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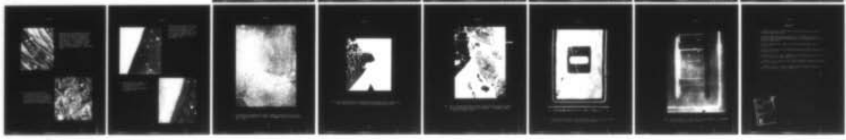

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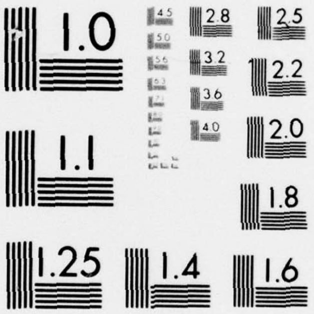

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PHOTOEMISSION ELECTRON MICROSCOPY: ANOTHER POWERFUL TOOL FOR THE MICROSCOPIST

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22 DECEMBER 1977

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UNITED STATES OF AMERICA

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20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

Photoemission Electron Microscopy, largely unknown in the United States, is an actively employed technique in several European laboratories. This report described microscope design, image formation and contrast considerations, resolution and depth of information, and application. Photographs illustrate varying applications in metals, ceramics and semiconductors.

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PHOTOEMISSION ELECTRON MICROSCOPY: ANOTHER POWERFUL TOOL FOR THE MICROSCOPIST

I. Introduction

A recent *ESN* (31-9:356) served as a brief introduction to photoemission electron microscopy (PEEM). This report is intended to provide a more complete description of PEEM, without seeking to be either exhaustive or exhausting. The rationale for issuing this report is that PEEM is largely unknown in the US.

Although PEEM was first described by Bruche in 1933 and continuing attempts at developments were made over the next 35 years (see Refs. 1 and 2), an operative microscope awaited the work in the late 1960s of Engel (Refs. 3, 4), who solved the problem of image brightness at high magnification and improved the resolution limit to 120 Å, and of the work of Graber *et al.* (Refs. 5-7), who solved the problems of maintaining a lasting contrast with photoemission, and of continuous heating stage microscopy.

While the method is referred to as photoemission electron microscopy, it would be more correct to delete photo. The essentials of the emission electron microscope (EEM) is that electrons are emitted from a sample surface and that the sample forms the objective of the microscope. There are four mechanisms for electron emission:

1. Field emission. This is the technique pioneered by the late E.W. Muller. While the results that have been obtained with field emission are occasionally spectacular, the technique is applicable to selected systems, and images of very limited areas are obtained.
2. Kinetic emission. This is the basis for scanning electron microscopy (SEM) and for microprobe analysis, both highly successful developments. The latter, used primarily for elemental analysis, differs substantially from EEM. SEM might be viewed, initially at least, as a competitor to EEM. In fact, the two methods are more complementary, a point to which I will return. The heart of kinetic emission methods is the release of electrons or ions by bombarding electrons or ions. Accordingly, one might term these high energy methods.
3. Photoemission. Photons are the bombarding particle in this method, bearing energies of only a few electron volts, substantially below the kilovolt or megavolt range of kinetic emission methods. It follows that the electrons that are emitted by impact with these photons are also low in energy. In essence, the photons serve as bearers of very local hot spots, "heating up" single electrons on collision. This suggests that one might accomplish a similar purpose by actually heating the sample sufficiently, and this leads to the final release type:
4. Thermionic emission. Here, as just stated, the sample temperature is sufficiently elevated that a few electrons, enough to be useful

in microscopy, are excited to a great enough degree to be "boiled off" from the sample surface. While this method follows in a logical manner from photoemission, historically thermionic emission preceded it in application for obvious reasons; it is considerably simpler to heat a sample than to bathe it with the strong flux of ultraviolet light needed in photoemission.

Not surprisingly, each method has its advantages and disadvantages, which we will review below. We turn first to a description of the photoemission electron (PEE) microscope, which includes the capability to operate as a thermionic-emission electron (TEE) microscope.

II. Microscope Design

In overall schematic design, the PEE microscope resembles conventional metallurgical microscopes. In the latter, light is reflected from the object, then collected and focused for observation by a set of glass lenses; in the PEE microscope, photons excite electrons from the object (e.g., sample), and these electrons follow a path through magnetic lenses. By contrast, in transmission and scanning electron microscopes, the guidance of electrons precedes incidence on the sample (although there may be additional steering to bring the scattered electrons to a detector). Despite this similarity in generic type to optical microscopy, the actual physical instrumentation of the PEE is distinctly more readily associated with other electron microscopes since all electron microscopes share the common inclusion of vacuum features and electron-guidance lenses.

Figure 1 shows a schematic view of the PEE microscope. The specimen holder (1) supports the sample (4) whose surface is to be imaged. Ultraviolet light from four high-pressure mercury-vapor lamps (3) is reflected from a highly polished anode plate (5) onto the sample surface. Emitted electrons are accelerated in a static field along a path of 5 mm through 50 kV. The electrons then pass through the anode aperture into a three-stage columnar magnet and are projected onto a fluorescent viewing screen (9). A camera is situated below this screen. Magnifications are variable between 10^2 and 10^4; resolution varies between 150 Å and 300 Å, depending on the specimen material. At temperatures in excess of about 1,000C, thermionic emission begins to become effective, and the uv-light sources may be switched off. The combination of photo- and thermionic emission allows a continuous study of materials from room temperature to 2,000C directly. In the photoemissive mode, the extension of the operating range to cryogenic temperatures can be envisioned.

The energy density of the uv illumination is high—several W/cm^2—and bathes an area of sample of about 0.25 mm^2. The use of high-pressure mercury lamps provides a spectral range from 270 mm into the visible region. The lower range is particularly important since the emission of electrons drops off steeply with wavelength so that few materials emit sufficient electrons when the incident photon wavelength approaches 325 mm and above.

PEEM is based on integral-image generation; scanning is not helpful since the light-spot size is too extended. This apparent disadvantage is balanced by the short exposure times required in PEEM—0.2 sec to 60 sec, depending on material and magnification. This is important in applications in which sample morphology changes in time due to underlying kinetic processes, particularly at high temperatures, and it is desired to record with movie equipment. In addition, short exposure times reduce the consequences of surface contamination; see below.

Construction details will depend on the manufacturer, of course. Here we describe the Balzers Metioscope KE3, the unit in use by over 10 institutions. Figure 2 presents a sectional view of the KE3. Electron focusing and steering is provided by lenses. During operation a vacuum of about 10^{-7} Torr is provided by conventional ion diffusion/rotary pumping (not shown) in conjunction with a liquid-nitrogen cold trap. The specimen is faced downward in the specimen stage, with a 40-50 v differential being maintained below the anode; the anode is constructed of highly polished chrome-nickel steel to provide full reflection of the uv light from the lamps and is grounded. Recording is done on the fluorescent screen or photographic plate. Samples are loaded into the KE3 by tilting the specimen holder into a position where it can be lowered into a vacuum lock. Then further rotation allows the surface to be cleaned by ion bombardment. A motorized cross table allows any location in a 3 mm × 3 mm area on the specimen to be examined. An electron-beam evaporation source provides carbon-layer deposition, and a quenching device aids rapid sample cooling. Radiant heating is used for slow heating and cooling of 12-mm-diam. cylindrical specimens, in the range from room temperature to 1,200C. Electron beam heating is used for rapid heating and cooling of 1-mm-diam. specimens in the range from room temperature to 2,000C and also for heating tensile specimens in the range up to 1,200C.

III. Image Formation and Contrast Considerations

As is also true in SEM, there are three main contrast phenomena in PEEM. These are:

1. Relief (topographic) contrast. This contrast should, ideally, reflect the actual relief of the sample's surface, without complication from other contrast phenomena.
2. Grain orientation contrast. Here, the difference in the crystallographic orientations of adjacent grains should be shown to best advantage.
3. Material contrast. The goal here is to distinguish between various materials, either of substantially different composition or different phases in a single alloy separately.

Relief contrast is the least distinctive factor in PEEM; SEM is distinguished by its excellence in relief contrast. This brings out the interesting fact that PEEM and SEM are complementary in their strengths and weaknesses, as supported by the discussion below concerning grain orientation and material contrast.

The inferiority of the PEE microscope in developing topographic contrast is due to a variety of factors. For one, other contrasts (i.e., grain and material contrasts) confuse it. It follows that topographic contrast is best observed in the simplest of systems—single crystalline materials, amorphous materials, or very simple binary alloys. Even then, fidelity in reproduction of topography is reduced by the ever-present electric fields that develop near a sample's surface. Since the emitted electrons, whether in PEEM or TEEM, are low-energy electrons, even the relatively mild fields that develop cause electron trajectories en route to deviate away from the specimen's surface.

A relief contrast emerges that is strong in PEEM (actually, generally stronger than in SEM) but not as faithful in reproduction. In fact, the lesser relief contrast associated with SEM is used to advantage there, in providing good images of surfaces with very large relief variations. In the special cases of small variations in relief in homogeneous materials, PEEM may actually surpass SEM.

The result of these considerations is that PEEM is acknowledged to be generally inferior to SEM for relief contrast. It is logical, then, to hope that PEEM might excel in image contrasts for very smooth surfaces, and this proves to be the general rule.

In its applications on the observation of flat surfaces, PEEM becomes a strong extension of conventional metallurgical microscopy.

Both orientation and material contrast both arise from the same cause—the variation of work function at the surface of different grains or different materials, respectively. These contrasts are a reproduction of work-function topography. It is a fortunate fact that the work function varies sufficiently strongly between different grains or materials to provide the necessary contrast that underlies PEEM; the intensity of the photoemitted electron-flux rises varies rapidly, from near zero, in a short photon-wavelength region.

Since the work function at the surface is of prime importance here, and since it is sensitive to the "chemistry" of the surface, one might predict that surface coverage by contaminants could play a crucial role in PEEM. Again, this prediction is largely borne out. Its consequences may be beneficial or detrimental. Where, for example, the contrast between two grains might be small at pristine surfaces, contamination may, and frequently does, enhance the contrast. That is good. What is unfortunate is that the contrast may shift in time even though the underlying sample structure remains stable or, more seriously, that the contrast will not directly reflect with time the variations of structure that are occurring. Various laboratory "tricks" may be necessary to minimize this difficulty. Nevertheless, the strong effects of surface contamination apparently rule out the major use of PEEM in another application in which it could have conceivably excelled—the actual chemical analysis of alloy phases.

IV. Resolution and Depth of Information

The resolution of the PEE microscope is closely related to the depth below the surface from which information is gathered: the smaller the depth, the greater the surface imaging fidelity and resolution. Here, again, the low energy of the electrons that probe the material in PEE microscope is used to advantage. The penetration of the incident photons is not, in itself, important; however, the energy transfer is determined by the energy of the incident photons, and this in turn, determines the distance below the surface from which photoemitted electrons can be derived to form the image. This depth varies from 100 Å in metals to 500 Å for non-metals, even though the uv penetration may be of the order of 1 m. Similar resolution is obtained in SEM for relief contrast, wherein secondary electrons (with relatively low energy) are utilized. But for flat surfaces, it is necessary to use the more energetic backscattered electrons as well, and this increases the depth of information by about an order of magnitude.

V. Applications

Figure 3 presents a classical application of PEEM. In this figure of the structure of a white cast-iron, three phases are to be seen: Cementite is etched and appears as dark; there are also white, unetched needles of martensite in a background of austenite. Although there are compositional differences between these three distinct regions, the main effect is structural (i.e., orientational).

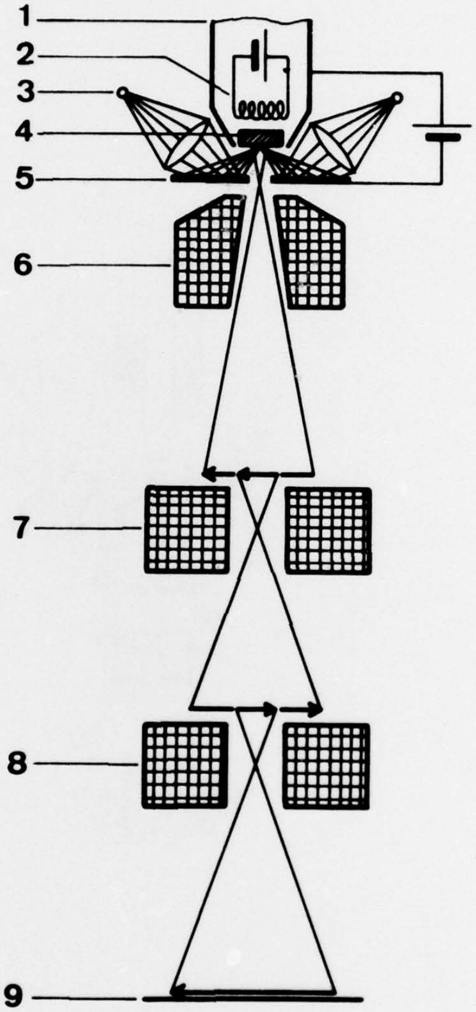
Figure 4 demonstrates that it is not necessary to have any compositional differences in order to display orientational differences. The figure shows slip lines and deformation twins on a polished unetched surface of deformed beryllium-bronze.

Other examples of the use of PEEM in deformation studies are presented in Figures 5 and 6. Figure 5 shows brass that has been cold-worked to a 6% deformation. The deformation has produced considerable twinning and the α- and β-phases are evident, in addition. Figure 6 shows the cleavage surface of a zone-melted single crystal of tungsten. The ability of PEEM to follow relief contrast under favorable circumstances is demonstrated here.

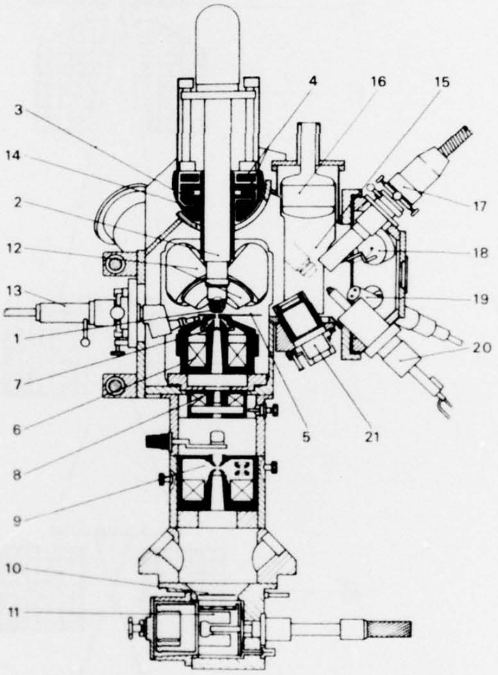
The ability of the PEEM to follow continuous changes in a material is presented in Figures 7 and 8. Figure 7 shows the sample in an as-deposited condition. Chrome-nickel steel had been deposited on a glass substrate and appears at the left. To the right of the interface, an additional deposition of aluminum was made. After an extensive high-temperature diffusion, the micrograph is modified to that shown in Figure 8. The formation of intermetallic compositions at the interface is evident. In addition, dendritic structures have appeared and grown at the surface of the aluminum deposit, representing diffusion through the original thin (1200-Å) aluminum layer.

Figures 9 and 10 show application of PEEM to non-metals. In Figure 9 we see the surface of a nickel sample that was oxidized *in situ* at 900C at an oxygen pressure of 10^{-4} Torr. The oxidation process can be observed continuously with movie attachments to the PEE microscopy. This is demonstrated even more graphically in Figure 10, where the specimen is a refractory brick material consisting of ZrO_2 (gray), Al_2O_3 (white), and a glassy matrix (black). The lefthand figure was taken at 700C, in the photoemissive mode; the righthand figure was taken at 1700C in the thermionic emission. The melting of the glass and its attack on the alumina (Al_2O_3) is apparent.

Figure 11 presents a rather different application of PEEM. Here there is a micrograph of a section of an integrated circuit. The differentiation between variously doped portions is well established on the left in this figure, but is poor on the right. The surprising aspect, for those of us conditioned to accept that cleaner is better, is that the righthand photo shows the microcircuit section <u>after</u> it has been cleaned by ion bombardment.

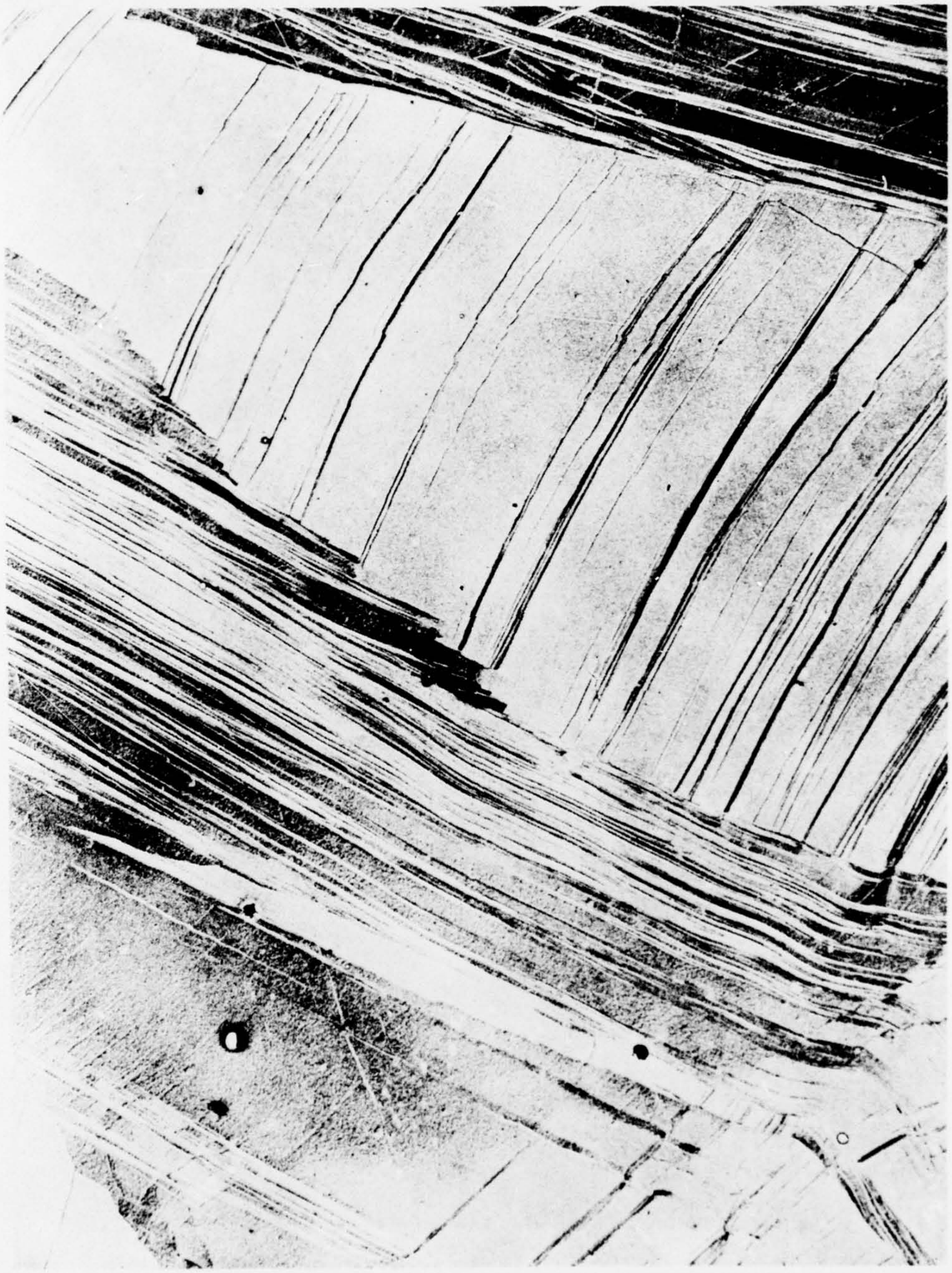


1. Schematic view of the photoemission electron microscope. 1-Specimen holder; 2-Specimen heater; 3-Ultraviolet lamps; 4-Specimen (solid); 5-Pierced anode; 6-Objective lens; 7-Intermediate lens; 8-Projection lens; 9-Fluorescent screen. (L. Wegmann, *Journal of Microscopy* 96, 1, 1972)



2. Cross-section of the photoemission electron microscope (Metioscope KE3). 1-Specimen, 2-Specimen holder with heating device; 3-Specimen rotating stage; 4-Specimen displacement stage; 5-Anode interchanging device; 6-Objective lens with stigmator; 7-Aperture diaphragms; 8-Intermediate lens; 9-Projector lens; 10-Screen; 11-Plate camera; 12-uv illumination systems; 13-Neutral particle gun; 14-Tilting specimen support; 15-Preparation chamber; 16-Cooling trap; 17-Ion gun; 18-Surface temperature probe; 190Evaporating source; 20-Specimen cooling device; 21-Airlock; 22-Specimen chamber. (L. Wegmann, *Microstructures*, Aug/Sept 1971)

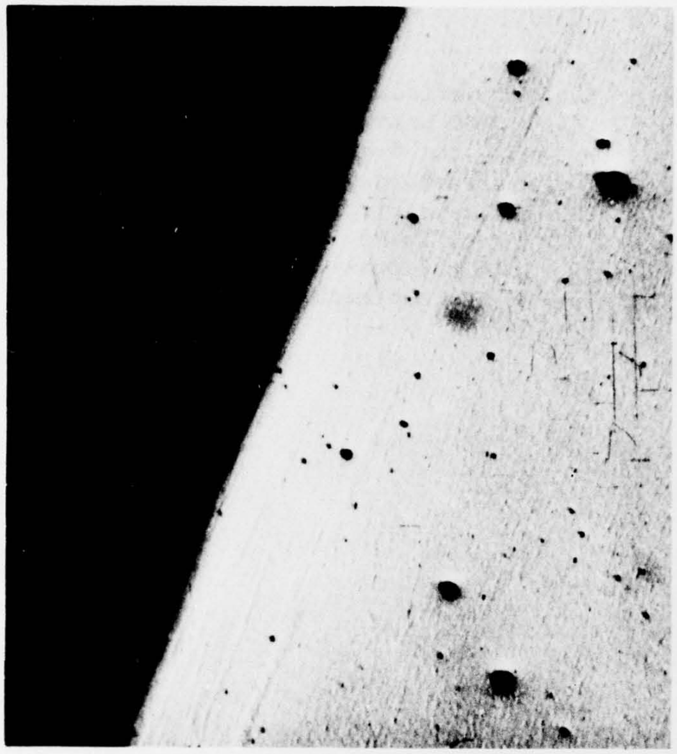
3. Photoemission micrograph of white cast-iron. The cementite (dark) is etched, whereas the white needles of matersite in the autentite are unetched. (L. Wegmann, *Journal of Microscopy*, 96, 1, 1972)



4. Photoemission micrograph of deformed beryllium-bronze. Slip lines and deformation twins on the polished unetched surface. (L. Wegmann, *Journal of Microscopy*, 96, 1, 1972)

5. Photoemission micrograph of a cold-worked brass with 6% deformation. Note the β-grains in a deformed α-structure. The deformation of the α-matrix is evidenced by deformation twins. (L. Wegmann, Fifth International Congress on X-Ray Optics and Microanalysis, 9 September 1968)

6. Photoemission micrograph of a cleavage fracture of a zone-melted single crystal tungsten. (L. Wegmann, Fifth International Congress on X-Ray Optics and Microanalysis, 9 September 1968).

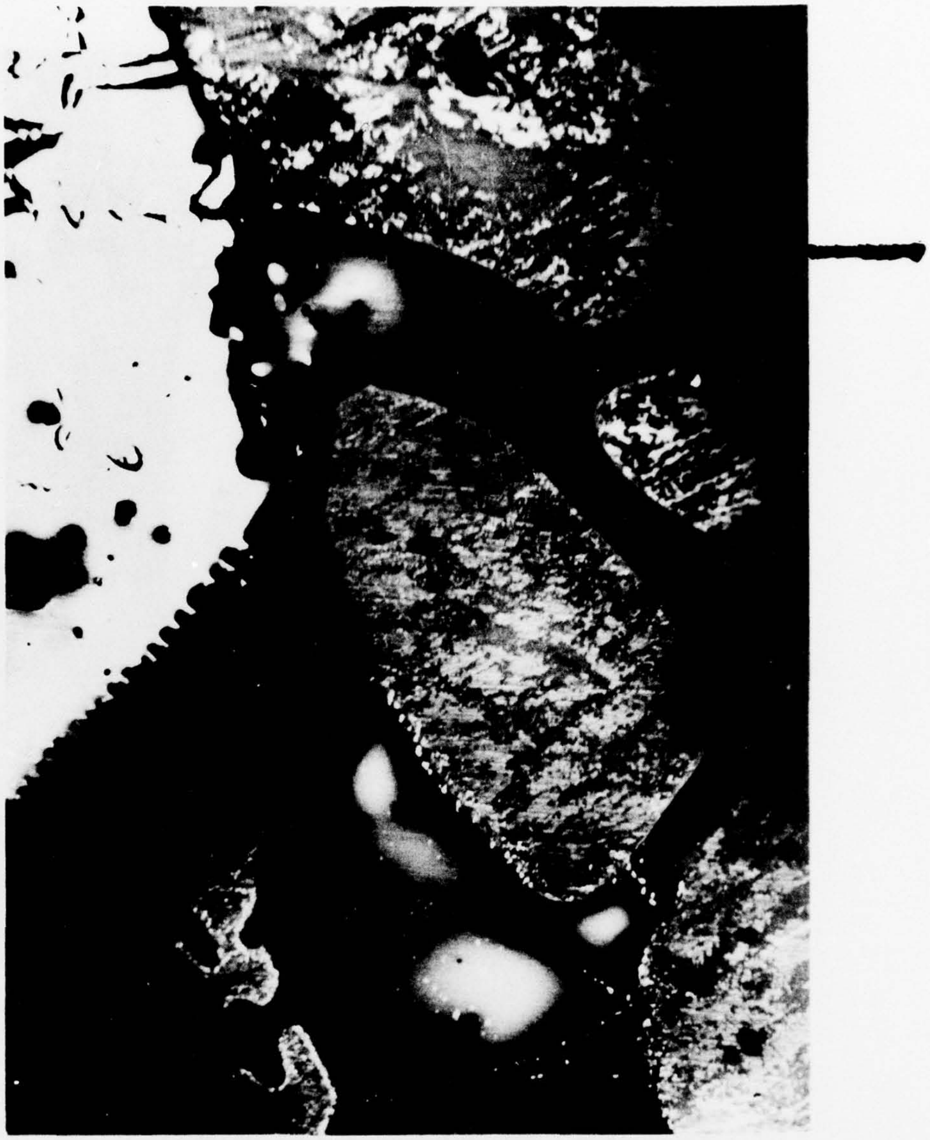


7. Chrome-nickel (left) deposited on a glass substrate. At the right is an aluminum layer, 1200 Å thick, deposited on one side of the chrome-nickel layer. (L. Wegmann, Balzers Report, September, 1969)

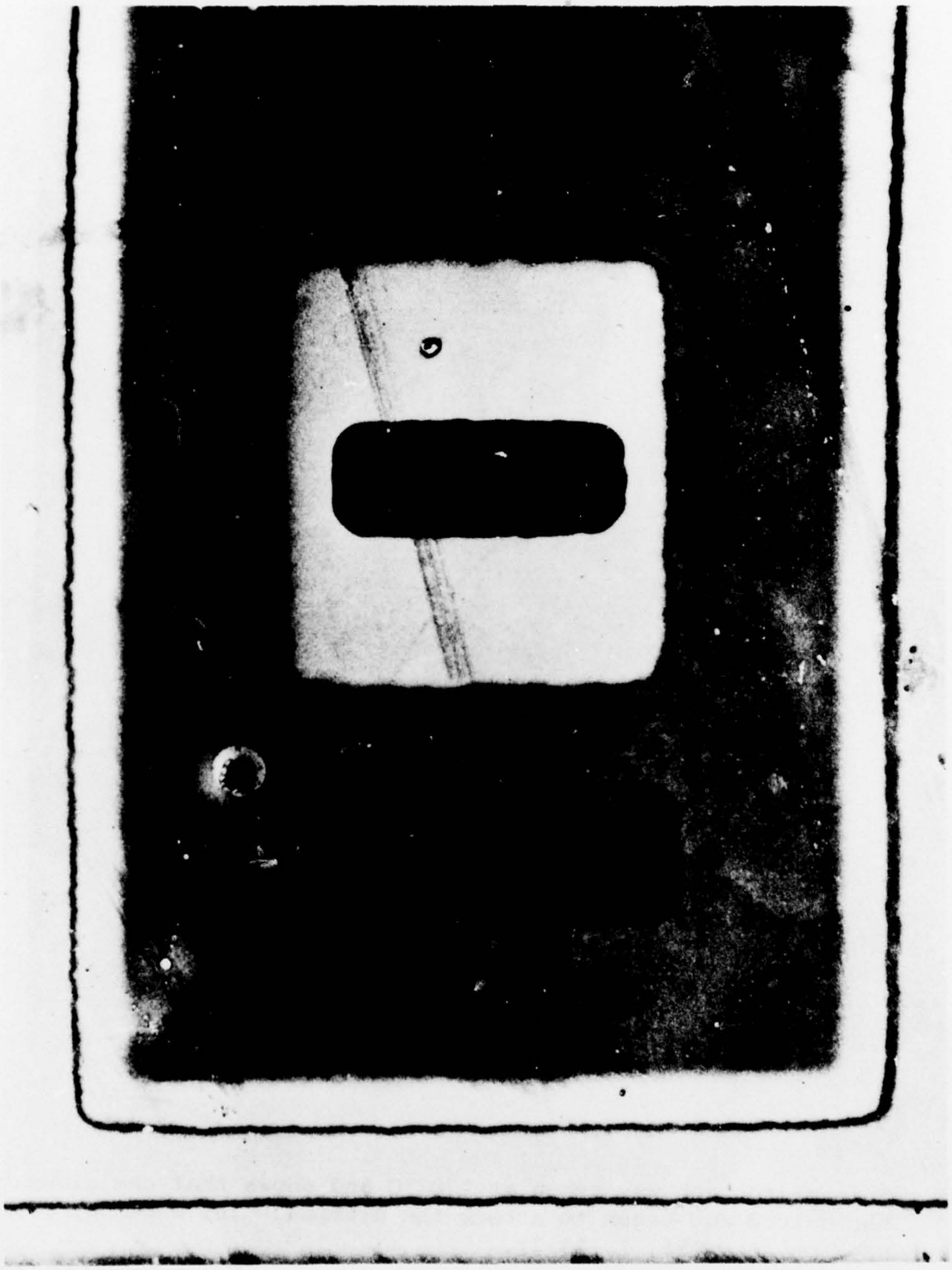
8. Same specimen as Figure 7 a after extended diffusion treatment at 740° C. (L. Wegmann, Balzers Report, September 1969)

9. Photoemission micrograph of a nickel surface oxidized at 900°C *in situ* at an oxygen pressure of 10^{-4} Torr. (L. Wegmann, *Journal of Microscopy* 96, 1, 1972).

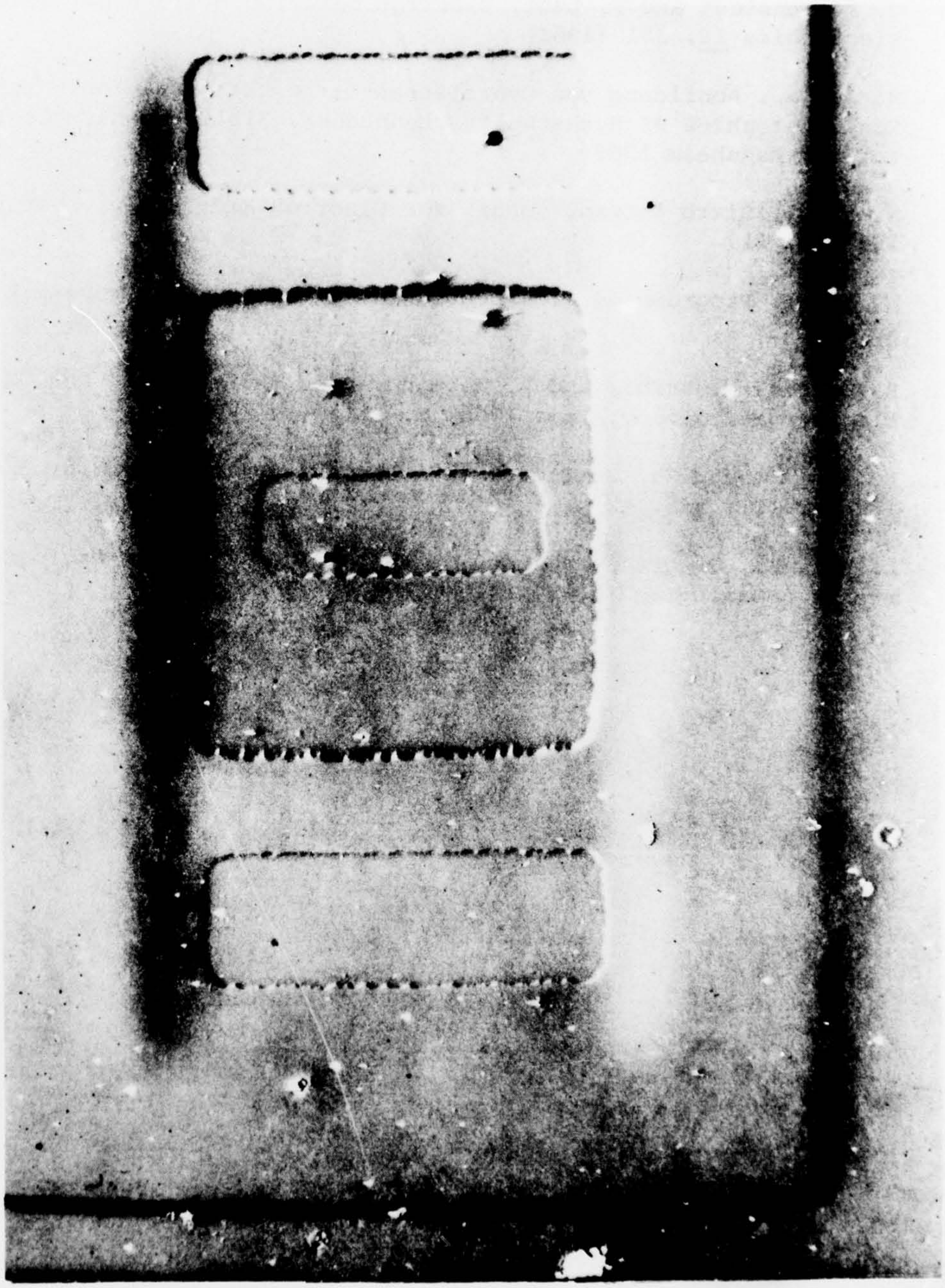
10A. Highly refractory brick consisting of ZrO_2 (grey), Al_2O_3 (white) and a glass matrix (black). Photoemission micrograph taken at 700°C.



10B. This micrograph was taken at 1700°C and shows that the glass matrix has melted and begun to attack the alumina. (L. Wegmann, *Journal of Microscopy* 96, 1, 1972).



11A. Photoemission micrographs of an integrated circuit. The circuit here is shown before cleaning, indicating strong contrast.



11B. Here the circuit is shown after a short cleaning. (L. Wegmann, *Journal of Microscopy* 96, 1, 1972).

REFERENCES

1. G. Mollenstedt and F. Lenz, Electron Emission Microscopy, Adv. in Electronics 18, 251 (1961)
2. H. Seiler, Abbildung von Overflachen mit elektronen, Ionen und Rontgenstrahlen BI Hochschultaschenbucher, Bibliographisches Institüt AG, Mannheim 1968
3. W. Engel, Sixth Intern. Congr. for Electron Microscopy, Kyoto, 1966, p. 217
4. W. Engel, Programm der 13. Deutschen Tagung für Elektronenmikroskopie, Marburg 1967, p. 58
5. R. Graber, M. Bribi, and L. Wegmann, Proc. Fourth Eur. Reg. Conf. on Electron Microscopy, Rome 1968, p. 111
6. L. Wegmann and Ch. Zaminer, Sixth Plansee-Seminar, Vorabdrucke, Reutte 1968, V. II, Art. 42
7. L. Wegmann, Progress towards a Metallurgical Electron Microscope, Prakt. Metallographie, 5, 241 (1968)