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Observation of Magnetic Domains by Means of the Bitter Colloid Method

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TECHNICAL DOCUMENTARY REPORT NO. ASD-TDR-63-83

March 1963

Directorate of Materials and Processes
Aeronautical Systems Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

Project No. 7371, Task No. 737103

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28-701C, 400, 5-21-63

FOREWORD

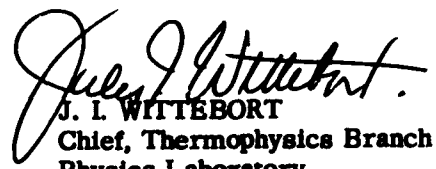
This work was part of the in-house research of the Electronic and Magnetic Materials Section, Physics Laboratory, under Project No. 7371, "Applied Research in Electrical, Electronic, and Magnetic Materials," Task No. 737103, "Applied Research on Magnetic Materials." The work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. Robert J. Patton and Karl J. Strnat were the project engineers who did the research.

This report covers work from Oct 1961 to June 1962.

ABSTRACT

Experimental equipment has been developed for the light-microscopic observation of ferromagnetic domains by means of the Bitter technique. The design of an electromagnet-microscope stage which can accommodate both bulk samples and thin sheet strips is described. The formula for the preparation of the colloidal iron-oxide solution is given. Photographs of domains on silicon-iron transformer sheet illustrate the quality of the pictures and the resolution which can be obtained with the set-up.

This report has been reviewed and is approved.



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INTRODUCTION

Ferromagnetic Domains

A ferromagnetic material below its Curie point normally consists of a large number of small regions, the so-called magnetic domains, each of which is magnetized to the same value of the "spontaneous magnetization," M_s. The direction of the magnetization differs from domain to domain, however, and in the demagnetized state the magnetic moments of all regions cancel out to a resultant moment of zero for the entire sample. Upon application of a magnetizing field, domains having their magnetization near the field direction grow at the expense of their less favorably oriented neighbors - thus shifting walls between domains and altering the pattern. As the field is increased, these wall motions are followed by a rotation of the magnetization vectors in all domains closer to the direction of the field. By the latter process, the domain walls eventually disappear and, at saturation, the sample is ideally one large, single domain.

This picture was first put forth as a hypothesis by P. Weiss in 1907 (ref 1) and later refined by many other workers. For a recent survey see article by H. J. Williams and R. C. Sherwood (ref 2).

Bitter Patterns

This domain structure could be made visible for the first time more than 20 years after it was postulated by P. Weiss. Independent of each other, F. Bitter (ref 3) and L. von Hamos and P. Thiessen (ref 4) developed essentially the same technique which is described in the following paragraphs.

A drop of a colloidal suspension of iron oxide in a liquid is placed on a polished surface of a specimen. The fine ferrimagnetic particles are attracted to the domain boundaries by the strongly inhomogeneous stray fields which exist there and form a pattern which can be observed under a microscope. Particles will also accumulate on grain and phase boundaries, voids in the sample, or on surface scratches - generally, around everything that disturbs the uniformity of the magnetic flux near the surface. These irregularities will not move when the magnetic field is changed, but the domain boundaries will.

The patterns thus obtained represent, of course, only the surface structure. Special precautions are necessary to make sure that the patterns are really characteristic of the magnetic domain structure existing at the same depth underneath the surface. On specimens which have been mechanically polished, misleading "maze-patterns" can often be observed (figure 1). These have been attributed to strains in the surface layer or to systems of microscopic scratches, brought about by the polishing, which lie preferentially in certain crystallographic directions (refs 5 and 6). Also, a thin layer of amorphous material can be produced by heavy polishing which masks the crystal structure and, hence, the magnetic structure underneath. Properly conducted electrolytic polishing removes the deformed surface layer and permits observation of the true magnetic domain arrangement.

Manuscript released by the authors 10 January 1963 for publication as an ASD Technical Documentary Report.

Application of the Bitter Technique in this Laboratory

The experiments described in this report were undertaken to support two research programs: A study of the magnetic properties of rare earth intermetallic compounds and an investigation of ferromagnetic thin films. In the latter, the Bitter technique will be used as an alternative to magnetooptic techniques (ref 6) for observing the domain structures of thin metal films on which magnetooptic constants are to be measured and correlated with magnetic data. On specimens of rare earth alloys we expect to use the technique to see domains and also to distinguish phases with different magnetic properties. This application is based on the fact that, at least in a specimen magnetized perpendicular to the surface, the colloidal particles will accumulate in greater density over regions that are more strongly ferromagnetic than adjacent areas of a metallurgical section.

THE APPARATUS

Preliminary Experiments

In our first attempts to observe domain patterns on specimens of transformer sheet steel, the sample was simply placed on the stage of an upright metallurgical microscope* and magnetized with a permanent magnet mounted underneath. The magnet was moved to change the field strength (which could, of course, not be quantitatively determined in this case). A very inconvenient feature of this arrangement was that, when the field was changed, the magnetic forces deformed the stage slightly and moved the sample sufficiently to bring the domain pattern out of focus.

To remedy this, a small but heavy electromagnet was built which took the place of the normal microscope stage. This was still unsatisfactory because the pole pieces moved slightly when the field was altered. The final solution was to make the stage completely rigid by means of soldered-in copper spacers.

The colloidal solution used successfully in our early experiments was obtained from Dr. K. Kronenberg of the Indiana General Corporation. The solution later coagulated and we had to make our own by using the recipe given in appendix A.

Magnet and Sample Holder Design

Figure 2 is a photograph of the final version of the electromagnet. The geometry is such that the "stage" which holds the specimen slides under the microscope objective while the energizing coil is in a place where it will not interfere with the microscope. The coil consists of 4200 turns of No. 25 AWG enameled copper wire wound on a Plexiglas form. The magnet core is made of mild carbon steel. To ensure rigidity, a heavy copper block was sweated between the two long legs of the yoke. Two different specimen support stages were built. They can be interchanged and secured to the yoke such that good and reproducible magnetic contact is obtained. Both magnetize the sample parallel to its surface (transversely to the optic axis of the microscope) in the center where the patterns are observed.

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* American Optical Co., Research Microscope Model No. C5LX-OA.

Stage A (see figure 2) is for use with thin sheet or film specimens. The pole pieces are spaced rigidly by a soldered-in copper block. The top of the center portion (copper block and ends of pole pieces) is ground flat and well polished. If the best magnetic contact with sheet samples is desired, the underside of the specimen must also be polished. With thin film samples on a nonmagnetic substrate (such as a glass microscope slide) there will, of course, always be the gap introduced by the thickness of the substrate. This reduces the maximum magnetizing field which can be reached, but also eliminates any noticeable effect of the remanence of the steel yoke. For massive samples in good contact with the pole caps, these remanence effects can normally not be neglected.

Stage B (see sketch fig 3) is used with bulk samples. The poles pieces have polished faces normal to their axis. Their distance can be adjusted to the sample length up to $1\frac{1}{4}$ in. The specimens should have a cross-section not too different from that of the magnet's poles ($\frac{15}{16}$ in. diameter). For best magnetic contact, the sample should have two flat faces, mutually parallel and normal to the side on which the pattern is to be observed.

The Electrical Circuit

Figure 4 shows schematically the magnet's power circuit. The D. C. power supply, P. S., is variable between 0 and 28 V with a built-in wire-wound potentiometer. This control is used to adjust the maximum field needed in the experiment. (The steps are too coarse to use this potentiometer exclusively in traversing a magnetization curve.) The coil current is reduced to roughly the needed value by means of the rheostat R1; fine adjustment is done with the stepless resistor, R2. These resistors, the reversal switch R.S., and the switch S bridging R1 plus R2, permit adjustment of the field to most points on the hysteresis loop and stepless scanning of portions of it; also, the reproduction of the same gross magnetic state of the sample by the procedure outlined in appendix B.

MICROSCOPIC OBSERVATION OF DOMAIN PATTERNS

The Microscope

The magnet described before was used in combination with, both, an American Optical Company research microscope in this laboratory (identified by footnote earlier) and a Zeiss microscope* (located in the Technical Photographic Division at Wright-Patterson AFB). Figures 5 and 6 are photographs of the two microscopes with the magnetic stage in place. The Zeiss instrument has considerably better resolution and is equipped for convenient and rapid photographic recording. The photomicrographs (described next) were obtained with it.

Sample Preparation

The following is a description of the procedure used in preparing the transformer sheet steel samples on which the photomicrographs, figures 7 through 10, were taken. The technique will vary with the material to be studied. However, it can be expected that for all iron-rich alloys a procedure similar to the one described will be successful.

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* Zeiss Ultraphot II camera microscope

Rectangular specimens of the dimensions 0.7 cm wide and 2.5 cm long were cut off the sheet, ground flat, and moderately polished on one side. Then they were carefully mounted in the fashion standard for metallographic samples, i.e., with the unpolished surface exposed. This surface was given a careful mechanical polish. The sample was then removed from the mount and electro-polished in a bath of concentrated phosphoric acid with 15 percent chromic acid added. During polishing the etching current was held constant at 10 amperes for a period of one minute. Since a good deal of heat is generated by this process, it is advisable to water cool the etchant. Current densities at the surface of the sample ranged from 2.8 to 6 amp/cm^2 depending on the sample size and whether or not both surfaces of the sample were etched simultaneously.

For the microscopic observation, the sample was laid across the pole caps of stage A (described earlier), a drop of the colloidal solution applied on the electrically polished surface and covered with an extra-thin microscope cover glass.

Discussion of Bitter Patterns

To familiarize the investigator with the Bitter technique and to explore the possibilities and limitations of the apparatus, several specimens were prepared of commercial, poly-crystalline, silicon-iron transformer sheet of unknown history. In a number of locations on the samples, sequences of domain patterns were photographed while the magnetic field was varied in steps through the range in which the major changes in the pattern occurred. As expected for poly-crystalline samples of this kind, the patterns are quite complex and do not lend themselves to an easy interpretation. The following pictures are therefore intended primarily to show the appearance of Bitter patterns and the contrast and resolution which were obtained.

Figures 7 and 8 represent a fairly uncomplicated region of the sample. In figure 7, which was taken at low field strength, spike-like domains are visible in the lower center and along the left margin. The spikes, particularly those in the middle, appear uniformly darker than their surroundings. This indicates that the component of the magnetization normal to the surface is larger in the spike domains than in the adjacent regions and resulting in a layer of surface poles. Immediately above this layer the product of field and field gradient is high and, therefore, the colloid particles are attracted to the spikes. (This is not the usual appearance of domains. In most cases, the normal magnetization component will be the same in adjacent domains. The colloid will accumulate only along the domain boundaries and form fine lines which separate regions of equal appearance.) Figure 8 shows the same area after the magnetic field had been raised to nearly saturate the sample. The spike pattern has disappeared and the entire visible area seems to be one domain. The two near-vertical lines composed of many heavy, dark spots are probably not domain boundaries but the outline of a mechanical defect lying inside the sample. Both lines grew more distinct as the magnetic field was increased; the left line was completely immobile while the other one shifted about 0.3 mm to the left. The many small etch-pits visible in the photograph indicate that the current density applied in the electro-polishing was not high enough.

Figures 9 and 10 show a different portion of the sample surface where three grains intersect. Each grain exhibits a distinctly different type of colloid pattern. In figure 9 (low field strength) the spike-pattern in the upper right corner resembles that of figure 7. When the field was increased, the spikes disappeared and gave way to an array of nearly horizontal walls below a large domain covering the upper third of the grain. In the grain which constitutes the lower half of the picture, there are also several small spike domains visible in figure 7 which disappeared when the field was increased. The many small rectangular

areas which barely changed position or size with the field are most likely not regular domains but small grains of a second phase, or regions of high coercive forces caused by local stresses or precipitation, or even surface imperfections. The third grain (upper left) exhibits a rather complicated pattern of elongated domains. The lower portion maintained its general habit when the field was increased; the domains in the upper half rearranged. However, there remained a great number of walls; the field strength was not sufficient to saturate the grain.

APPENDIX A

RECIPE FOR THE COLLOIDAL SOLUTION OF IRON OXIDE (Ref 8)

Dissolve 2 grams of $FeCl_2 \cdot 4H_2O$ and 5.4 grams of $FeCl_3 \cdot 6H_2O$ (or equivalent amounts of the sulphates) in 300 ccm of hot water and add with constant stirring 5 grams of NaOH dissolved in 50 ccm of water. Filter to remove salt and excess sodium hydroxide. Rinse the precipitate in filter several times with water and finally once with 0.01 N HCl. Then transfer the precipitate to one liter of $\frac{1}{2}$ percent soap solution and boil for a short time. The former precipitate will now have become entirely colloidal with the exception of a very small quantity of undispersed oxide which should be removed by filtering while hot. It is interesting that the success of the method depends entirely on the peptization of the precipitate with HCl before it is added to the water-containing soap which serves as a protective colloid. A drop or two of the colloidal magnetite placed on the magnetized specimen will give an ample supply of sol particles for forming a pattern.

APPENDIX B

REPRODUCTION OF THE SAME MAGNETIC STATE

To reproduce a given macroscopic magnetic state of the sample, i.e., the same point on the same hysteresis loop (see figure 11) the following procedure has to be observed: A field is applied which produces a magnetization higher than the highest to which the sample has been subjected before—preferably saturation magnetization M_s (point 1 in figure 11). This field is reversed several times to stabilize the hysteresis loop. The field is then reduced from $+H_s$ (point 1) to H_2 to reach any point 2 above the remanence point 3. To reach points between 3 and 6 the field is reduced to zero from $+H_s$, the polarity reversed, and a smaller field H_4 or H_5 switched on. One may proceed from point to point in our numerical sequence. However, going back to a previous point (say, from 5 to 4) has to be done through saturation in both directions (e.g., $5 \rightarrow 6 \rightarrow 1 \rightarrow 4$). If one would simply reduce the field from H_5 to H_4, a so-called "minor loop" (as drawn in figure 11) different from the "major" hysteresis curve would be traced. What was said here for the upper branch of the hysteresis loop applies in an analogous way to the lower branch. Point 6 (saturation in the minus-direction) then takes the place of 1 as a starting point from which the field strength is to be increased monotonically.

Points on the virgin curve $0 \rightarrow 1$ (dashed line in figure 11) can be reached only by raising the field strength from zero after complete demagnetization. The latter can be accomplished by heating the specimen above its Curie point and cooling it in the absence of a field, or by placing the sample in a slowly alternating field whose amplitude must initially suffice to saturate the sample and is gradually reduced to zero.

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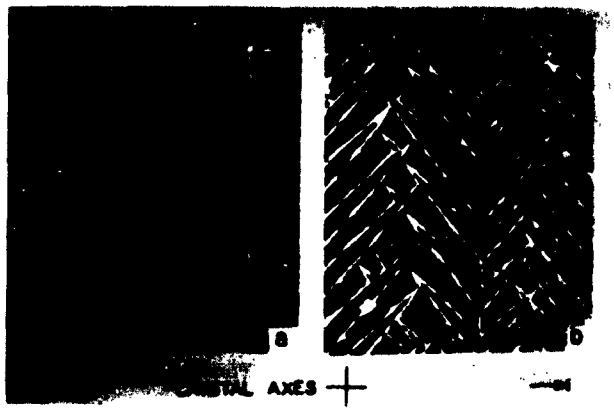

Figure 1. Effect of Polishing upon Powder Patterns

(a) "Maze Pattern" after Mechanical Polishing

(b) Same Area after Electrolytic Polishing (Taken from Ref 5)

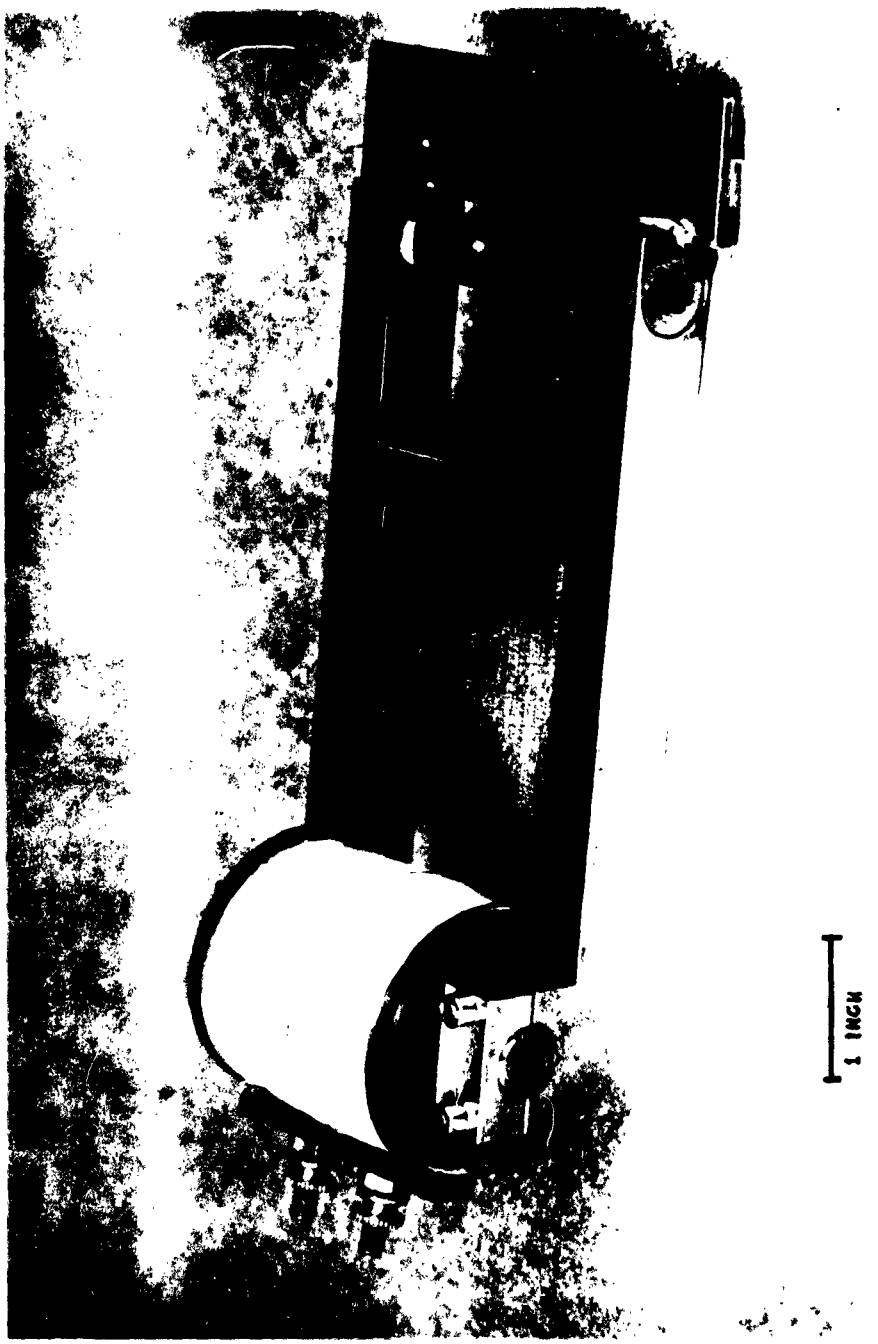

Figure 2. Electromagnetic Microscope Stage With Sheet Specimen Holder (A)

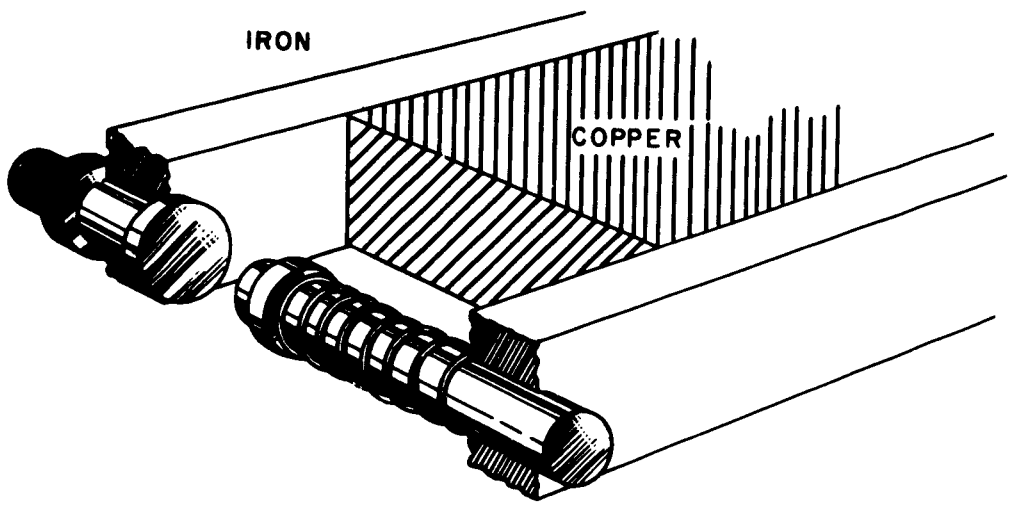

Figure 3. Bulk Specimen Holder (B)

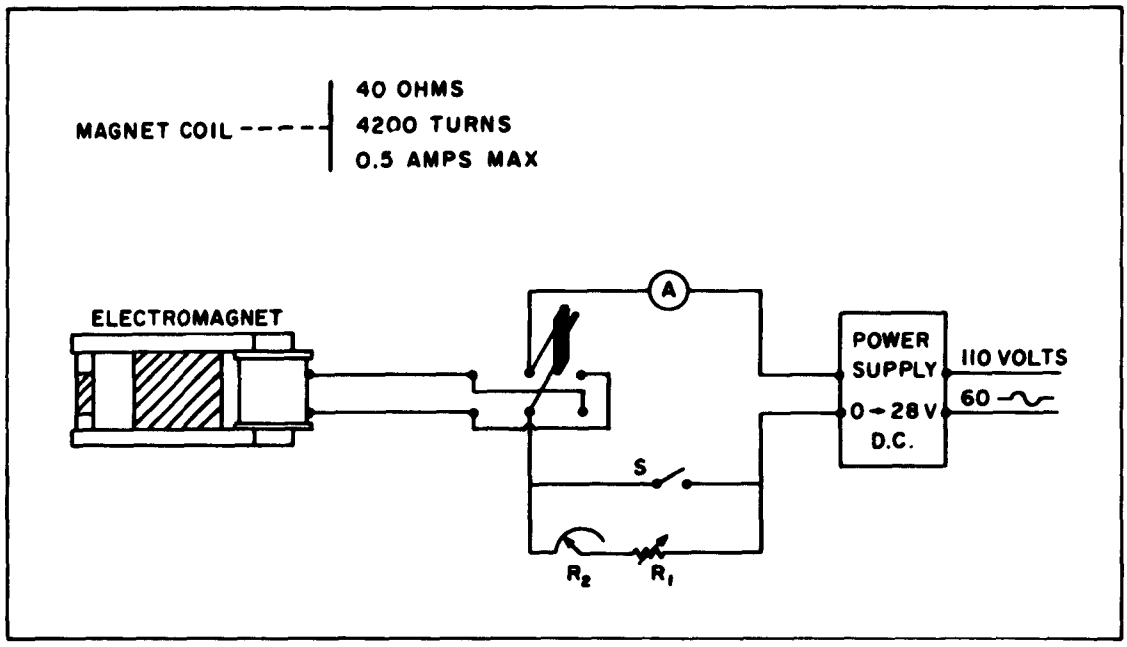

Figure 4. Magnet Power Circuit

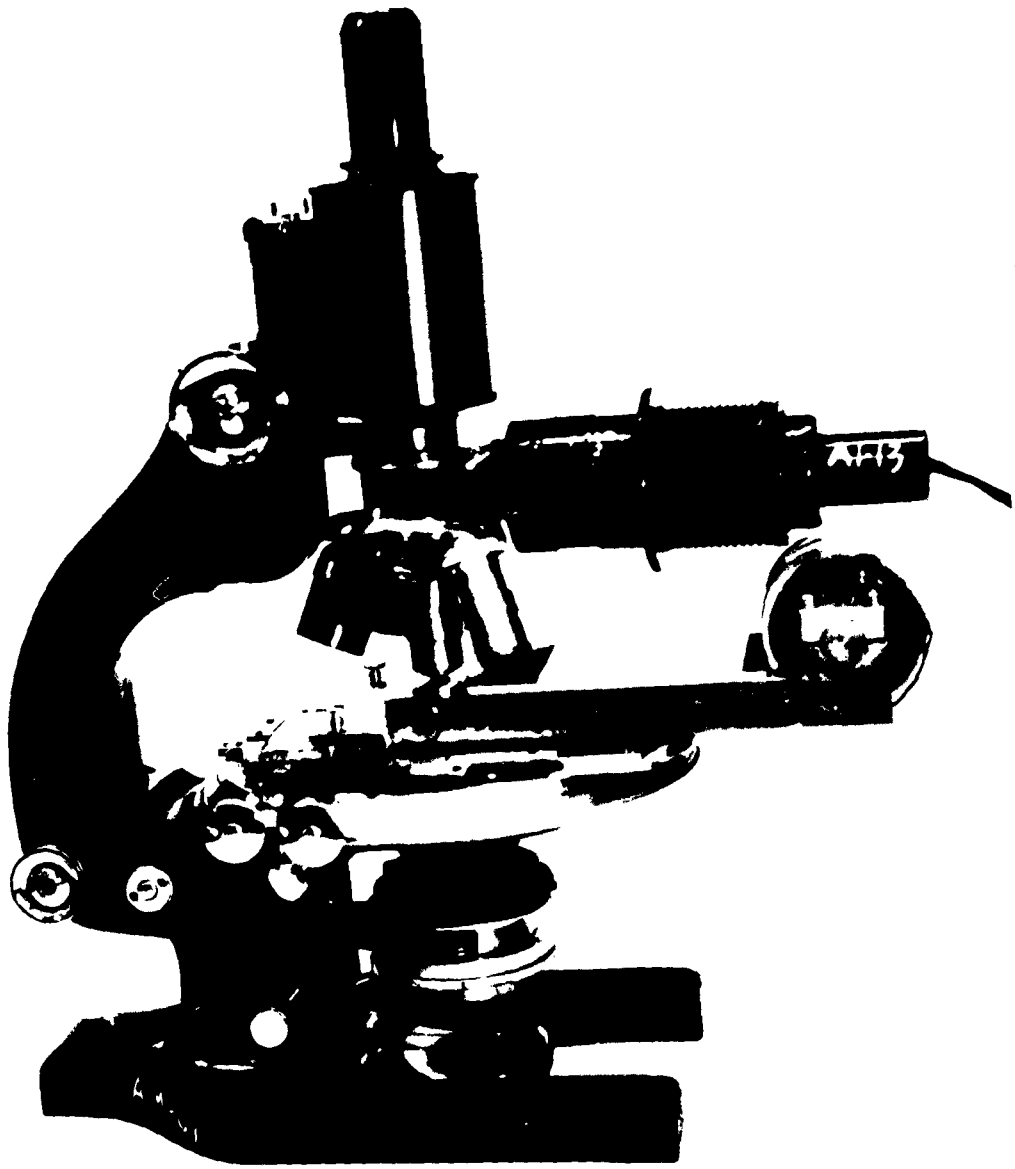

Figure 5. American Optic Company Microscope

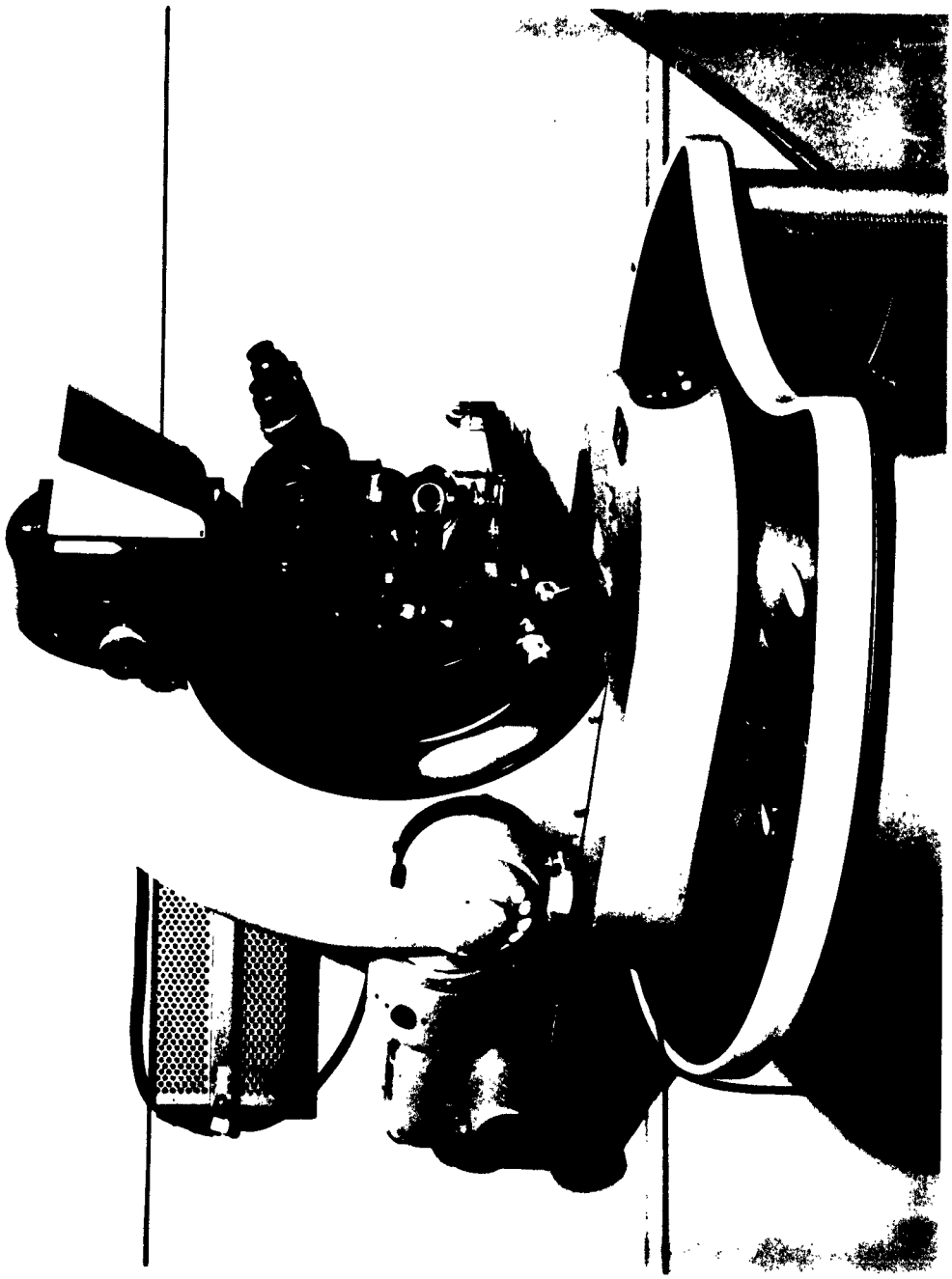

Figure 6. Zeiss Ultraphot II Microscope

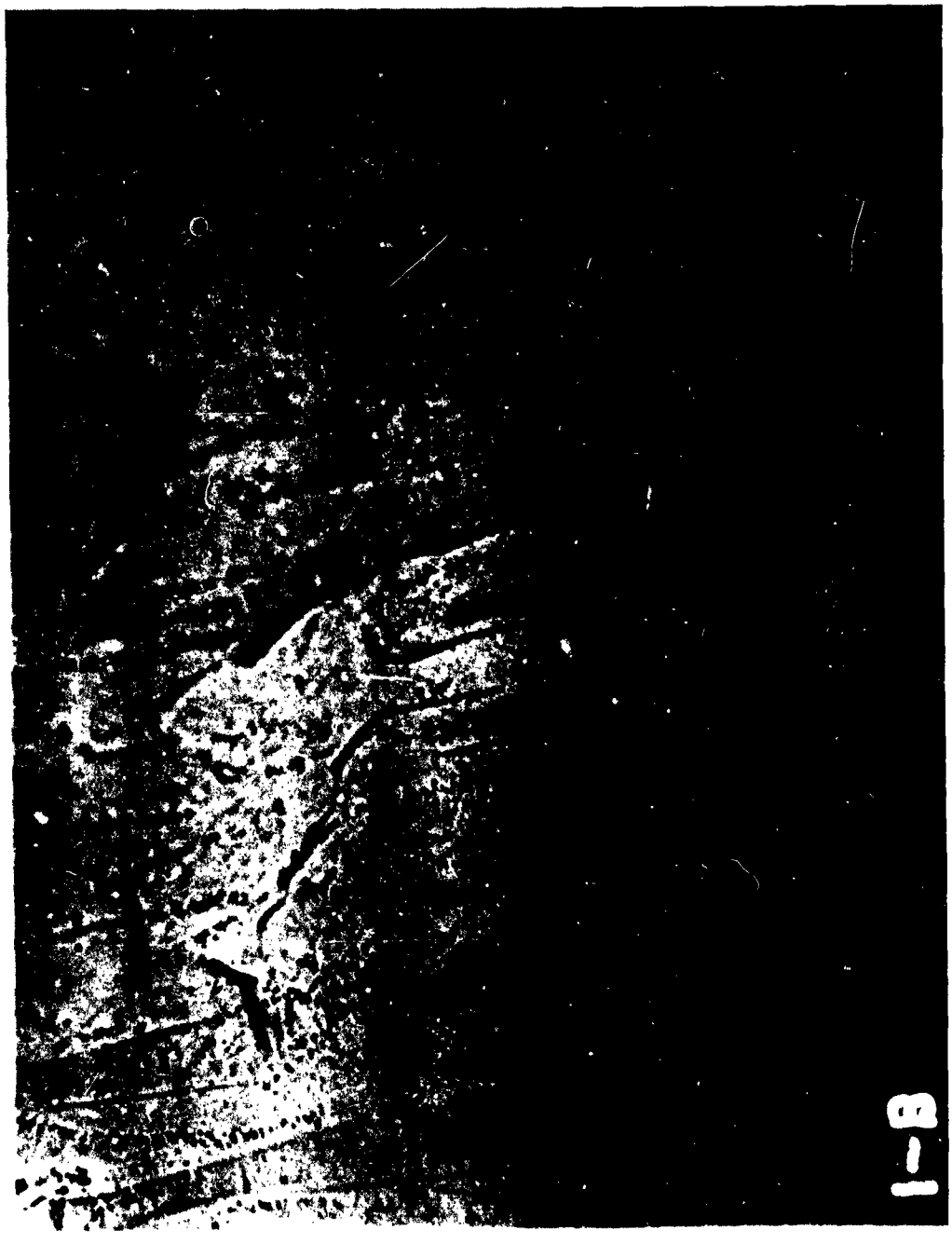

Figure 7. Bitter Pattern Observed on Fe-Si Steel Specimen, Region A, Low Field

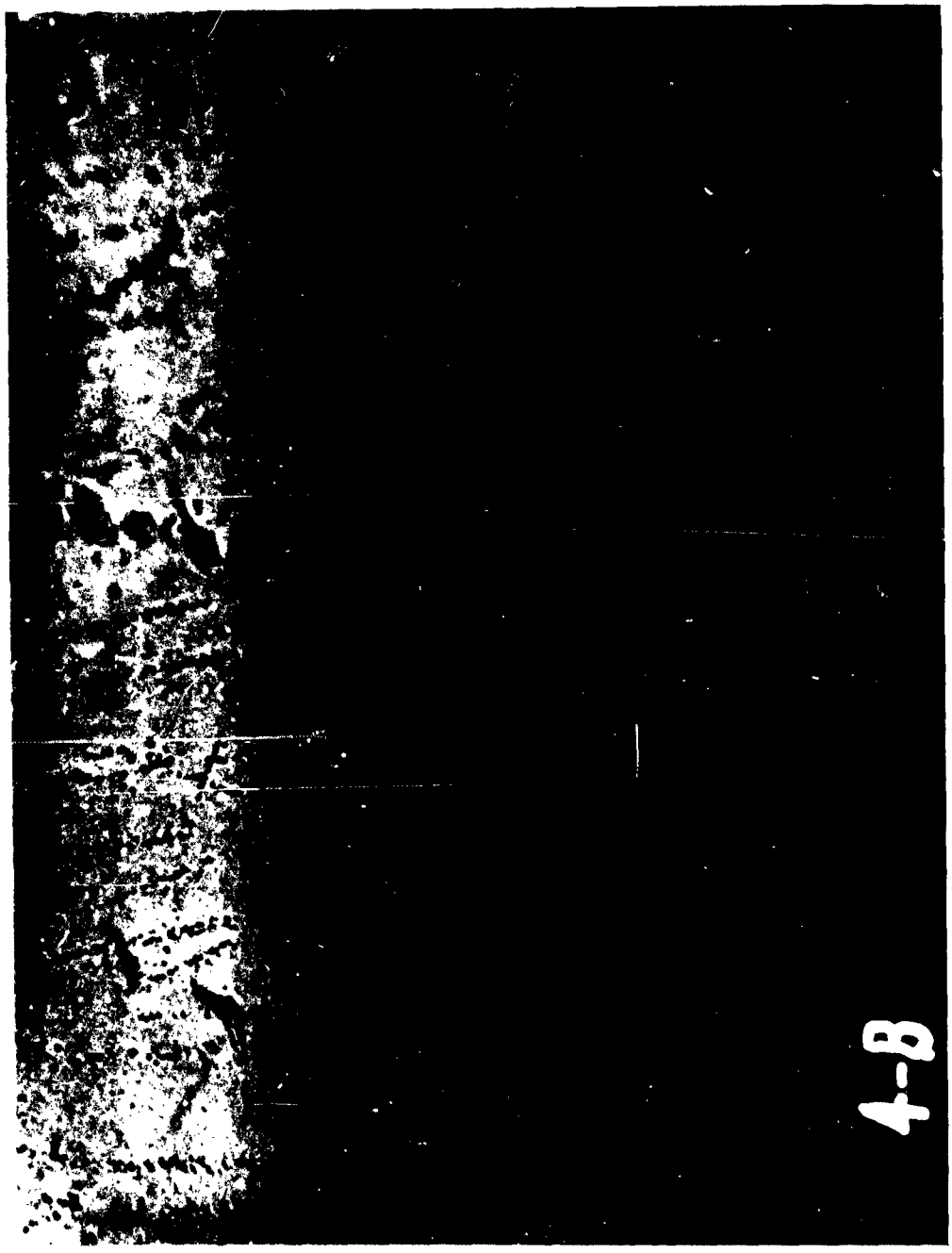

Figure 8. Pattern on Fe-Si Steel, Region A, High Field

Figure 9. Pattern on Fe-Si Steel, Region B, Low Field

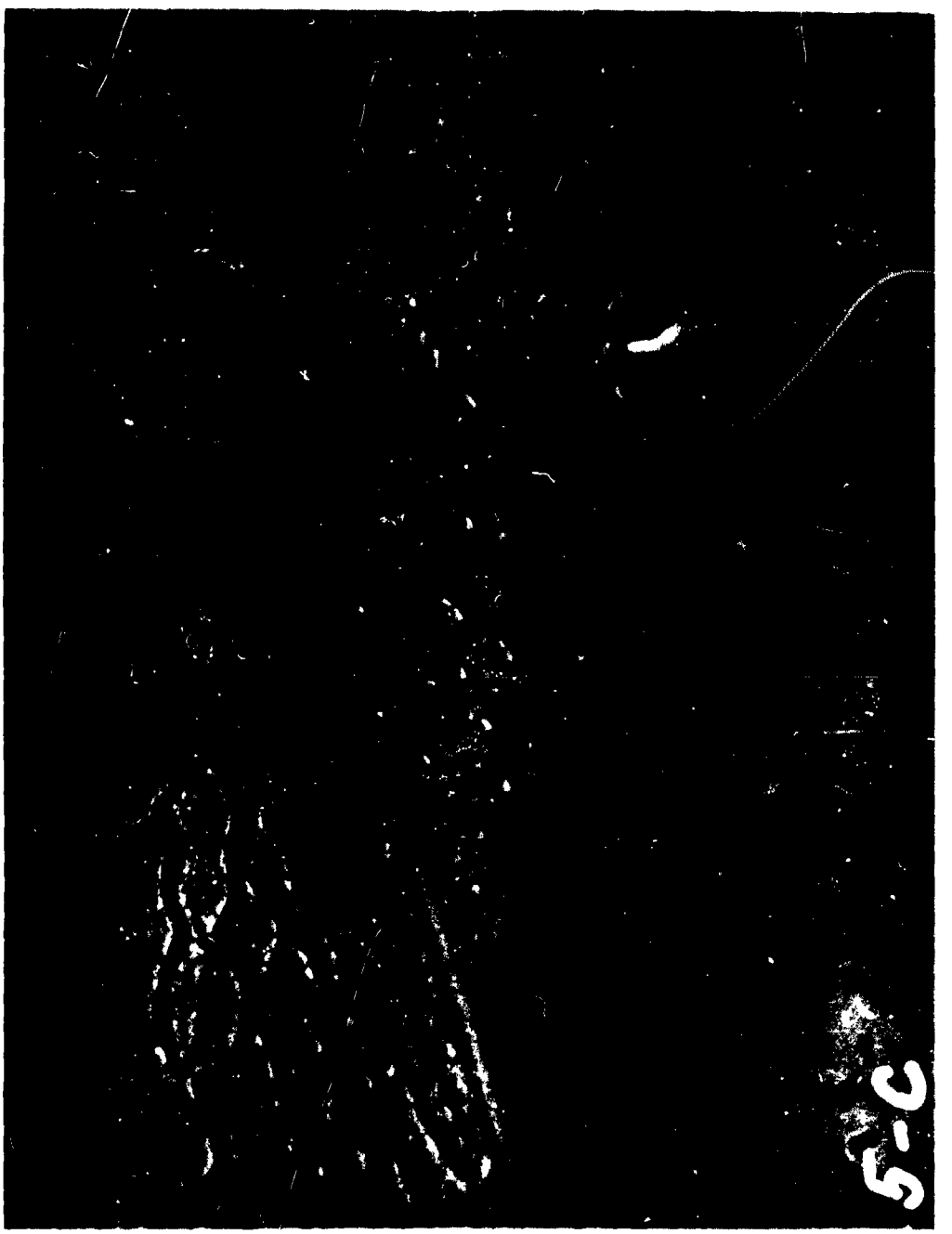

Figure 10. Pattern on Fe-Si Steel, Region B, High Field

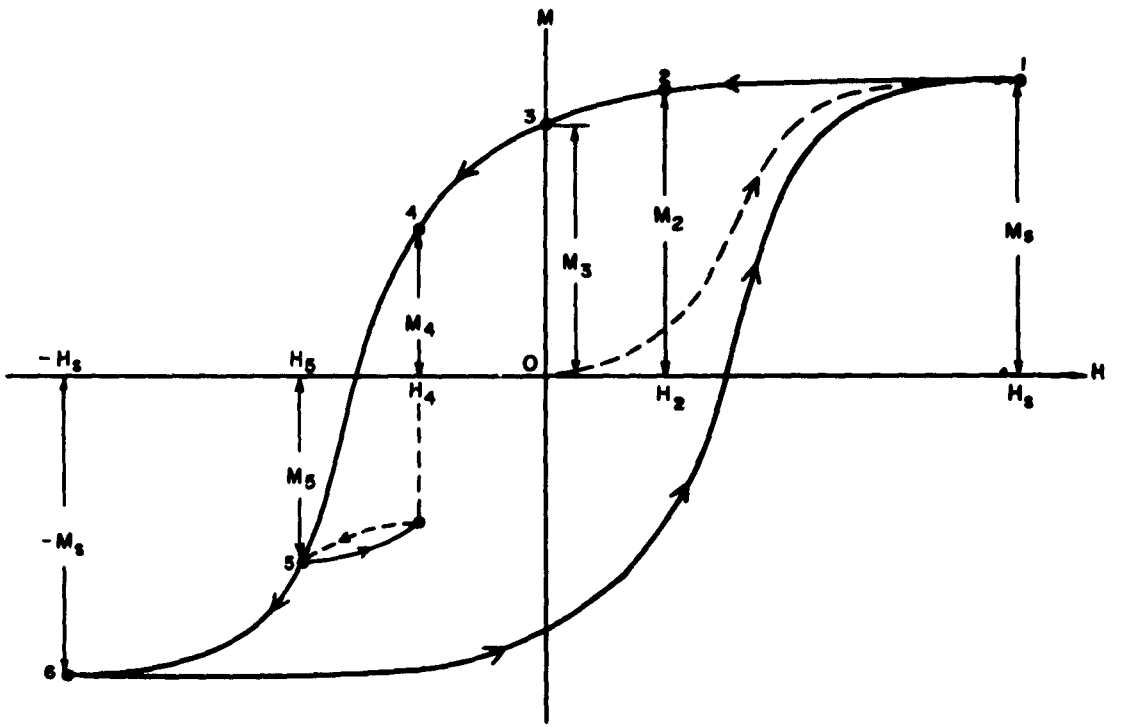

Figure 11. Hysteresis Loop

Aeronautical Systems Division, Dir/Materials & Processes, Physics Lab, Wright-Patterson AFB, Ohio.
Rpt No. ASD-TDR-63-83. OBSERVATION OF MAGNETIC DOMAINS BY MEANS OF THE BITTER COLLOID METHOD. Final report, Mar 63, 21p. incl illus., 8 refs.

Unclassified Report

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3. Magnetic Susceptibility
4. Magnetic Effect
5. Magnetic Measurement

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