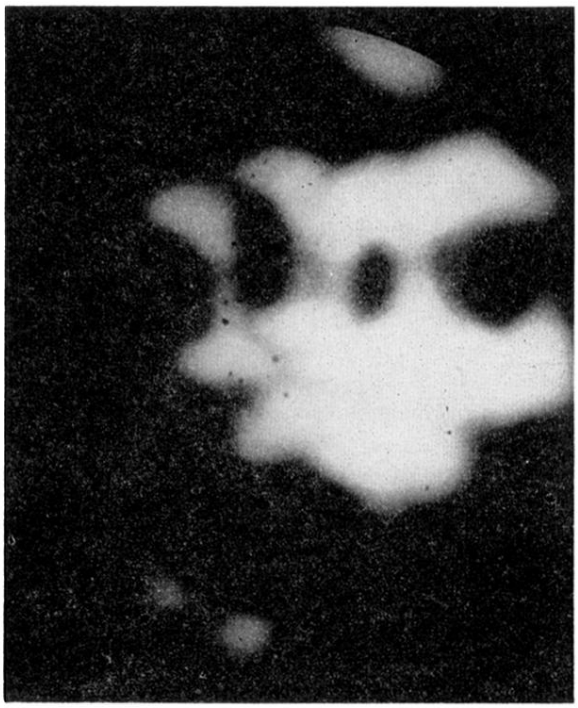

FIG. 2. Typical field emission pattern from titanium crystal that has not been heated above its transformation temperature. Pattern shows no long-range symmetry.

FIG. 3. Field emission pattern from titanium crystal that has been heated above its transformation temperature. Long-range hexagonal symmetry is discernible but imperfect.

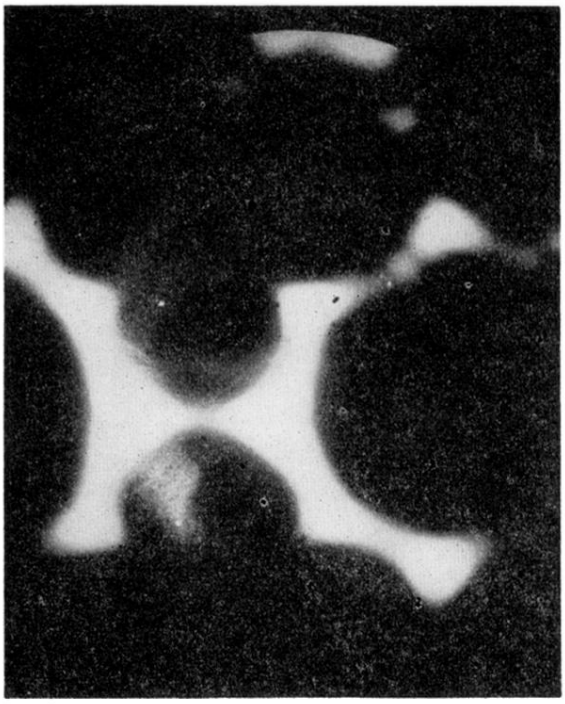

FIG. 4. High-temperature field emission pattern from titanium showing cubic symmetry.

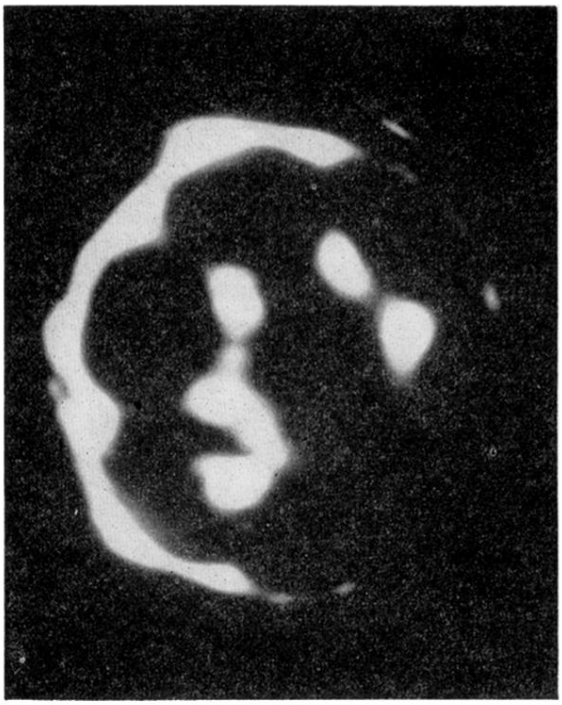

FIG. 5. Low-temperature field emission pattern from a titanium crystal that has been cooled in the presence of an electric field.

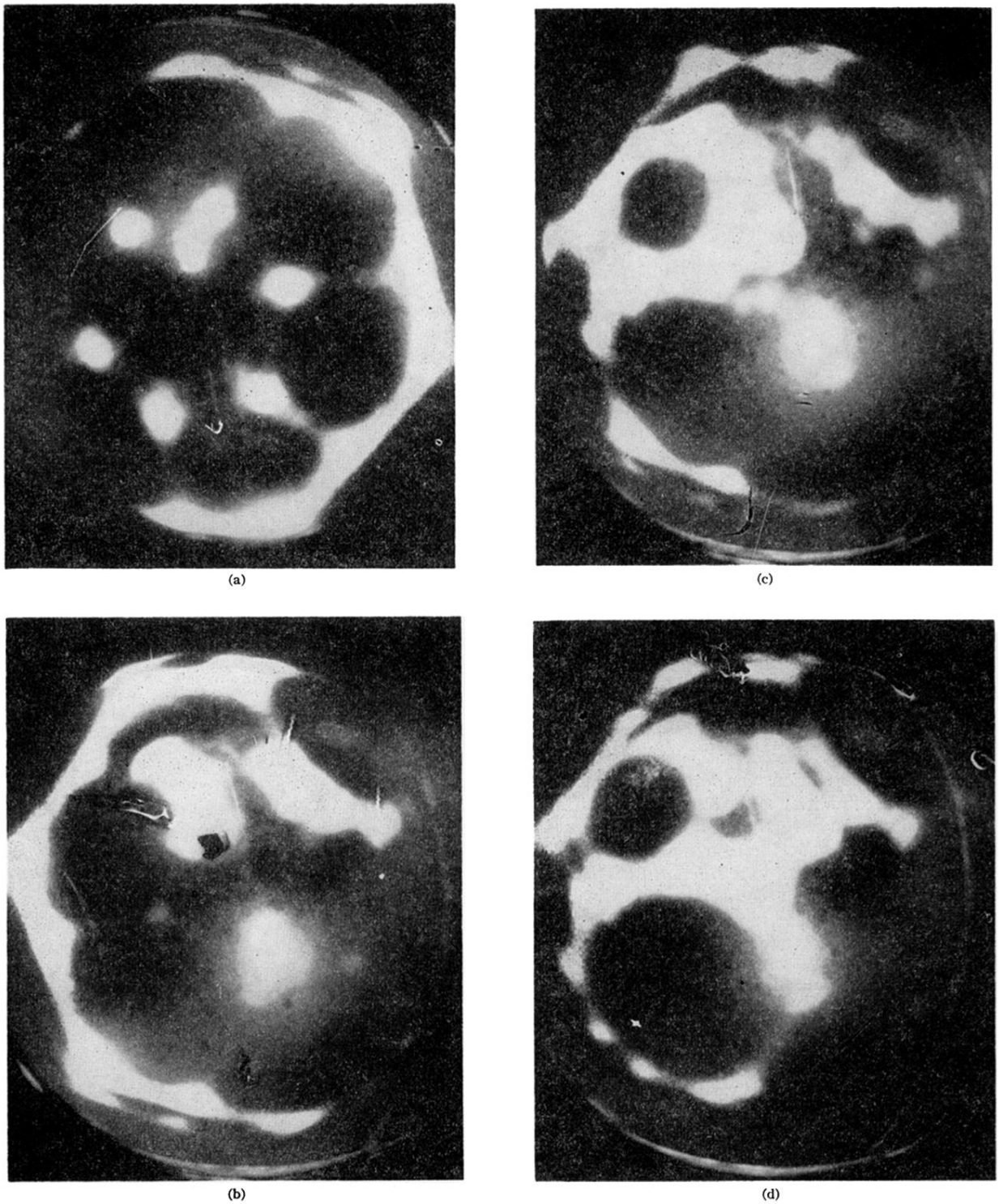

FIG. 6. Series of patterns for a titanium crystal that was heated through its transformation temperature with electric field applied. (a) Hexagonal pattern from crystal at temperature below 800°C. (b), (c), and (d) Patterns from crystal heated to successively higher temperatures. (e—on opposite page) Cubic pattern from crystal at termperature *circa* 1000°C.

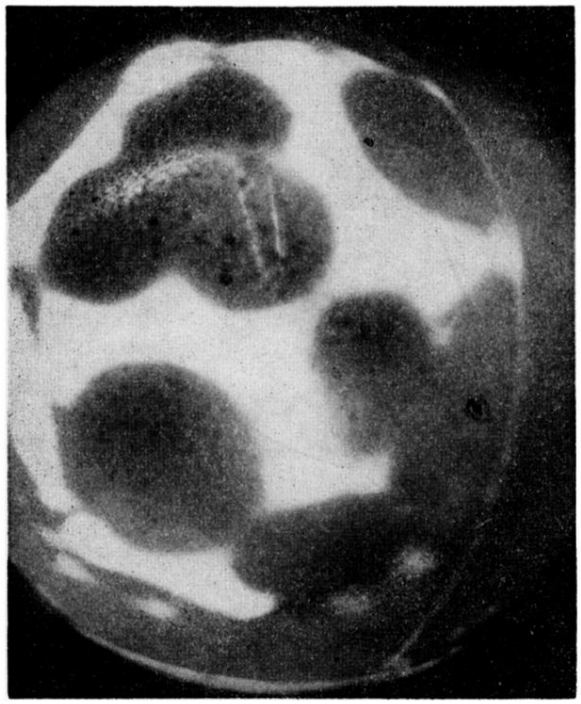

FIG. 6(e). Figs. 6(a)-(d) on opposite page.