

THE ATOMPROBE® AT WORK

by

GEORGE CHAPLENKO, D. O. LANDON and A. J. MITTELDORF

“AND when a smith dips an axe . . . in chill water with a great hissing, then he would temper it, for whereby anon comes the strength of iron.” Homer’s *Odyssey* thus records man’s early success in transforming the properties of metals to suit his needs.

Metallurgy has come a long way since then. The field has lost almost all its aura of art, guild-secret brews having been replaced by formulations dictated by theory and guided by modern analytical techniques. Among these, the most basic is still a microscopic examination of the polished and etched surface of the metal. To the expert the microscope reveals the “personality” of the alloy, its discreet phases, the results of any heat treatment, the presence of any intermetallic compounds, foreign inclusions or unalloyed materials placed there intentionally or otherwise. In fact, the wondrous microcosm of a metal sample under the microscope is as meaningful to the metallurgist as that of the stained cell to the biologist. Light-colored crystals in a sample of steel dotted with black spots are immediately recognized as ferrite with spheroidized carbides indicating that the metal is soft, possibly in the annealed state. Differently heat treated, the same alloy may undergo a structural change, needle-like particles of martensite—a sign of extreme hardness—replacing the ferrite crystals.

It has long been realized that the microstructure holds the key to the basic understanding and improvement of alloy properties. How to determine the composition of local areas ranging from 2 microns in diameter to 50 microns has been the challenge. Micro-drilling and brute-force hand gouging to pry out all-but-invisible chips for spectrographic analysis were quickly found to be less than satisfactory; few technicians boast the skill and patience such delicate manipulations demand.

Need ultimately found a solution—albeit an expensive one—in the electron microprobe, an enormously complex device which provides analysis without recourse to physical separation of the specks from their matrix. An electron beam is directed to a selected sample area under an evacuated microscope, stimulating emission of a characteristic x-ray spectrum. In the decade since its inception, the electron microprobe has become a most powerful metallurgical tool, furnishing elemental composition with speed and accuracy far beyond any other technique. Since the sample is not destroyed, its spectrum can be displayed on a television screen for study as long as desired. At appropriate settings areas rich in a particular element may be scanned and at the flip of a few switches the picture may be changed to reveal iso-concentration levels for another element. Spatial resolution as

small as 1 micron has been demonstrated. And the probe can zero in on the tiniest inclusion, trace a grain boundary, diffusion zone or corrosion deposit—all while its executive director is seated comfortably before his hundred-thousand-dollar console viewing a familiar-looking bright, large screen.

Significantly, the x-ray approach has, until now, not been matched by a commercial emission spectrographic instrument. Early investigators, their work predating the development of the electron probe, stumbled over at least two hurdles. One was how to constrain the spark so it sampled exactly where the auxiliary electrode pointed; conventional sparks burst into uncontrolled coronas. In 1939, Scheibe and Martin (1) found a solution by encasing the auxiliary electrode in an insulating quartz capillary. The reward for struggling with this spark straight jacket was a spatial resolution as small as 200 microns. Thanheiser and Heyes (2) resorted to a tiny hole drilled in a sheet of mica to restrict the sparked area. They also set the sparking device into the objective of a microscope to improve aiming accuracy. Areas as small as 60 microns were analyzed in this fashion. The second problem was optical speed; the low light output of the faint discharge hindered photographic detection. Scheibe and Martin tackled this with some success by placing the discharge at the normal entrance slit position, an approach taken by several researchers thereafter. Exposure time was an hour or two.

Although neither the quartz capillary nor the pin-hole in a mica sheet represented a truly convenient approach to getting the spark where it was wanted, the former seems to have won out with the small community of pioneers who continued to keep the spark of microspectroscopy alive for the next fifteen years. Murray, Gettys and Ashley (3) succeeded in controlling the spark still further by drawing capillaries out to 30 micron diameters. Bryan and Nahstoll in 1947 (4) conducted a classic study of the composition of phases in a PbCuNi bearing alloy by this method. As late as 1953, Brandt (5) still enlisted the capillary. In 1956 Hurwitz (6) found that he could direct a traversing discharge in a track 500 microns across merely by sharpening a silver counter electrode to a fine point.

None of this work was successful in reaching the really interesting areas below 50 microns and for this discouraging reason the literature of the Fifties abounds with articles on other subjects. A breakthrough came in the early Sixties with an intensive project undertaken by Vogel and Kneip (7) at Mallinckrodt Chemical Works. Like Hurwitz, they discarded the cumbersome quartz capillary, finding that they could reduce the burn by electropolishing the auxiliary electrode to a tip radius of 1 micron. Reducing the gap to around

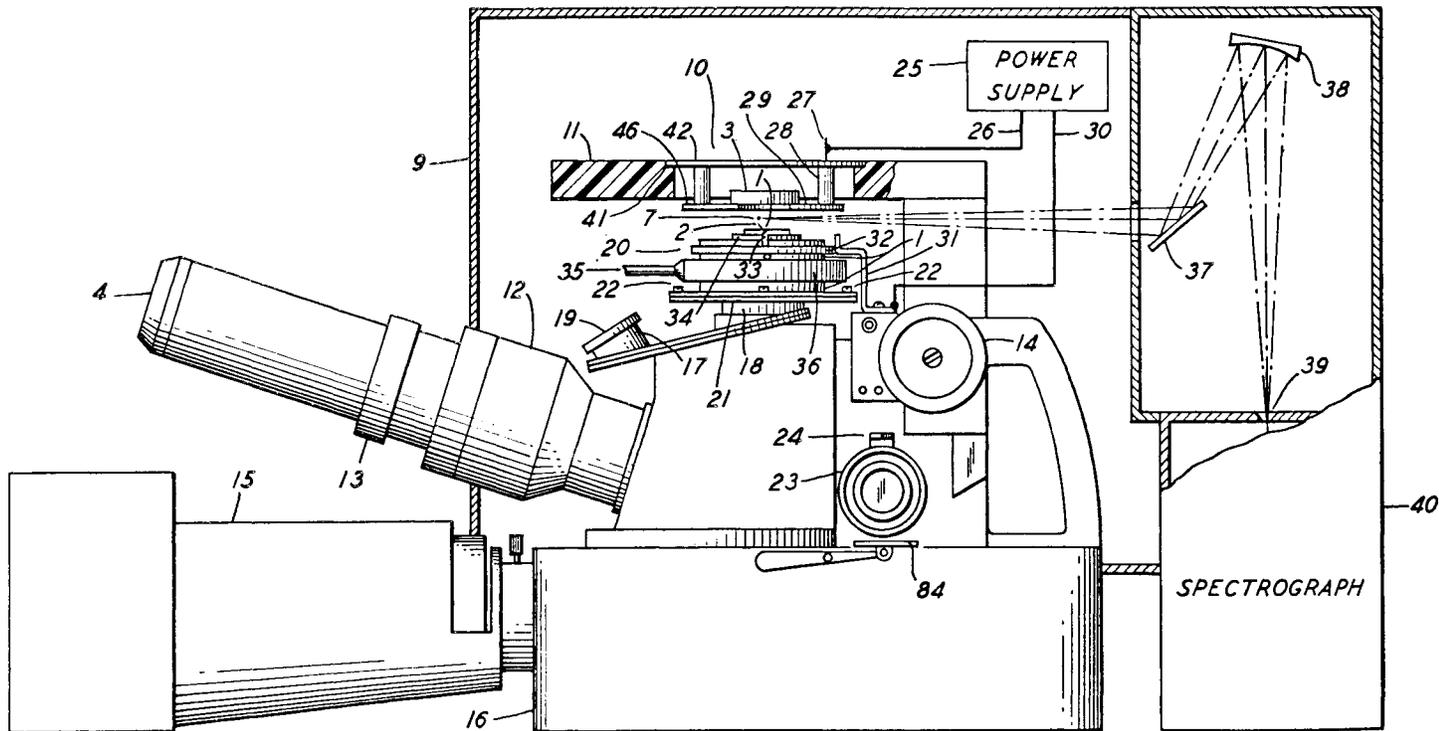


Fig. 1—Outline drawing as it appears in the Spex Atomprobe patent application.

30 microns and optimizing the discharge parameters, they confined the spark to a 5-10 micron area and were able to aim it with an accuracy of 2 microns.

Although Vogel and Kneip amply demonstrated the feasibility of their technique, it was not immediately accepted as a new method for micro-analysis because their apparatus lacked the convenience expected of modern instrumentation.

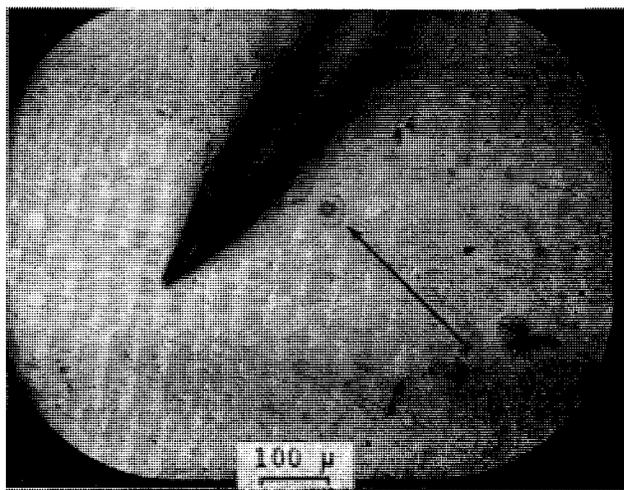


Fig. 2—Aiming accuracy and spark confinement are illustrated by this 15 micron diameter spark crater inside an inclusion approximately 40 microns across.

Like their predecessors, they were light limited and found it necessary to replace the spectrograph entrance slit with the spark gap. Spectra from this system consisted of dots with fuzzy edges and could not be read on a conventional microphotometer. Viewing the sample and aligning the spark were also tedious since these operations were separated, the counter electrode and objective being mounted in different positions on a sliding turret.

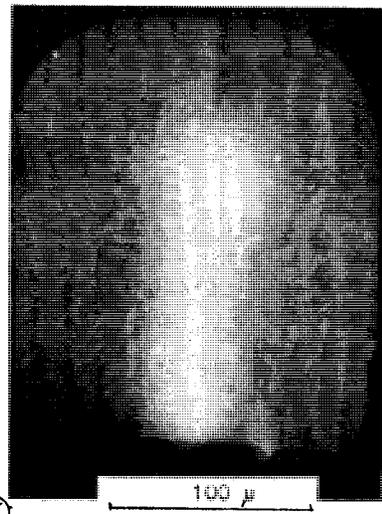
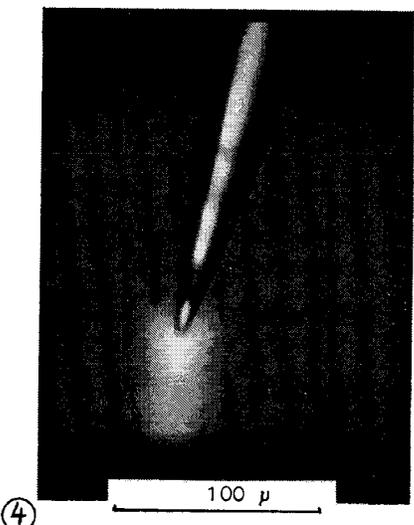
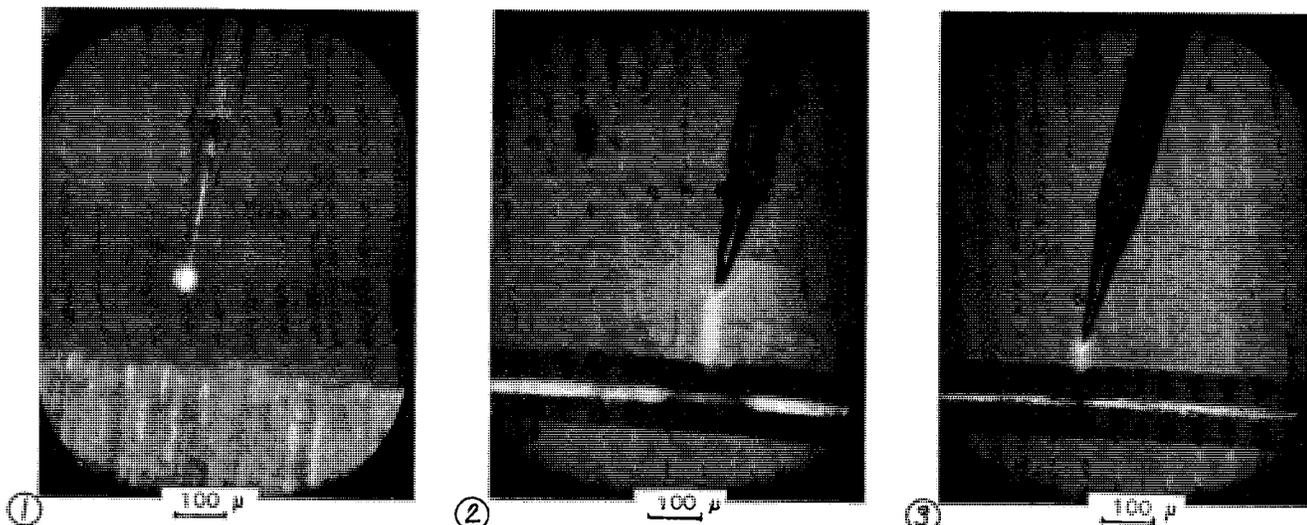
Undertaking the development, refinement and commercial manufacture of the Mallinckrodt device, we, at Spex, have come up with the design shown in Fig. 1. For convenience, we chose and modified an inverted-optics metallurgical microscope. Our electrode holder, rather than being built into an unoccupied objective lens turret position, is mounted on top of the viewing objective. The task of indexing is thereby immensely simplified. Once set up, the cross-hair reticle of the microscope is permanently aligned with the spectrograph and the electrode tip, centered in the viewing field, is automatically aligned with the slit. The faint spark may be observed during exposure, the tip of the counter electrode is clearly visible (Fig. 2) and so good is the aiming accuracy that we are easily able to center a 15-micron diameter spark burn within a 40-micron inclusion. A built-in Polaroid camera lets one supplement the spectrographic data with before-and-after photomicrographs. A spectrographic camera photographs the stationary spark or can be motor driven either alone for surface analysis or in synchronism with a traveling stage for diffusion or distribution studies. Because the photographic speed (f/6.8) of our spectrograph is at least 20 times faster than those employed earlier, not only can the slit be retained but exposure times are usually no more than 15 seconds. Moreover the flux transmittance of our instrument provides sufficient intensity for recording non-integrated photoelectric data.

Our circuitry for producing a microspark is not unlike that devised for ordinary spark work. To confine the spark to a small area, the power requirement of the oscillatory discharge is minimized by keeping the spark gap below 50 microns and by electro-chemically sharpening the electrode to a fine tip. Despite the weak appearance of the spark, however, its power density is comparable with that of a conventional macro spark as evidenced by the fact that spectra of the two are quite similar. To provide several types of spark to suit the analytical circumstances, the excitation voltage and discharge parameters—capacitance, resistance and inductance—may be varied. Tungsten electrodes prepared almost automatically in seconds with the device shown in Fig. 3 maintain their sharp point for several minutes of sparking, a period generally long enough to analyze a complete sample. Spectra of the counter electrode, incidentally, are not normally detected. Contamination from one determination to the next seems negligible but a short preburn will provide insurance for the cautious.

Fig. 4 shows photographs of the spark first at a magnification of 100X, then at 400X. There is very little corona; the discharge has a cross-sectional diameter of around 25 microns. Depth of the crater even after about 3 minutes of sparking is less than 5 μ .



Fig. 3—ATOMPROBE electrode pointer.



ATOMPROBE: PROFILE OF THE SPARK

TOP ROW - x100 MAGNIFICATION

1 - CORONA DUE TO REVERSED POLARITY (POINT NEGATIVE)

2,3 - SPARK WITH 150 μ AND 40 μ GAP

BOTTOM ROW - x400 MAGNIFICATION

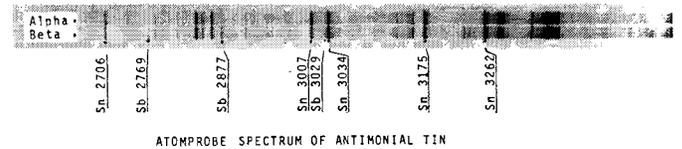
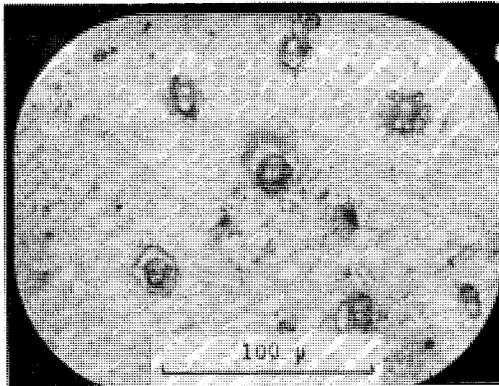
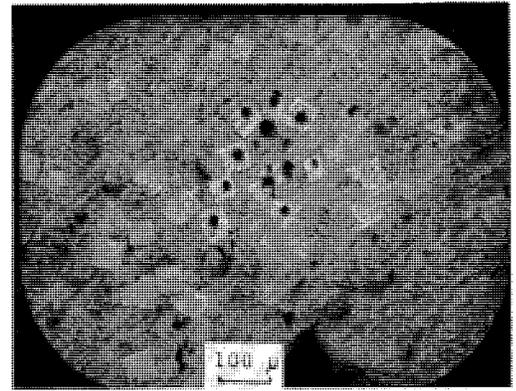
4 - SPARK WITH 45 μ GAP

5 - SURFACE CONFINEMENT OF SPARK: NO MEASURABLE CRATER PRODUCED EVEN AFTER 3 MIN OF CONTINUOUS OPERATION.

Fig. 4



Fig. 5
Antimonial Tin;
Alpha is the matrix
and Beta the
antimony-rich
phase.



The spectrograms of 15 second exposure on a Kodak 103-O plate indicate without reservations the qualitative difference in the antimony content of the beta and alpha (matrix) phases. As usual with spectrographic techniques, the difference between 89% and 50% tin is not readily seen. Having no standards and realizing that the composition of beta cubes has been well known for years, we did not pursue this investigation further.

Zinc-base Alloy

Another specimen brought before us was a zinc-base alloy misbehaving in machinability. Sure enough, its metallogram exhibited a quirk: tiny, bright inclusions that occurred in irregular patches (Fig. 6). Recognizing a foreign substance was, however, as far as the metallographer could go. Could the Atomprobe be more enlightening? In Fig. 7, the spectra of the matrix and inclusions can be compared. Chromium is immediately identified as the intruder and this keystone clue led to a now obvious conclusion. Someone had dumped chrome-plated scrap into the melting pot!

Fifteen seconds of sparking produced a spectrum with enough chromium lines for positive identification. A trivial calculation based on this detectability of chromium will elucidate the extreme sensitivity of the Atomprobe. Averaging 10 microns in diameter, each inclusion contained no more than 4 nanograms of chromium. That photographic operation of the Atomprobe can give meaningful, unquestionable data is thus demonstrated.

Table I. summarizes the pertinent parameters of photographic operations of the Atomprobe, as they were here utilized.

Table I. Photographic Operating Parameters

Spectrograph		Source	
Slit	50 microns x 2mm high	Voltage	1750
Plate	Kodak 103-O	Capacitance	20 pico F
Wavelength coverage	2500-3500A	Inductance	200 μ H
Exposure	15 seconds	Resistance	200 ohms
		Analytical gap	30 microns

DURING this shake-down period we were willing recipients of an array of specimens offered to help us investigate the various characteristics of our new instrument. We twiddled knobs methodically, one by one, finding ways of changing spark parameters and excitation voltage to optimize results of either photographic or photoelectric readout. We tested our prowess on a multitude of samples: free-machining steel, bearing bronze, die-casting alloys of aluminum and zinc bases, artfully prepared binary alloys and (of course!) Spex high-purity metals. Various modes of operation of the Atomprobe evolved from this work; we are here describing results to date which illustrate some advantages as well as limitations of these.

Our 1700 Spectrometer, incorporated in the instrument system, is convertible from photoelectric to photographic readout with the turn of a lever which positions a 45° mirror in the exiting light path diverting it to the camera. The f/6.8 speed is amply fast to record the spectrum in a few seconds. The spectrograph-component of the Atomprobe includes a kinematic mount for interchangeable gratings but for the work herein reported it was equipped with a 600 groove/mm grating. All data were taken in the first order in a 1000A area centered at 3000A (the blaze of the grating).

Antimony-Tin Alloy

The upper left-hand photograph of Fig. 5, is a pretty photomicrograph which emerges when a binary alloy containing 11% antimony in tin is polished and etched. Perfect cubes about 50 microns on a side—an antimony-rich beta phase—appear in random orientation. This and the photomicrograph on the right were taken at 100X with the Polaroid camera of the Atomprobe before and after sparking. The lower photomicrograph, at 400X, shows the shape and indicates the depth of crater produced by sparking for a typical period of 15 seconds. Note the marksmanship attainable by a near-novice.

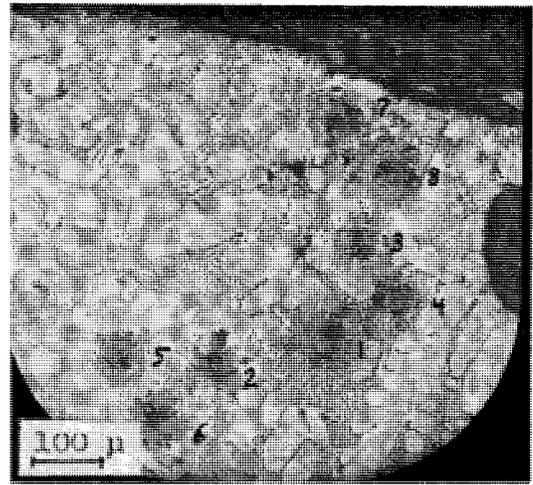
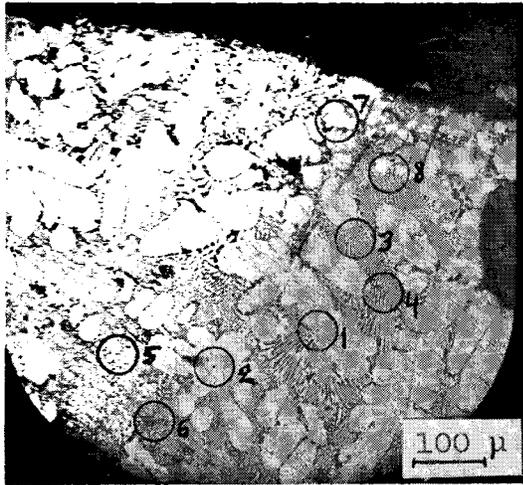


Fig. 6—Zinc die-casting; left, before and right, after sparking. Irregularly-shaped inclusions are high in chromium.

Manganese Bronze

Taking a cue from direct-reading spectrometers dominating the field of routine macro analysis, we reasoned that the photographic approach, while ideal for qualitative surveys and excellent for semiquantitative work, cannot compete with photoelectric detection for quantitative measurements. But the Atomprobe is basically a spectrometer, designed for high photoelectric throughput, for transmitting a known line to a detector and for scanning smoothly over that line. So we put it to work on a proprietary alloy of manganese bronze which, under the microscope, appeared to contain mysterious unidentified foreign objects. A few of these inclusions, which ranged in size from 10 to 1000 microns, were shown in Fig. 2. When their spectra and that of the matrix is compared (Fig. 8), it is evident that only the inclusions are predominantly iron. High concentrations of iron and boron were detected photoelectrically. (The spectral region covered photographically did not include the sensitive boron line pair at 2495 and 2496A.)

Wondering whether these elements constituted an intermetallic compound, we took several intensity ratios of boron 2496A to iron 3020A. Were these to fluctuate, we would con-

clude that either our method was poor or the elements were randomly sprinkled throughout the inclusions. Actually, the ratio of the two lines was found to stay remarkably constant for repetitive burns taken in different areas of a large inclusion (Fig. 9 and 10).

Chances are that this is an intermetallic compound although from these ratios we would not deny the possibility of a uniform mixture. What is not left to question is the remarkable repeatability of the Atomprobe, indicative of the reproducibility of the sparkings as well as the constancy of composition.

The boron and iron were determined with the Atomprobe in a "stored energy mode", in which the spectrometer is set to, and allowed to dwell on, the wavelength of the line being measured. A capacitor in the storage circuit is charged with a fixed potential and then connected to the discharge circuit and spark gap. The energy emitted by the spark is detected by a photomultiplier, and amplified through a picoammeter, the time-constant of which is commensurate with the duration of the discharge. Traced on a fast-response recorder, the deflection is approximately proportional to the total intensity of the spark.

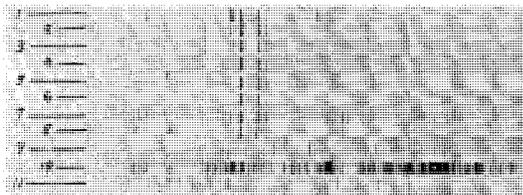


Fig. 7—Zinc-base alloy spectra illustrating the difference in composition of the matrix (1-6) and inclusions (7, 8). Reference spectra are: Tin (9), Chromium (10) and Nickel (11).

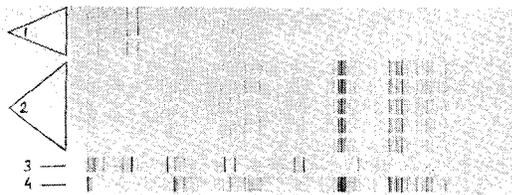


Fig. 8—Manganese-Bronze spectra: (1) is the matrix, (2) an inclusion (3) and (4) are reference spectra of Tin and Iron respectively.

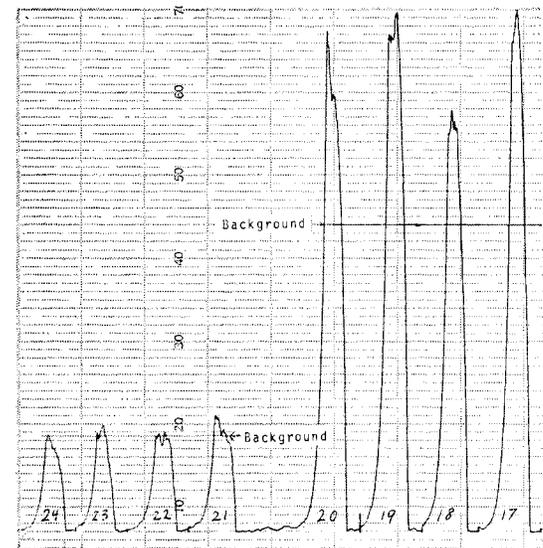


Fig. 9—Boron (2496.78A line) in an inclusion (17-20) and in the Manganese-Bronze matrix (21-24).

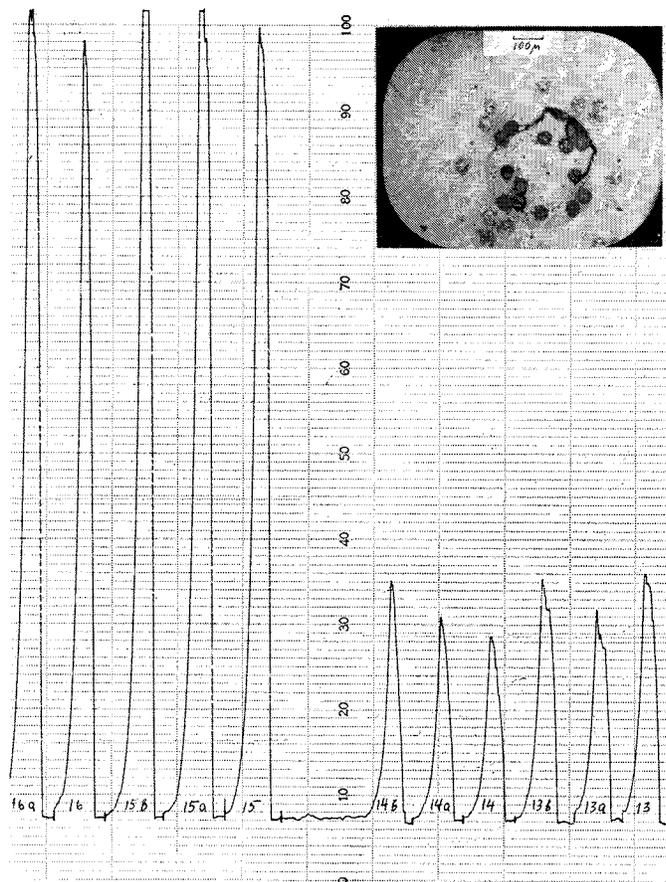


Fig. 10—Repetitive tracings of Iron (3020.64A line) in the matrix (13-14B) and in the inclusion (15-16B), illustrating precision of the "stored energy mode."

Copper—Cupronickel

For the study of diffusion of one metal bonded to another Hurwitz' (6) scanning technique was adapted to the Atomprobe. Sacrificing a spanking new quarter, in which a layer of copper is sandwiched between two 10% nickel-90% copper layers, we spark-scanned across the polished interface for two minutes. The spectrum (Fig. 11) was taken on a plate moving at a rate proportional to that of the microscope stage. Copper is seen to be notably uniform while the gradual build-up of nickel lines is evident. Of course the scanning mode can be recorded photoelectrically as well.



Fig. 11—Simultaneous moving plate and positional traverse from copper to cupronickel, reading top to bottom.

One of the shortcomings of the scanning mode as just described is the width of the track which, though a factor of 10 better than that of Hurwitz' and others, still approaches 50 microns. When scanning at a speed sufficiently low to detect the elements of interest, the dwell time is so long on any one area that the spark wanders laterally as it seeks the path of minimum electrical resistance. To overcome this a variation referred to as step-scanning was developed. Here in place

of the continuous spark, an interrupted discharge is applied. By driving the stage at a constant rate while the spark is turned on and off in a ratio of one second to four seconds, we obtain a perforated track (Fig. 12) about 10 microns wide and a unique, easily interpreted photoelectric bar tracing. The locus of the nickel 3414A maxima corresponds to the variations in concentration of nickel (Fig. 13).

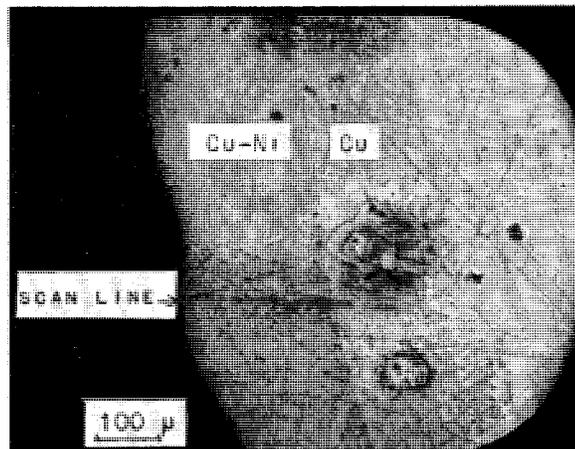


Fig. 12—Step-scan with stored energy excitation. Scan line is about 10 microns wide.

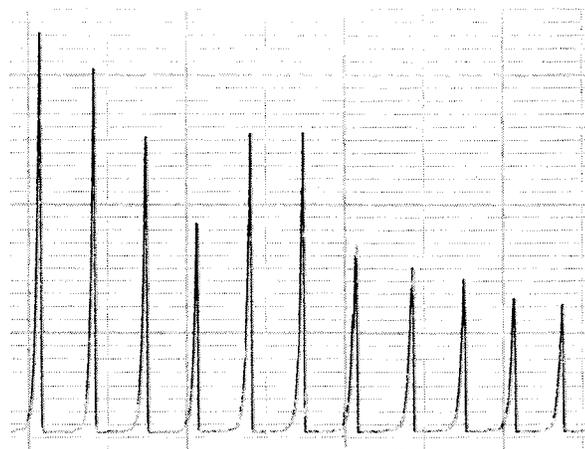


Fig. 13—Distribution of Nickel (3414.76A) in explosive-welded sandwich.

Tantalum Explosively Bonded to Steel

The analysis of an explosively-bonded metal pair presented a paradoxically interesting point: the marked difference between the lines listed in handbooks as *raies ultimes* and the most sensitive lines found with the Atomprobe. *Raies ultimes* are defined as the last spectrum lines of an element to sink into the background when the concentration of the element is reduced to vanishing values. The Atomprobe, on the other hand, detects lines of an element present in heavy concentrations, but localized. The Atomprobe, in this sense, is a micro analytical tool as distinguished from one designed for the detection of trace elements.

The micro-analytical problem at hand was a study of the diffusion of tantalum welded to steel. The handbooks list nine sensitive spark lines in the region from 2635 to 3406A. Our initial attempts were frustrating when we failed to identif

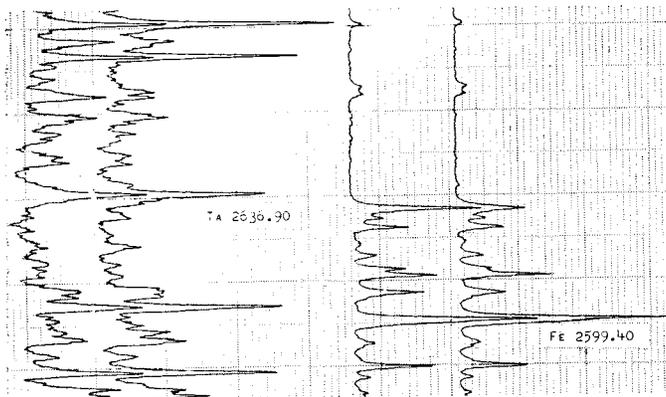


Fig. 14—Wavelength scans of Tantalum and Iron layers.

any of the lines photographically. The appearance (Fig. 14) of the spectrum of the steel layer differed notably from that of the tantalum layer, however, the latter showing a number of lines ultimately identified as tantalum. The 2636.9A line was singled out as being relatively free of background and iron interference. For Fig. 15, the spark was scanned across the interface between the two metals while the spectrometer "sat" first on the tantalum line, then on iron 2599.4A. The traces are juxtaposed so the rate of increase of the one element can be followed and compared with the decrease of the other.

Integrated Microcircuit

Deadline time at hand, we wish to squeeze in a few words on yet another promising application of the Atomprobe: the analysis of integrated microcircuits, those confetti-sized wafers which already have stripped the size and weight of electronic packages to a small fraction of their ancestors! Deposited and etched in successive multitudes of layers, resistors, capacitors, diodes, transistors and their "wiring" are so miniaturized that seeing the components, let alone analyzing them, requires a microscope. To provide a conductive path for the Atomprobe, many of the connectors at the outside of a microcircuit wafer were shorted together and the entire unit mounted face-down

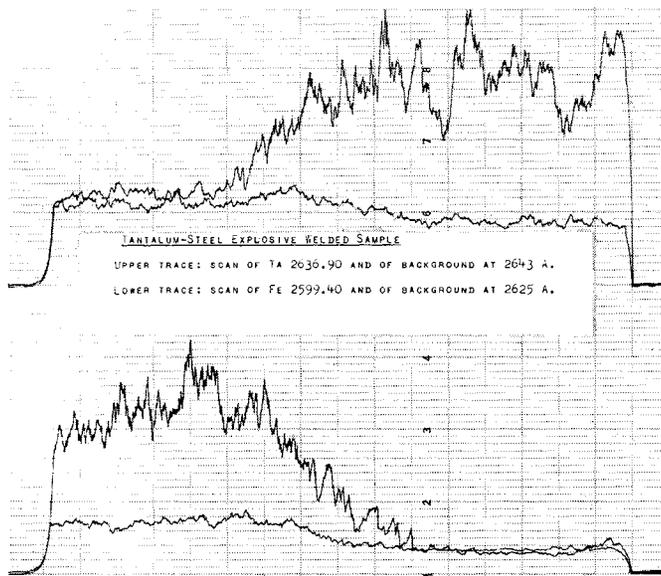


Fig. 15

on the microscope stage. Fig. 16 is a photomicrograph of the wafer before and after sparking to it. The light-colored areas are conductive; the darker, insulating. Several spark scars are visible, one at a boundary between a conductive and non-conductive area. Naturally, the insulating section remained unsparked.

The first and only micro-spectrogram taken of the wafer took us by surprise. Instead of the silver conductor our intuition led us to expect, the "wiring" turned out to be aluminum. Alas, no other elements were evident in the spectrum and we must reluctantly go to press knowing full well that some of the little rectangles outlined beneath the surface probably contain N-doped silicon, some P-doped silicon, tantalum, and possibly other secret ingredients. They will probably show up the day we see this in print. Oh well, that's cliffhanging progress!

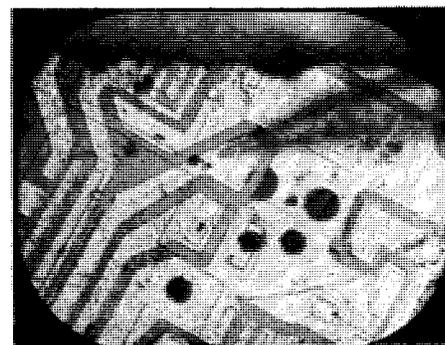
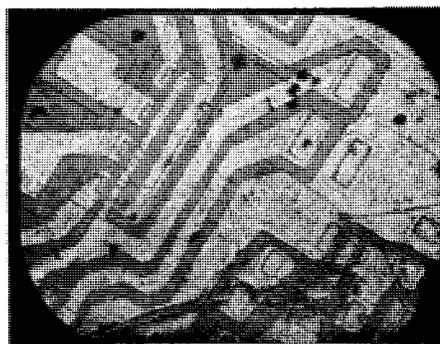


Fig. 16—

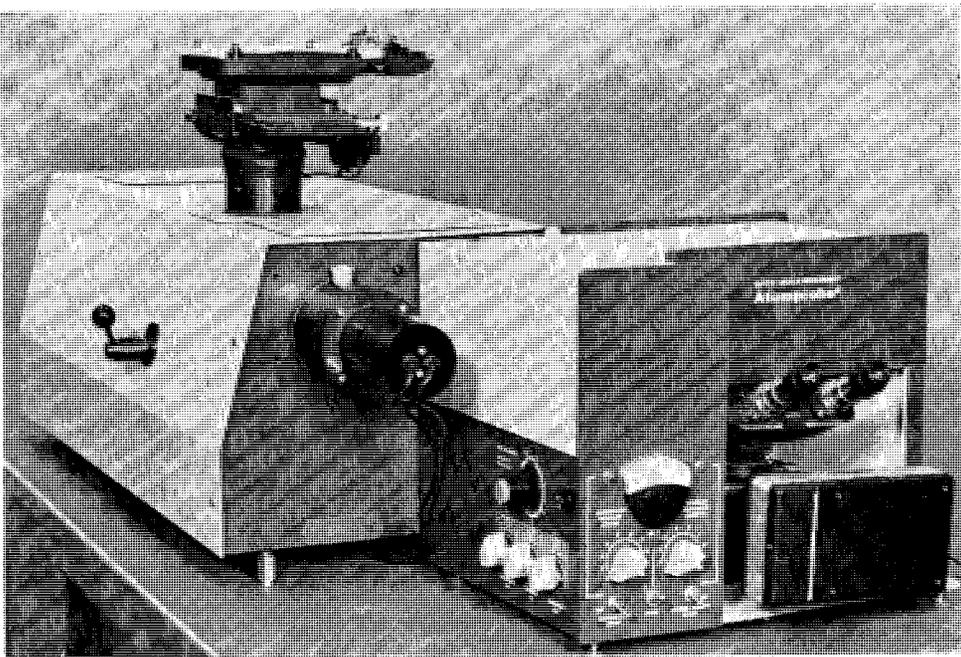
Photomicrographs of a 2 x 2 mm integrated circuit, before (above) and after (right) sparking.

Acknowledgments

We had the germ of an instrument without problems, methods without samples, answers without questions. We wish to thank the following for their timely cooperation in supplying the missing links: Arno Arrak, Grumman Aircraft Company; Walter Battis and Donald LaVelle, American Smelting and Refining Company; C. Manning Davis, International Nickel Company; Kap Suk Yoon, The Singer Company.

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