

SPECTROGRAPHIC ANALYSIS OF GRAIN BOUNDARY  
SEGREGATES IN CAST MONEL METAL

by

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### Abstract of Conclusions

Calcium will precipitate in grain boundary segregates when present in Monel Metal.

Magnesium remains in solution in Monel Metal except when lead is present. Lead and magnesium precipitate in grain boundary segregates.

The high voltage spark has an etching action on cast Monel Metal, removing the grain boundary material.

The arc is more satisfactory than the spark for detecting small percentages of lead and tin in Monel Metal.

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IntroductionGeneral:

The maturing of the steel age has fostered a rapid trend to metallic alloys which have been rapidly developed in an effort to secure specific properties not possessed by the few materials available at the turn of the last century.

A problem especially pertinent to the building of ordnance materiel is that of corrosion. Since this materiel is generally used under conditions where adequate maintenance facilities are not available or may be stored for periods of many years with a minimum of maintenance, it is highly desirable to find materials which possess the high physical properties required in service and, at the same time, are resistant to corrosion. Recently at Watertown Arsenal, investigations have been conducted to determine the extent to which Monel Metal is applicable in ordnance construction.

Monel Metal is a nonferrous alloy of approximately two thirds nickel and one third copper. It is resistant to corrosion and possesses physical properties comparable

with good steels. There are several grades of Monel Metal used, each being distinguished by the amount of alloying elements, other than nickel and copper, present in the metal.

Specific:

In 1935, an investigation was made by Captain S. L. Conner, of Watertown Arsenal, to determine the practicality of centrifugally casting Monel Metal of the various grades. Experimental castings were made from melts of thirteen different compositions. The results were found to be uniformly good with the exception of two castings containing lead and tin which were unintentionally introduced in the melt. Tin and lead were not present in any of the other castings.

The only other essential difference in composition between the two poor castings was that one contained about three and one half per cent aluminum, while the second contained one tenth of a per cent aluminum, the greater amount having been added for hardening. Test specimens made from the two castings showed poor properties. The tensile strength was the same as the yield point. The reduction of area and elongation were zero. Micrographs of the castings showed that the metal was dirty, there were inclusions in the grains and segregations on the grain boundaries.

It was believed that the poor quality of the metal was due to the grain boundary material in these two castings. The test specimens broke with an inter-crystalline failure which was attributed by the investigator to segregations of tin and lead on the grain boundaries. These two elements were not present in the other castings though they showed inclusions similar to those in the poor metal.

To verify this conclusion and to determine the elements present in the grain boundary segregations, this thesis was undertaken. The problem being one of local analysis, the spectrograph was used.

## II

General Theory

A discussion of the theory of spectroscopy or spectrographic analysis is beyond the scope of this work. There is much in the literature available for anyone desiring fundamental work. "Spectroscopy" by E.C.C. Baly, "Metallurgical Analysis by the Spectrographs", by D. M. Smith, and "Foundations and Methods of Chemical Analysis by the Emission Spectrum" by Gerlach and Schweitzer are excellent. However, certain aspects of spectroscopy as applied to this work are worthy of detailed considerations. It has been the author's observation that too frequently investigators, in reporting their work, omit important details, a knowledge of which is necessary to duplicate their results. I refer especially to the electrical circuit employed.

A spectrograph is an instrument designed to break up light into its constituent wave lengths to form a spectrum which is photographically recorded. The foundation upon which qualitative analysis by the emission spectrum rests, is the fact that an element which has been rendered luminous, emits certain invariable lines which are characteristic of the element.

The means of excitation are the low voltage arc or the high voltage condensed spark. The arc spectrum is the spectrum of the atom while the spark spectrum is the spectrum of the ion and contains lines distinctive to itself. It must not be supposed, however, that the arc spectrum contains no spark lines or the spark spectrum no arc lines.

It is therefore evident that the nature of the light source is a primary consideration if the desired results are to be obtained. In this investigation, the arc was discarded at the outset as a source due to the fact that the metallic electrodes melted. This defeated the purpose of the work since the problem was one of analyzing the exposed surface of the electrodes.

The method of illumination used was the electric spark obtained by the discharge of a high potential current from a step up transformer with a condenser in parallel with the spark gap. The sparks were due to the discharge of the condenser and were caused to pass through a self-induction coil in series with the spark gap and between the surfaces of the metal being investigated.

The spark discharge tends to excite lines which are relatively weak in the arc spectrum. These lines are due to the ionized atom and, in general, the state

of ionization depends on the intensity of the spark discharge. Therefore, the size of the condenser is an important matter in spark spectra. The condenser, whatever its capacity, must be charged to sufficient potential to discharge across a gap of about one eighth inch. The capacity of the condenser determines the quantity of electricity which passes in each individual spark, or in other words, the intensity of the spark. The degree of ionization existing depends upon this intensity.

The spark spectrum contains lines due to the oxygen and nitrogen of the atmosphere. The presence of these air lines is not a disadvantage since their wave lengths are known and they may be used as standards in an approximation of unknown lines. Also in a comparison of different spectra, they will serve to correctly orient the two spectra, being present in both. The air lines may be made to disappear by introducing a self-induction coil in the circuit.

Considerable study has been made to determine the mechanism of the spark. An interesting summary of this work is given by Baly in "Spectroscopy" in which he states in part: "Metal lines were due to oscillatory discharges, and all were curved so that they

must start from the electrodes and travel with decreasing velocity towards the center, the speed being calculable from the curvature of the lines; also it was noticed that this metallic discharge takes place after the discharge through the air. The mechanism of this is evidently as follows: The spark first passes extremely rapidly through the air, a single discharge; this vaporizes the metal which then spreads across the spark gap, conveying the current. The velocity of travel of the metallic vapor varies with different metals from 1300 to 400 metres a second, and appears to be quicker with metals of low atomic weight, but varies for different lines of the same metal."

## III

Equipment

This investigation was made in the spectrographic laboratory at Watertown Arsenal. The equipment of this laboratory is similar to that of most industrial spectrographic laboratories with the exception that a diffraction grating is used rather than a prism. The most apparent advantage of the grating lies in the constant dispersion over the whole spectrum as compared with the crowding of the prism spectrum toward the visible end.

The essential components of the grating spectrograph are the activating apparatus, the collimating lens, the mechanical slit, the grating, the cassette or film holder and the arrangement for holding the cassette in proper alignment. In order to be in proper adjustment, the mechanical slit, the grating, and the cassette must lie on the circumference of a circle whose diameter is equal to the radius of curvature of the grating.

For the reader not familiar with the spectrograph, the following illustrations will give a clearer conception of the apparatus.

### Figure 1

Figure 1 shows the activating apparatus, the collimating lens and the mechanical slit.

Both alternating and direct currents are available for the source. The electrode holder is equipped with cross and longitudinal feeds. As used in this work, the electrodes were mounted, one above the other, and moved uniformly at right angles to give a spark from a constantly changing surface which would at the same time be always focused on the slit.

The collimating lens is a quartz glass lens with a focal length of 24 inches.

The mechanical slit is a 20 m/m slit. The parallel steel jaws of the slit are held together by a spring and the width of the slit may be varied by a screw feed which is graduated in .005 m/m divisions. The length of the slit may be adjusted by a diaphragm with a V-shaped opening which slides across the front of the slit.

Fig 1

- 1. Electrode Stand
- 2. Colimating Lens
- 3. Mechanical Slit

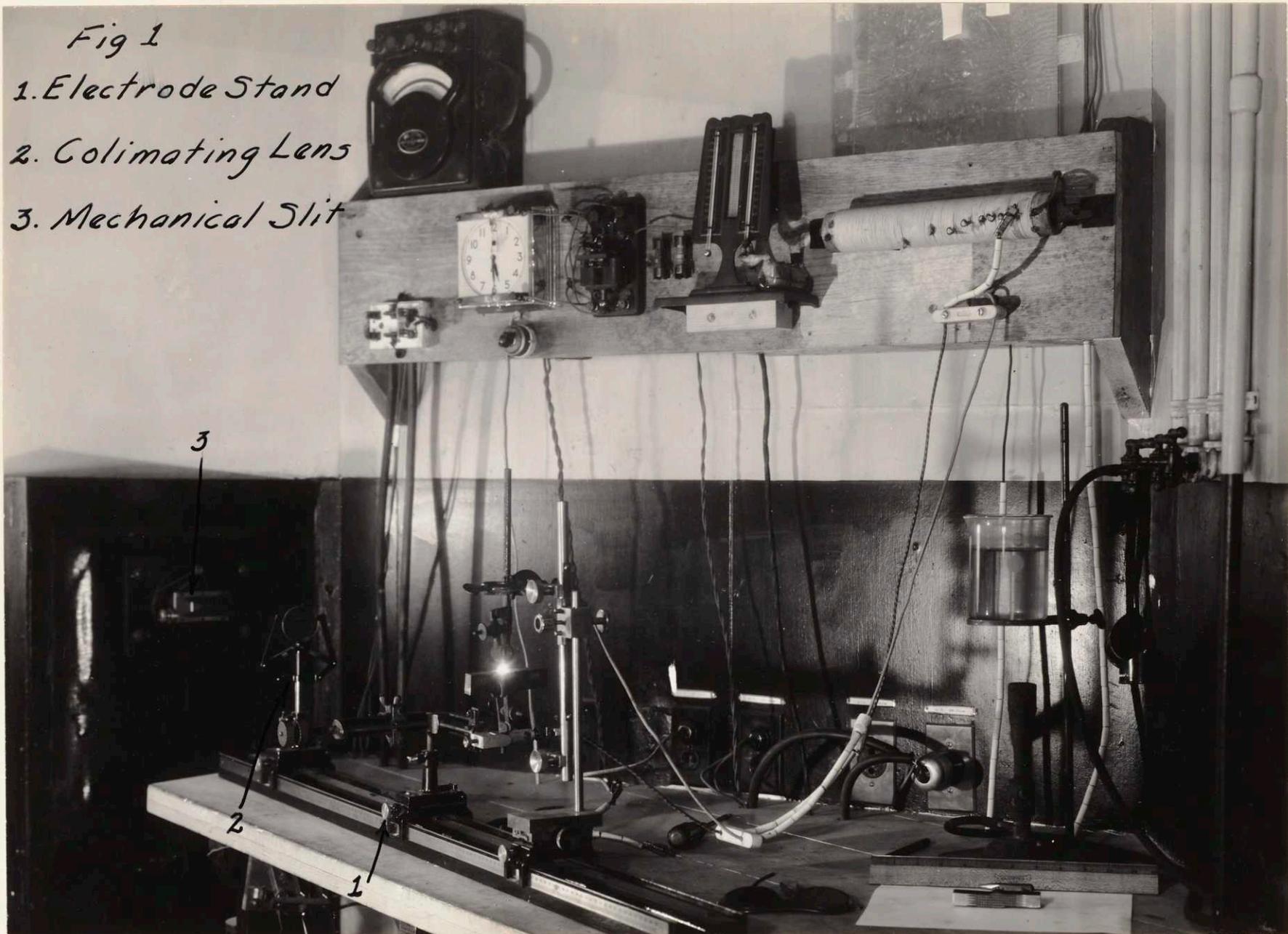
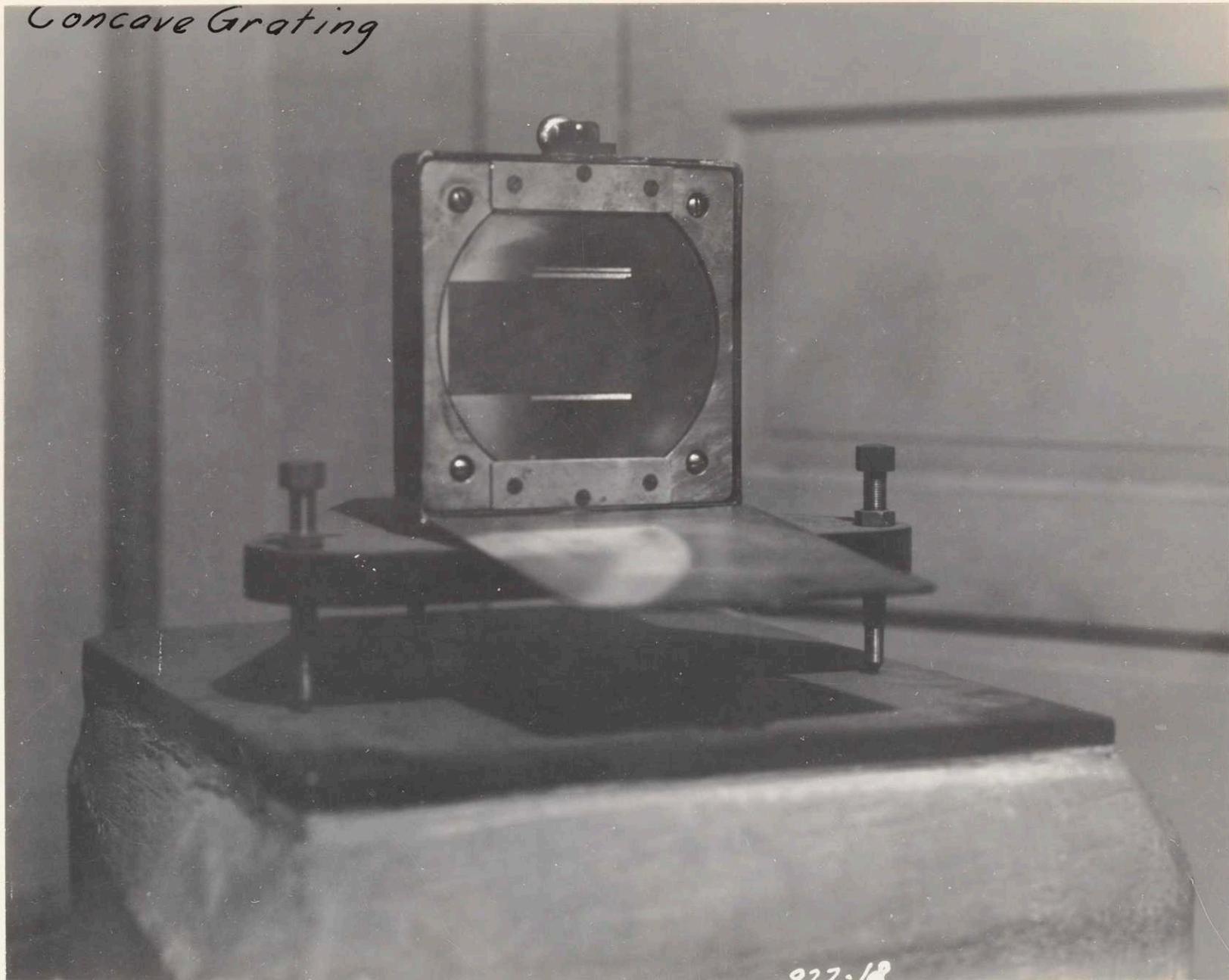


Figure 2

Figure 2 shows the concave grating of the laboratory.

This grating is a three meter radius of curvature mirror ruled fifteen thousand lines to the inch. It is mounted upon a concrete pedestal for freedom from vibration and stability.

*Concave Grating*



927-18

Figure 3

In Figure 3 is shown the shutter from the grating side. This is actuated by the solenoid coil to the left which is electrically connected to a switch in the source room so that the shutter may be opened or closed at will.

The cassette carries the film holder and rests upon a circular track of two rails and a center guide. It is free to be moved to any position on the track. A slide on the center guide keeps the cassette in proper focus on the circle.

The track rests on three concrete blocks. Set screws are provided on the blocks for adjusting the track to the proper curvature.

Fig 3

- 1. Shutter
- 2. Cassette
- 3. Film Holder
- 4. Track

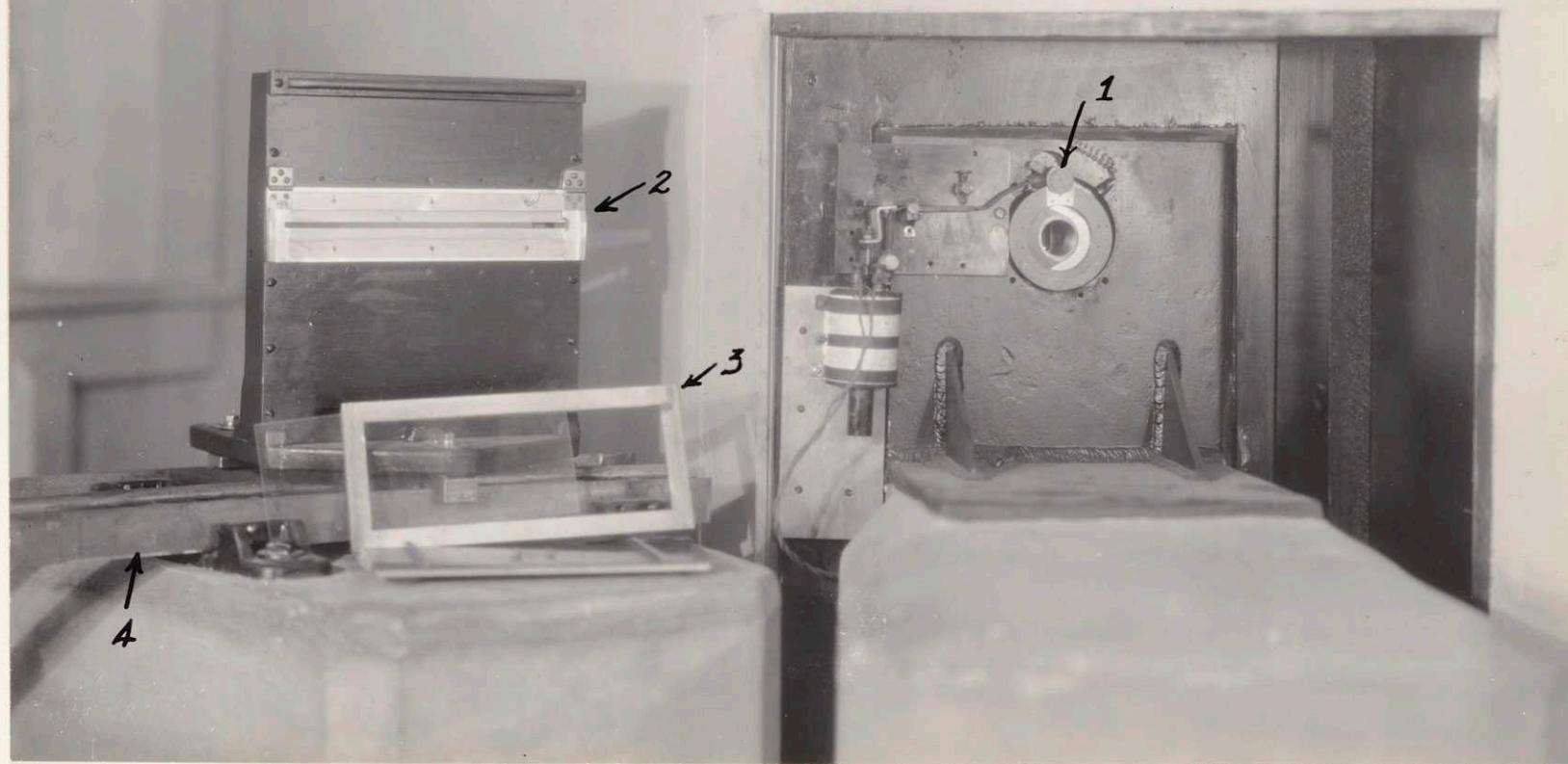
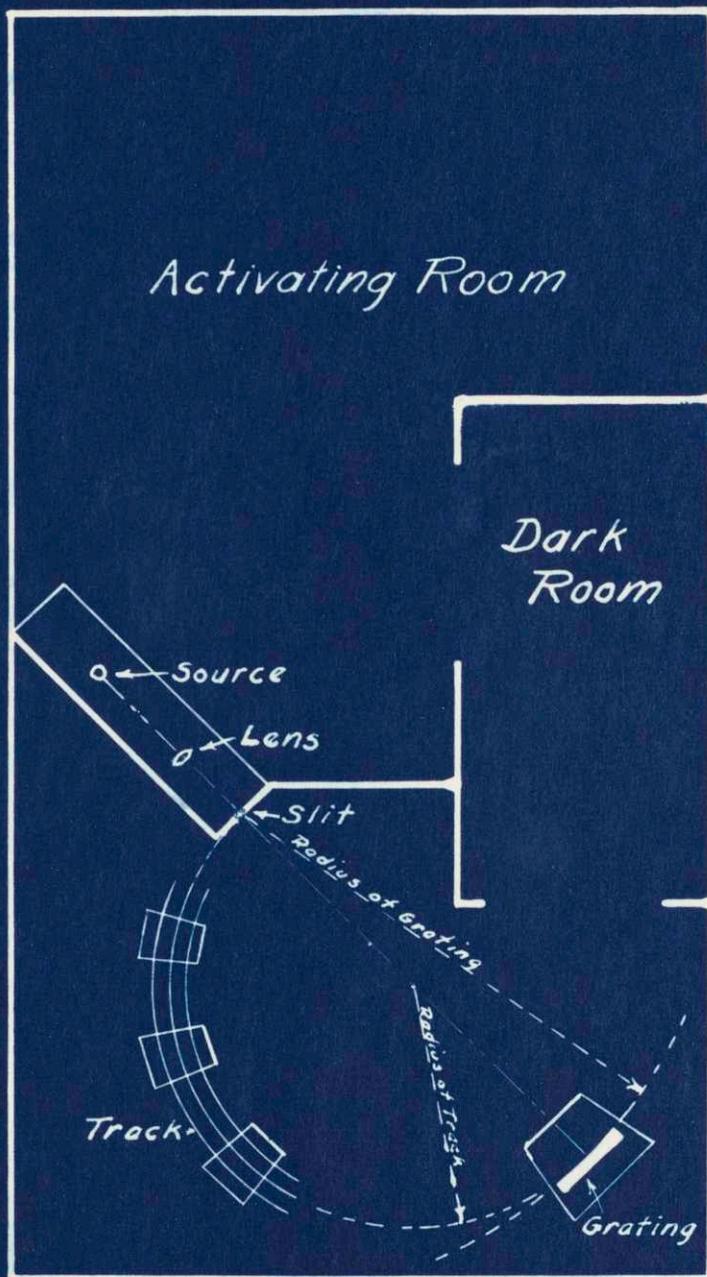


Figure 4

Figure 4 shows the set up of the spectrographic laboratory. This drawing is not to scale.

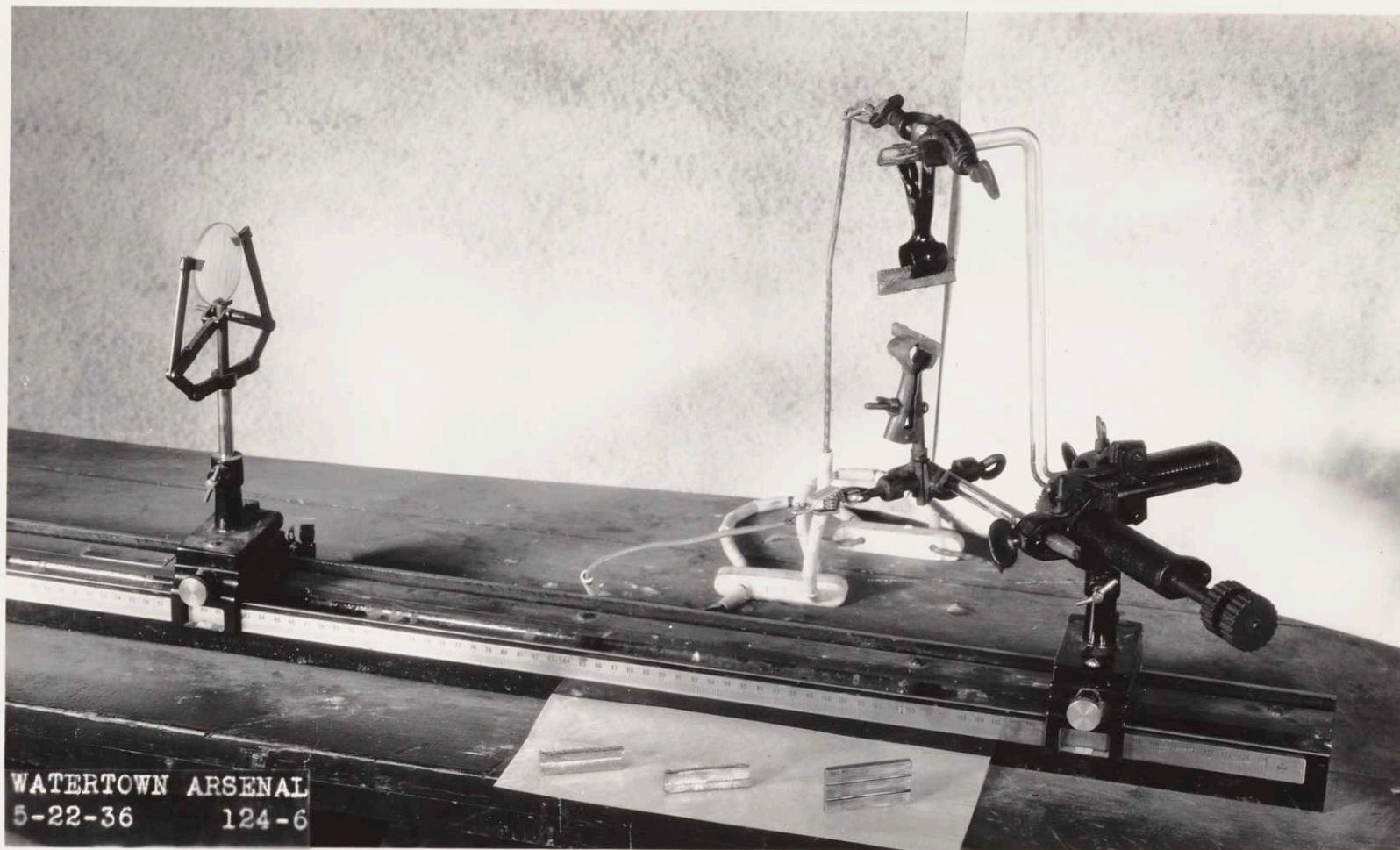


Spectrograph Lab.  
 Watertown Arsenal  
 J.A. Barclay

Figure 5

Figure 5 shows a view of the electrode holder and the method of mounting the electrodes.

In the foreground is one of the samples as prepared and one which has been fractured.



## IV

Procedure

The problem at its inception appeared to be one of qualitative microanalysis of the elements present in the grain boundaries of the poor metal. Obviously it would be a tedious if not impossible task to separate sufficient grain boundary material to analyze by wet chemical methods and the results of such procedure would be doubtful. However, since the test specimens of the Monel Metal showed no elongation and broke with an intercrystalline failure, a layer of grain boundary segregates is exposed on the surface of the fracture. This layer of grain boundary material would contain its constituent elements in a much greater concentration than the average percentage shown by wet chemical analysis provided there were segregations of alloys or impurities in the grain boundaries.

For analysis of this surface layer of material the spectrograph was used, the source of light being spark excitation.

As the surface was sparked a small amount of the surface material was volatilized. Since each successive time the surface was sparked, the amount of grain boundary

material was decreased, the intensity of the lines in the spectra would likewise decrease.

A similar problem was investigated by Gerlach and Schweitzer who made a spectrographic study of the grain boundaries of gold containing small percentages of lead, which was brittle metal, and they determined that the lead existed in the grain boundaries. They reported, "We have carried out a set of special experiments regarding the intensities of the lines of lead, in one case with lead in gold, in another with lead in tin. Tin plus  $n\%$  lead did not exhibit this phenomenon of the decrease in the intensity.

A spectrogram was taken of a sample of Au plus  $1\%$  Pb and under it a spectrum of Sn plus  $1\%$  Pb. Since gold has a very small vapor pressure relatively to tin, the spectrum of the latter is considerably more intense than that of gold. The times of exposure were then so varied that a line of lead in the spectrum of Au plus  $1\%$  Pb acquired exactly the same intensity as the same in the spectrum of Sn plus  $1\%$  Pb. Next the spectra of other specimens, i.e. Au plus  $0.1\%$  Pb and Sn plus  $0.1\%$  Pb, Au plus  $.01\%$  Pb and Sn plus  $.01\%$  Pb were photographed so that the intensity relations between the lines of primary substances Au and Sn remained exactly the same

as those obtaining in the correctly coupled 1% Pb spectra. In practice this is accomplished by reproducing the condition of equality of intensity of a coupled pair made up of an Sn line and an Au line. The selected line of lead in the gold and tin spectra will continue to exhibit the same intensity. Experiments made upon other lines of Pb have verified this result. This shows therefore, that for the spark discharge between electrodes made up of Au plus n% Pb, after sparking of the exposed grain boundaries, the lead behaves exactly as though it were distributed therein as uniformly as in the tin.

These experiments demonstrated yet a further fact in metallographic chemistry. When the specimens of gold contained a little copper in addition to lead, approximately of the order of the lead content, the copper was found to exhibit precisely the same grain boundary effect as the lead. Gold copper, on the other hand, without lead showed a permanently constant copper line intensity. From this it may be inferred that the copper and lead are structurally arranged in the same manner. The brittle grain boundary layer is accordingly either an Au-Pb or a Pb-Cu compound. If silver happened to be present as well, the intensity of the Ag spectrum lines was found

to remain constant, which showed that the silver was evenly distributed in the gold. Etching experiments with nitric acid showed moreover that the copper vanished with the lead, not so the silver; whereas in lead free alloys the copper, like the silver, showed itself to be completely protected by the gold.

To the interpretation of the above experiments in terms of grain boundary effect, i.e. as experimental evidence for the assumption that lead occurs between the crystalline granules of the gold, it might be objected that in the course of the unavoidable heating of the electrode surface, lead volatilizes more rapidly by reason of its high vapor pressure than the gold, much in the same way as it is practicable by heating brass in vacuo to distil out the constituent zinc. There are, however, a number of experimental data which disarm this objection. In the first place, we have in this connection the above mentioned experiments demonstrating the equal relative sensitivity of the lines of lead in gold and tin. Next, there is no intelligible reason why specimens containing lead to the extent of 0.1% upwards should behave differently from those of lower concentrations since all specimens were examined in precisely the same manner. What supports our interpretation more forcibly than any other argument is the fact that the copper in gold

containing lead behaves exactly as does the lead.

Finally, analyses of tin contaminated with a small proportion of mercury do not show this effect although in this case similar differences in the vapor pressures of the primary substance and the secondary substance are present."

No quantitative results were attempted in this investigation, all changes in intensity of lines being considered as relative to the initial spectrogram of each sample. The change in relative intensity indicated only the relative change in the amount of the element excited in the spark.

The primary requisite to spectrographic work is a thorough knowledge of the spectra of the elements studied. Such study involves the measurement of many lines and careful study of the spectra of pure elements. To the beginner this may seem tedious, however it is well worth while for one soon learns to identify the persistent lines of the spectrum by visual inspection. The procedure is then rapid and verification of lines may be made by comparison with film records of identified lines.

For this preliminary investigation, samples were cut from the two poor castings. These were designated P-1 and P-2. They were analyzed by Watertown Arsenal as follows:

P-1Chemical Composition

<u>C</u>	<u>Mn</u>	<u>Si</u>	<u>Ni</u>	<u>Cu</u>	<u>Fe</u>	<u>Al</u>	<u>Mg</u>	<u>Sn</u>
.305	.60	.185	65.07	28.35	1.86	3.44	.006	.08
			<u>Pb</u>	<u>P</u>	<u>Ca</u>			
			Tr	.002	.01			

Physical Properties

<u>Y. P.</u>	<u>T. S.</u>	<u>Elong.</u>	<u>Red.of Area</u>
59,000	59,000	0	0

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P-2Chemical Composition

<u>C</u>	<u>Mn</u>	<u>Si</u>	<u>Ni</u>	<u>Cu</u>	<u>Fe</u>	<u>Al</u>	<u>Mg</u>	<u>Sn</u>	<u>Pb</u>
.22	.56	1.69	65.02	29.60	2.72	.11	.026	.03	Tr
			<u>P</u>	<u>Ca</u>					
			.023	.014					

Physical Properties

<u>Y. P.</u>	<u>T. S.</u>	<u>Elong.</u>	<u>Red.of Area</u>
26,000	26,000	0	0

These samples were compared with two from the castings showing the best properties. These were designated G-1 and G-2 and were of the following composition:

G-1Chemical Composition

<u>C</u>	<u>Mn</u>	<u>Si</u>	<u>Ni</u>	<u>Cu</u>	<u>Fe</u>	<u>Al</u>	<u>Mg</u>	<u>P</u>	<u>Ca</u>
.21	.56	.20	63.67	30.75	1.30	3.30	.006	.003	.01

Physical Properties

<u>Y. P.</u>	<u>T. S.</u>	<u>Elong.</u>
69,000	97,500	30%

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G-2Chemical Composition

<u>C</u>	<u>Mn</u>	<u>Si</u>	<u>Ni</u>	<u>Cu</u>	<u>Fe</u>	<u>Al</u>	<u>Mg</u>	<u>P</u>
.215	1.04	.135	65.10	31.80	1.30	.16	.205	.024
			<u>Ca</u>					
			.010					

Physical Properties

<u>Y. P.</u>	<u>T. S.</u>	<u>Elong.</u>
33,000	73,000	27.9%

A study was made of the spectra of the elements known to be present in the metal and then the spectrum of the Monel Metal samples was considered. The investigation turned naturally to the first order spectrum since the shortest possible time of exposure was desired and because of the small percentage of lead and tin present, it was necessary to use the order giving the greatest conservation of light.

The metallographic conclusion that lead and tin segregate at the grain boundaries was assumed to be correct and verification attempted. A table similar to that given below was prepared showing the persistent lines of lead and tin and the lines of the spectrum 5 Angstrom units greater and less than these persistent lines. In this way lines were selected for study which were not close to other lines of the Monel spectrum.

<u>A. U.</u> <u>Wave Length</u>	<u>Element</u>	<u>Intensity</u> <u>Spark</u>
3644.39	Ca	4
3643.98	Dy	3
3643.18	Co	2
3643.16	Pt	6
3642.81	ScII	10
3642.68	TiI	3
3642.05	Ta	2

<u>A. U.</u> <u>Wave Length</u>	<u>Element</u>	<u>Intensity</u> <u>Spark</u>
3641.84	Cr	3
3641.66	Tb	4
3641.53	La	2
3641.41	W	10
3641.335	TiIII	10
3641.3	Cs	4
3641.25	Er	4
3640.64	Ru	2
3640.39	Fe	3
3640.34	Os	2
3639.86	Rb	5
3639.81	Cr	5
3639.6	Sb	3
<u>3639.584</u>	<u>Pb</u>	<u>10R</u>
3639.52	Rh	3
3639.44	Co	2
3638.80	Pt	3
3638.68	Er	1
3638.45	Tb	5
3638.30	Nh	5
3638.29	Fe	2
3637.83	SbI	6
3637.76	Ny	5

<u>A. U.</u> <u>Wave Length</u>	<u>Element</u>	<u>Intensity</u> <u>Spark</u>
3637.5	Se	10
3637.46	Ru	2
3636.59	Cr	3
3636.26	Lu	3
3636.22	Ir	3
3635.9	Cu	2

In studying the Monel Metal spectrum with the cut samples P-1 and P-2, the lines of lead and tin did not appear in the spectrogram. The current in the primary circuit was varied from 2 to 10 amperes in increments of 2 amperes and exposures of two, four, eight, sixteen, and twenty minutes taken without success. Attention was then turned to the arc as a means of excitation. In the spectrogram taken with the arc using 3 amperes and thirty seconds exposure time, the persistent lines of lead and tin were both present.

In his investigations of quantitative analysis by the internal standards method, D. M. Smith reports that traces of lead were more easily detected by the arc method. However, in the analysis of tin in lead, the spark method detected percentages of tin as low as .003%.

In the course of studying the Monel Metal spectrum, an unlisted nickel line was found. The wave length as determined from measurements with a dividing engine was 3548.31 Angstrom Units.

All spectrograms were recorded on Eastman commercial film. Because of shrinkage of the film, measured wave lengths could not give absolute accuracy in determining unknown lines. To positively identify lines, the spectrum of the metal being investigated was photographed

Spectrum 1 shows the method of identifying lines. This is a spectrum of Monel Metal with pure nickel superimposed upon it.

Spectrum 2 is one with inductance in the spark circuit. Note the absence of background as shown in 3 which is the same spectrum made without any inductance in the circuit.

1

2

3



with the flap of the cassette raised which recorded the full length of the lines. The flap was then lowered and an exposure made using a pure sample superimposed upon the original spectrum. This gave a short darker section in the center and coincided with the longer lines of the first exposure. (Fig. 6). Once a line was verified as existing in the spectrum by this method, it was considered sufficiently accurate thereafter to check its presence by comparison with another film. Since the spectrum of Monel Metal contains the many lines of nickel, accurate orientation was possible.

When the presence of lead and tin in the two samples of poor metal was verified, the investigation turned to the question of whether these elements existed as segregations in the grain boundaries and if the concentration was great enough to be recorded using spark excitation. Electrodes were prepared from the four castings selected. These electrodes were one inch wide, two inches long and one-eighth inch thick with a groove one-sixteenth inch deep cut along the width parallel to the longer axis. When broken along this groove, a fractured surface two inches long and one-sixteenth inch wide was exposed. The electrodes were then placed in the holder with their length along the axis of the arms. (Figure 5). The electrodes could then be moved so that the location

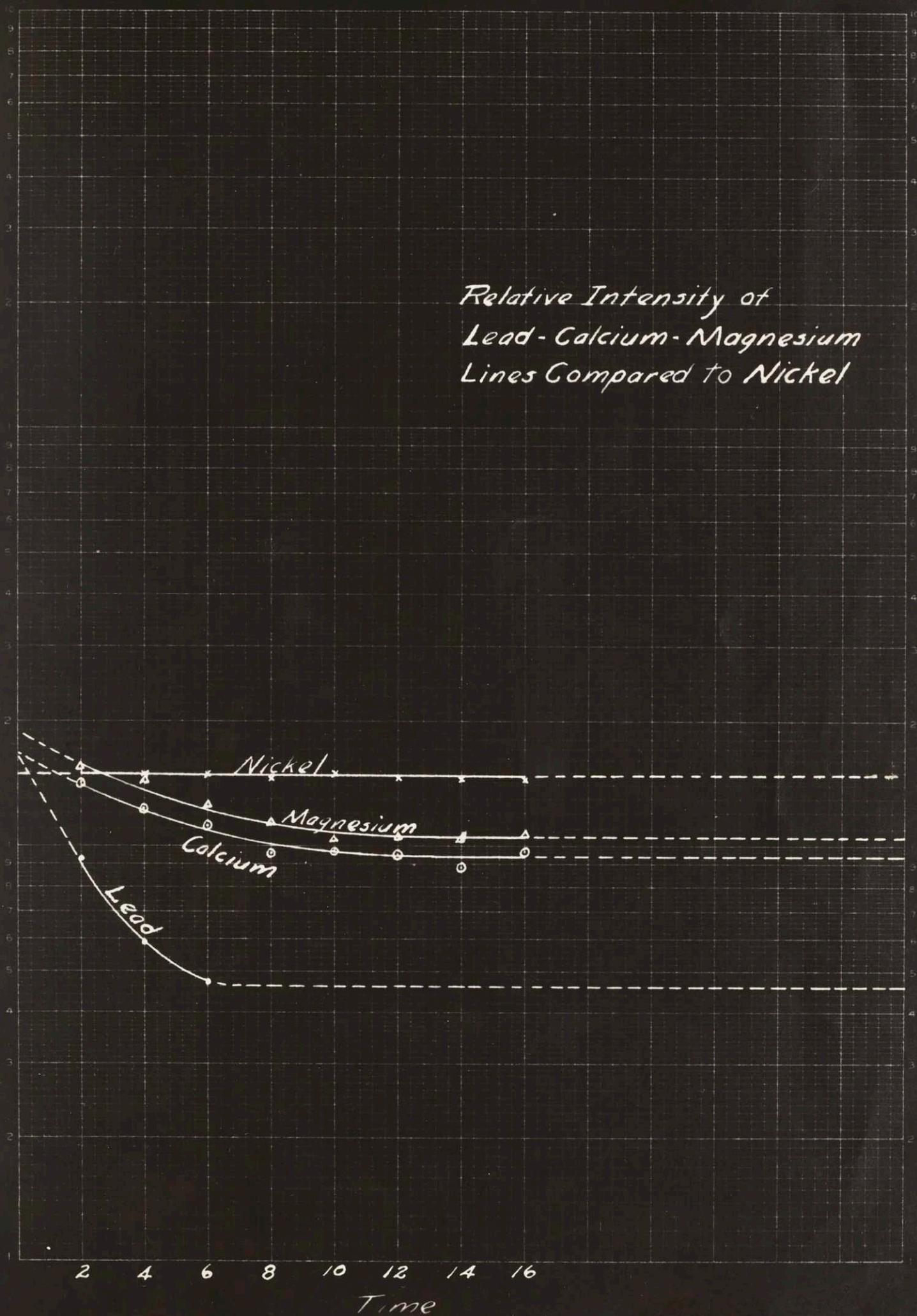
of the spark would remain constant with respect to the slit and at the same time the surface being sparked would be slowly changing.

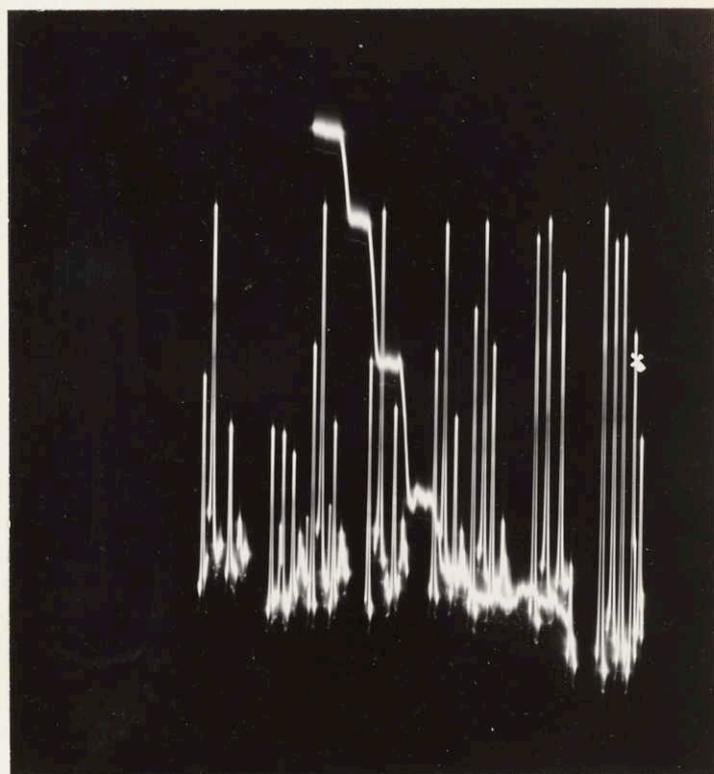
Since the spark vaporizes a small amount of metal from the surface being sparked, the amount of grain boundary segregations exposed diminishes with the length of time the surface is sparked. By constantly moving the electrodes so that the point of the spark was moving to a different point on the surface and recording the spectrum each time the fractured surface was completely sparked over, any lines due to material in the grain boundaries would decrease in intensity as the relative per cent of the element present on the surface decreased. The gap between the electrodes was adjusted to one quarter inch and they were moved at such a rate that the spark passed over the entire surface in two minutes. This time was used for each exposure.

The first spectrograms of the fractured surface did not show any lead or tin, but the persistent lines of calcium clearly showed a diminishing intensity with successive exposures. This was believed to be due to a surface contamination or embedded particles of the cutting wheel used to prepare the samples, since the original chemical analysis did not show calcium as being present. Gerlach and Schweitzer report that calcium and magnesium

The graph shows the diminishing intensity of the lines of lead, calcium, and magnesium with continued sparking, as compared to nickel which remains constant. This plot was made from the photodensitometer record shown.

*Relative Intensity of  
Lead-Calcium-Magnesium  
Lines Compared to Nickel*





0-100-100-1

Pb-4007

Ca-3933

3

Mg-2902

P-2 Fracture  
2 min Exposure - .065 lit - 4amps

were always present in the spectrum due to particles of dust in the air, however, this would not account for result observed.

Other samples were then cut with a hack saw and carefully washed in water and alcohol before fracturing. Precautions were taken not to touch the fresh surface and contaminate it in this way. These samples also showed the diminishing effect of calcium and subsequent chemical analysis showed .01% Ca present in three of the samples and .014% in P-2, proving that this element existed in the metal as an impurity.

An increase in the capacitance of the condenser brought the lines of lead and magnesium into the spectrograms with a most striking effect. The magnesium lines in the spectra of samples G-1 and G-2 remained constant while in the case of the other two samples of the poor metal the lines of both magnesium and lead diminished in intensity with successive exposures. The lead line, 4057 A.U. appeared strongest, though the persistent lines 3683 A.U., and 3639 A.U. were also present. These lines showed quite strongly in the first exposure and diminished until they disappeared in the fourth exposure. The magnesium lines 2795 A.U., 2802 A.U. and 2852 A.U. appeared in the sample containing .026% Mg and diminished until they reached a constant intensity in the

sixth exposure. With the sample containing .006% Mg, the persistent line 2795 appeared in the first two exposures only. J. S. Walker did quantitative work on the spectrographic analysis of magnesium and was not able to obtain satisfactory detection of this small percentage.

Unfortunately the prints of the spectrograms do not show the very light lines nor the striking effect of the diminishing intensity as clearly as the original films. A densitometer record was made from a spectrogram of sample P-2 and the relative intensities plotted, showing that the major constituent lines remain constant throughout the successive exposures while the lines of the elements present in the grain boundary segregations diminish successively until they reach a constant value. The extrapolations of these curves do not represent true intensities of the lines, but rather the intensity in an increment of time.

The lines of tin did not appear in the spectra at any time. It was therefore believed that the tin present in the Monel Metal was in solution in the grains rather than as a segregate on the grain boundaries, but the percentage present was too small to detect with spark excitation.

The spectrograms show the diminishing intensity of the segregated elements of the samples used. The successive order of each spectrum is indicated, being an exposure of two minutes and a single complete sparking of the surface of the electrodes. The lighter lines of the spectrum do not show as clearly in the prints as on the original films.

The identification of Sn in the two samples of poor metal is shown. The arc spectrum of P-1 and P-2 was photographed, and the spark spectrum of Sn superimposed upon it. The lines of Sn are indicated, the heavier center sections being the lines of the pure metal.

P-1

2 min - 3 1/2" .06 m/m slit

15  
14  
13  
12  
11  
10  
9  
8  
7  
6  
5  
4  
3  
2  
1

Pb 4057

Ca 3969

Ca 3933

Po 3693

Po 3639

Mg 2796

P-2

2 min - .065 lit - 3amps

5995  
3968-Ca  
43933-Ca

Pb 3683.

Pb 3639.

Mg 2852.

Mg 2805  
Mg 2798

9  
8  
7  
6  
5  
4  
3  
2  
1

Co 311

11/1/50

11/1/50

A-1 2 min exposure  
3/2 amps .06 amp slit

G-2 Limit exposure  
3 1/2 mps .06 sec

3995-Air  
3968-Ca  
3933-Ca

p.

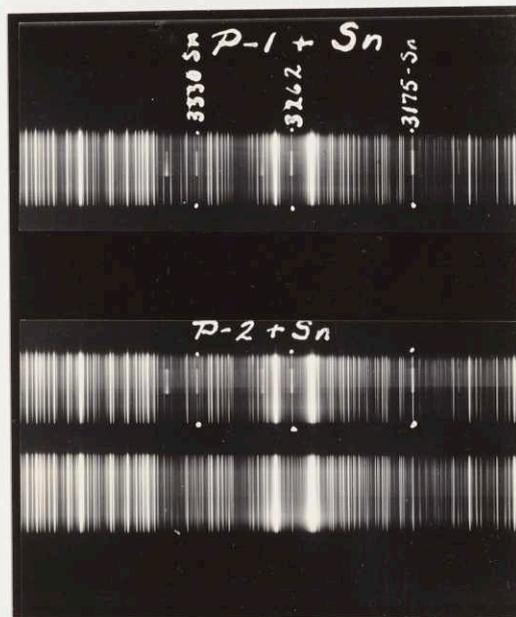
p.

p.

Mg 2102

Mg 2190

W. C. C. No.



The behavior of lead and magnesium may be due to the tin present forcing them out of solution to form segregates on grain boundaries, or the magnesium and lead may form the intermetallic compound  $Mg_2Pb$  which precipitates to the grain boundaries.

The lines of other elements present in the metal remained of constant intensity in all exposures which indicated that they were not a grain boundary constituent.

The two samples of good metal, G-1 and G-2, showed the calcium lines of the spectra diminishing in intensity in the successive exposures. It did not seem that this should be due to the surface layer of the fracture because these two metals were not brittle, but had a high percentage of elongation and did not fracture in an intercrystalline break as did the two poor castings.

An investigation was then made to determine the mechanical action of the spark on the metal. Samples of the casting were given a metallographic polish. The spark was then played over the polished surface and the specimens studied under the micrograph using magnification up to one thousand power.

It was found that a light sparking of the surface exposed the grain boundaries in small sections but not completely surrounding the grains. Increasing the

length of sparking time removed the grain boundaries around the entire grain. The grain boundaries appeared somewhat like craters, the violence of the spark apparently tearing away particles of the grain itself.

The spark did not confine itself to the grain boundaries though that material was preferentially removed. Marks upon the grains themselves were always found. These areas were slightly darkened and what appeared to be oxides of brilliant colors existed around the areas of the grains which were sparked. Best results with the spark etch were obtained when no inductance was used in the spark circuit and 5 amperes current in the primary circuit, the transformer ratio being 100 to 1. The etch made by the spark is much deeper than that produced by reagents. The latter can be removed with the polishing cloth but the spark etch was completely removed only with fine emery paper. The etch on the samples of poor metal was much more complete than with the good metals.

Time did not permit full investigation of spark etching and its application to other metals. The problem offers interesting possibilities and warrants further study. It may provide a means of solving many problems now perplexing the metallographer. The production of single crystals and the study of their properties

Figure 10

The polished surface of sample P-1 is shown in Figure 10. The metal is dirty and shows numerous inclusions. (X100)

Figure 11

The etch produced by dilute ferric chloride is in Figure 11. This is a light etch produced by immersing the specimen for five seconds. (X100)



Fig. 10

P-1 Polished Surface

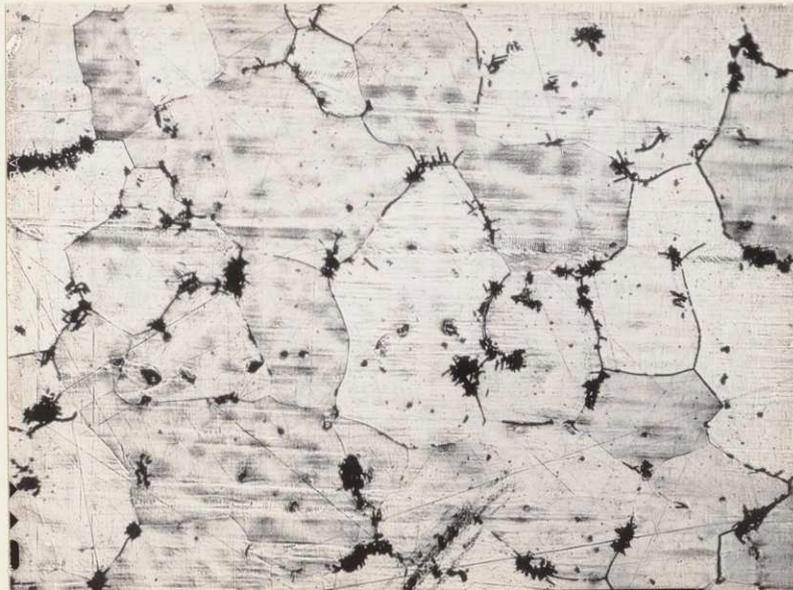


Fig. 11

P-2 Ferric Chloride Etch

Figure 12

Figure 12 shows the etch produced by nitric acid. This is a heavier etch than that produced by ferric chloride. (X100)

Figure 13

The etch produced by the spark is shown in Figure 13. The action on the edges of the grains can be clearly seen. The darkened areas in the interior of the grains appear to be oxides left around spots where the spark has struck the metal. (X100)

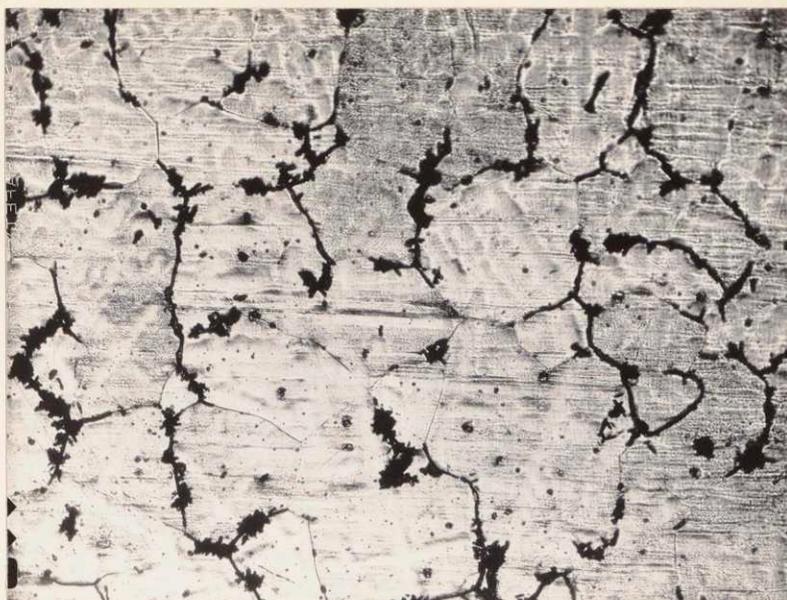


Fig. 12

P-2 Nitric Acid Etch

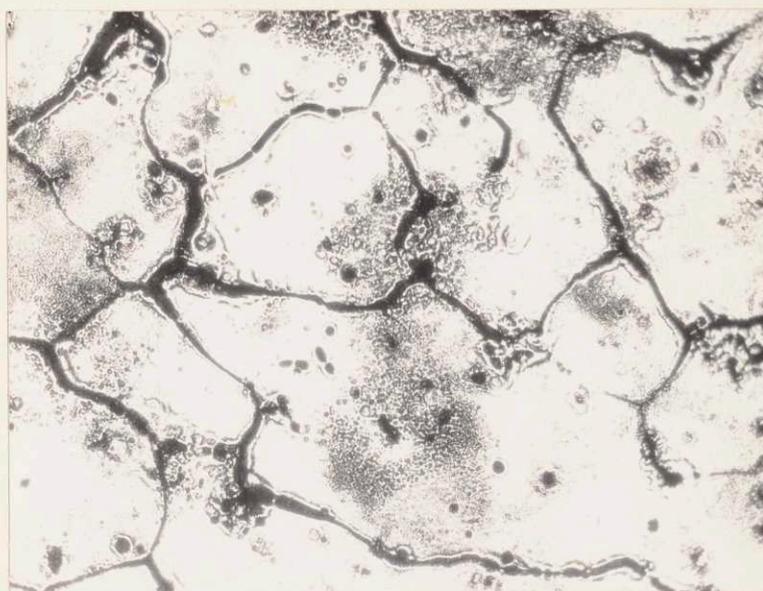


Fig. 13

P-2 Spark Etch

Figure 14

The action of a light spark passed rapidly over the surface of the metal is shown in Figure 14. The grains are not completely outlined and the grain boundaries are not enlarged. The flake-like areas are sparked spots in the grains. (X100)

Figure 15

The spark etch on a sample of the good metal is shown in Figure 15. The action appears more localized and the oxide deposit heavier. (X100)



Fig. 14

P-1 Light Spark Etch

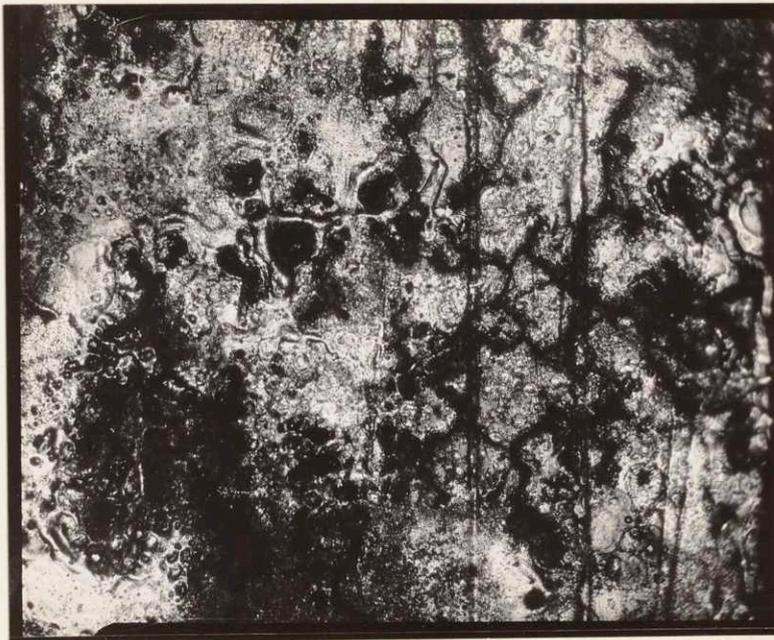


Fig. 15

G-1 Spark Etch

was largely prompted by a desire to eliminate the unknown effects of the grain boundaries since the properties of a metal are necessarily those of the crystal aggregate. If spectrographic analysis can be generally applied to grain boundary study, it will shed light upon this unknown factor.

## V

Discussion

To summarize the reasons leading to the conclusions stated: When the layer of grain boundary material exposed by the intercrystalline fracture is sparked a small amount of the material is volatilized. Each successive time the surface is sparked, the amount of grain boundary segregates decreases and the spectrum lines decrease in intensity until they reach a state of equilibrium with the constituents of the grains or the amount of the element excited becomes so small that it disappears from the spectrum. The equilibrium will be attained when the amount of grain boundary material volatilized is proportional to the time of exposure and the excitation of the grain constituents. The fractured surface should not be considered as having a uniform layer of segregates. The grains will be exposed in many places and those elements in solution will be excited, an equal amount in each sparking with a resulting constant intensity of the spectrum.

This is shown in the intensities plotted from the densitometer record.

The objection has been made that the effect obtained in the spectrum is due to these elements being

more readily volatilized than the other constituents of the metal. This might appear to be so but many facts disprove it.

In the case of magnesium, the diminishing intensity of the spectrum lines is shown in the spectra of the two poor metals while in the spectra of the good samples these lines remain of constant intensity throughout the successive exposures.

Again, the electrodes were not allowed to become hot. There was, of course, some heating but the electrodes could be comfortably handled after sparking.

If the effect was due to volatilization, a spectrogram made by confining the spark to a single spot should show this effect. When this was done, lead and magnesium lines did not appear in the spectrum but were only found when the spark was played over the surface of the electrode showing that these elements existed as scattered segregations through the metal. Calcium did show the diminishing effect when a single spot was sparked, but this may be explained by the etching action of the spark, calcium being more easily excited than the other elements and readily detected.

I may cite also, the work of Gerlach and Schweitzer, particularly their experiment in which tin contaminated with mercury was spectrographically analyzed. This

alloy did not show a preferential volatilization of mercury, the spectrum lines remaining constant in successive exposures.

To consider the reasons for lead and tin being detected in the arc spectrum and not in spark, the excitation is entirely different. The arc spectrum is essentially that of the neutral atom. The electrodes under the arc become heated above the melting point and therefore the segregations would be volatilized. Also, the surface layer is melted, causing many layers of grains to be excited and produce the spectrum of the elements in the volume of melted metal rather than that of a localized spot as with the spark.

The action of the high voltage spark in etching the grain boundaries is most striking. The material around the grains is certainly removed preferentially to that of the grain itself and this action was much more complete in the poor metal than in the good samples, though it seems the effect should be due to the structure of the metal rather than the constituents in its grain boundary.

From the mechanical viewpoint, the grain boundary segregates are removed until after continued sparking, the lines in the spectrum reach an equilibrium state when there is a uniform volatilization of the internal

regions of the crystals and grain boundaries. Since the grain boundaries are removed, the air gap will increase around the grains causing the current to flow through or along the surface of the grains.

The theoretical reasons for this occurrence cannot be justified without further investigation of the problem.

To consider the action of the spark, Schenck found that it presents three phases. The first a brilliant white straight line due to the first discharge through the unionized air. Then, curved lines of light which shoot out from the negative pole towards the center with diminishing velocity. When a streamer advances from one pole the other is dark. This is followed by a faint light which fills the gap for a certain length of time after the oscillations die out.

The spark lines of the spectrum are due to the curved streamers, the arc lines partly to the streamers but largely to the glow which persists after the streamers. The streamers do not carry the current since they travel with a continually diminishing velocity and before they reach half way across the gap the whole discharge has passed and the return oscillation started.

We may consider the grains or crystals of the metal as being positive atomic residues held together

by free metallic electrons while the segregations are of an amorphous nature with loose bindings of unsaturated valency. The latter are then more easily ionized by the flow of electrons and carried into the spark gap as ionized atoms.

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