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A Metallographic Study of
Copper Mattes

By
Edw. Torrence, Jr.

A METALLOGRAPHIC STUDY OF COPPER MATTES

by

Edward James Torrence, Jr.

A

T H E S I S

submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the

D E G R E E O F

BACHELOR OF SCIENCE IN GENERAL SCIENCE
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Approved by

Chas. J. Clayton

Professor of Metallurgy and Ore Dressing.

Metallographic Study of Copper Mattes

The metallographic knowledge of copper mattes or mattes in general for that matter, although extensive, is, to put it mildly, rather diversified. One authority, for instance, believes that mattes are sulphide dissolving compounds there being no eutectiferous series involved. Another believes that the matte constituents enter into a eutectiferous series, compounds being present. Still a third contends that there are no compounds formed but that a simple eutectiferous range exists between certain limits outside of which the end members of the series form solid solutions with each other.

In so far as there exists seeming absolute proof for all of the above versions, it was deemed worthwhile that an attempt be made to establish one or the other as being correct. It was for this purpose that the work yielding the results recorded in this paper was taken up. The data and photographs herein embodied resulted from a series of investigations carried on in the metallographic laboratories of the Missouri School of Mines.

Results of Previous Investigations

Messers Allan Gibb and R. C. Philp of Mt. Perry, Queensland, Australia, are the originators of the sulphide dissolving compound idea.¹ They classified mattes some-

¹Gibb and Philp, "The Constitution of Mattes Produced in Copper-Smelting, "T.A.I.M.E., XXXVI, 665 (1906).

what as follows:

Matte Names	% Cu	Color
Course Metal	35 to 55	Bronze
Blue Metal	55 to 70	Bluish purple
White Metal	70 to 75	White
Pimple Metal	75 to 85	Metallic copper

They found that when Cu, Fe and S constitute the whole matte they combine to form the compound $5\text{Cu}_2\text{S} \cdot \text{FeS}$ called by them "white metal" as noted above. They claimed to have very satisfactory proof for its being a compound. This proof is recorded at great length in their article but did not, however, include any photographic or microscopic evidence. Their proof although seemingly beyond any possibility of doubt, was nevertheless, rather narrow.

But, granting for the moment that this compound may exist, let us review the remainder of their hypothesis. They claimed that:

- (1) Cu_2S and FeS combine to form the compound $5\text{Cu}_2\text{S} \cdot \text{FeS}$ - white metal.
- (2) White metal enters into the composition of all mattes.
- (3) Fused white metal is capable of mixing in all proportions with fused FeS but separates during solidification.

In other words, their belief is that every matte

is a compound with either Cu_2S or FeS in solution or suspension according to the proportions present. This assumption naturally precludes the possibility of an eutectic being present. Microscopic evidence, however, establishes beyond any doubt the presence of a definite matte eutectic. This theory, held also by Peters¹, becomes upon the face of it, untenable.

Bornemann², Tammann³, Friedrich⁴ and Rontgen⁵ also have delved into the intricacies of matte equilibria with astonishing results. Some of the equilibrium diagrams proclaim compounds, others do not. The one predominant fact, however, is that no two of them agree. It would therefore be useless to present their ideas at any great length. More recent pyrometric data would seem to point to the non-existence of compounds in spite of all their proof to the contrary. Hofman⁶ gives a fairly reasonable diagram based it would seem on actual experimental data. His diagram points to a straight eutectiferous series between certain limits.

C. H. Fulton in cooperation with Ivan E. Goodner made an extensive study of copper-iron and copper-lead mattes and the evidence presented in their paper corroborates that of Hoffman to a certain extent⁷. They

¹Peters, "Principles of Copper Smelting"

²Metallurgie VI, 1909

³Zeit. Fur Anorganische Chemie XLIX, 1906

⁴Metallurgie V, 1908

⁵Metallurgie III, 1906

⁶Fulton's "Principles of Metallurgy", 296

⁷Fulton and Goodner, "The constitution of Copper-Iron and Copper-Lead-Iron Mattes," T.A.I.M.E., XXXIX, 584 (1908)

list the following constituents:

1. Substance "D" - Cu_2S or $\text{Cu}_2\text{S.Cu}$ or $(\text{Cu}_2\text{S.Cu})(\text{FeS.Fe})$
Varies from a gray-blue to a sky-blue color.

2. Substance "C" - FeS or FeS.Fe or
 $(\text{FeS.Fe})(\text{Cu}_2\text{S.Cu})$. The color varies from a light yellow to a gray brass yellow. Cavities and blowholes are very frequent in this substance.

3. A conglomerate; eutectic; called "B" - It is composed of interstratified plates of $(\text{Cu}_2\text{S.Cu})(\text{FeS.Fe})$ and $(\text{FeS.Fe})(\text{Cu}_2\text{S.Cu})$. Cu_2S - 21%; FeS -79%.

4. Substance "A"- Metallic Fe .

5. Substance "F"-Metallic Cu .

6. Substance "C"-Present as crystals of a purple color. It is thought to be ZnS but is unimportant because of its rare occurrence.

7. Substance "L"- PbS . Present in high lead mattes only. Under direct reflected light it presents a typical gray color.

8. A conglomerate; eutectic; called "K"- It consists of interstratified plates of $(\text{PbS})(\text{Cu}_2\text{S.Cu})(\text{FeS.Fe})$.

9. Substance "M" - Green in color. Occurs in long thin strips and is usually identified as slag.

Matte Constituents (Fulton and Goodner)

$\left. \begin{array}{l} \text{D} = \text{Cu}_2\text{S} \\ \text{C} = \text{FeS} \end{array} \right\} = \text{B the eutectic.}$

$\left. \begin{array}{l} \text{D} = \text{Cu}_2\text{S} \\ \text{L} = \text{PbS} \end{array} \right\} = \text{K the leady eutectic.}$

$\text{A} = \text{Metallic Fe}$

F = Metallic Cu

M = Slag

C = ZnS

Keeping the above varied ideas as to the constitution of mattes in mind, let us proceed to the work at hand - the determination of the correct hypothesis. That is, the justification of either the sulphide dissolving compound theory or the eutectiferous (with or without compounds) theory.

Plan of Proposed Work

Determination of Equilibrium Diagram.- It is proposed first to determine by the aid of cooling curves the equilibrium diagram to as exact a degree as is possible. Synthetic mixtures having matte proportions will be used for this work and both heating and cooling curves will be taken if conditions permit.

Study of Synthetic Mattes.- After having procured the necessary pyrometric data, specimens of both hot and cold mold pourings of the synthetic mattes will be taken, polished and microscopically studied. This part of the work is planned for the purpose of verifying the results obtained in the pyrometric determinations. It is believed that the constituents can be more accurately labeled by a microscopic study of a whole series of differently proportioned synthetic mattes than by a study of commercial mattes chosen at random.

Study of Commercial Mattes.- After having determined the identity of the constituents, their characteristics and the regions to which they are limited, it is further proposed that the subject of matte structure be investigated. It is thought that commercially produced mattes will be best adapted to this purpose. Specimens for structural study will, therefore, be taken from actual commercially produced mattes supplied by various copper producing companies throughout the United States.

Discription of Apparatus and Material

The materials used in the production of the synthetic mattes were a fairly pure grade of commercial FeS and a good grade of "white metal" in place of Cu_2S . The mixtures thus produced were melted in a Case gas-fired muffle equipped with a Case hydrocarbon burner and manufactured by the Denver Fire-Clay Co.

Pyrometer.- An alumel-chromel thermocouple was used in determining the cooling curve data and a Wilson-Maulen Millivoltmeter was used in measuring the E.M.F. produced.

Polishing Apparatus.- For the preparation of the specimens to be studied microscopically a set of horrizontal polishing wheels were used. The specimens were ground down on a small carborundum wheel. They were then smoothed

upon 00 emery paper backed by a brass wheel after which they were roughly polished on a canvas covered wheel using powdered alumina as the polishing material. The final polish was given on a felt covered wheel with jewellers rouge as the polishing material.

Photomicroscope.-Photomicrographs illustrating structure, constituent arrangement and relative proportions were taken and included as part of this paper. A large Reichert Photomicroscope was used for this purpose. It consists of an optical bench on which are placed an adjustable carbon lamp, a microscope and a photomicrographic camera. The above apparatus was manufactured by C. Reichert, Wein, Austria.

Developing and Printing Apparatus.- For the developing and printing of the photomicrographs the standard Mentol-Hydrochinon developing solution was used. The regular equipment generally associated with dark-rooms played its part in this work and need not be mentioned in detail.

Detailed Account of Work.

Determination of Equilibrium Diagram.-

In the determination of any equilibrium diagram the first step is the proportioning of the materials for the mixtures to be studied. For instance, if the end members whose equilibria are to be determined be the metals A and B then mixtures of A and B ranging from 100% A and 0% B to 100% B and 0% A are proportioned accordingly. The number

of mixtures will depend to a great extent upon the complicacy of the equilibria to be studied. If there is no pre-established knowledge on the subject it is of course best to have as great a number of mixtures as possible. In the case at hand, however, it was thought that mixtures taken at intervals of 10% would probably be sufficient but such was not the case entirely since it was found that more points would be necessary near the eutectic point in order to establish the curve.

These mixtures were melted in the small gas-fired Case furnace mentioned above the temperature seldom extending beyond 1300°C. This temperature was subjected to a fairly close pyrometric control for it is a well known fact that too high a temperature leads to sulphide decomposition.¹ Every possible precaution was taken to insure correctly proportioned melted mattes.

An attempt was made to obtain heating curves, especially for the high copper mattes (it was thought that there was some phase change below the eutectic line but this idea remained unconfirmed) but the attempt was unsuccessful owing to mechanical difficulties. The data that was obtained showed no new points and is not, therefore, included in this report.

The crucible containing the melted matte after being removed from the furnace was placed in an especially provided Silocel non-conducting container ^{a thermocouple} immersed in the

¹ Hofman "The Constitution of Ferro-Cupros Sulphides", T.A.I.M.E., XXXVIII, 142 (1908)

liquid and millivoltmeter readings recorded at intervals of 15 seconds until the matte had thoroughly cooled. The mattes while still hot were broken out of their containers and in all cases whether the Cu content was high or low "moss copper"¹ appeared. This "moss copper" is extruded from the cuprous sulphide which undergoes a dimorphic change² at about 1100°C³.

The thermo-couple used in deriving the above mentioned cooling curve data was standardized against C. P. aluminum and C.P. Lead. A curve was derived by which the millivoltmeter readings might be changed directly to temperatures. These temperatures (See Table I, page 9) were then plotted against compositions producing the diagram shown below.

Table I, Data for Equilibrium Diagram

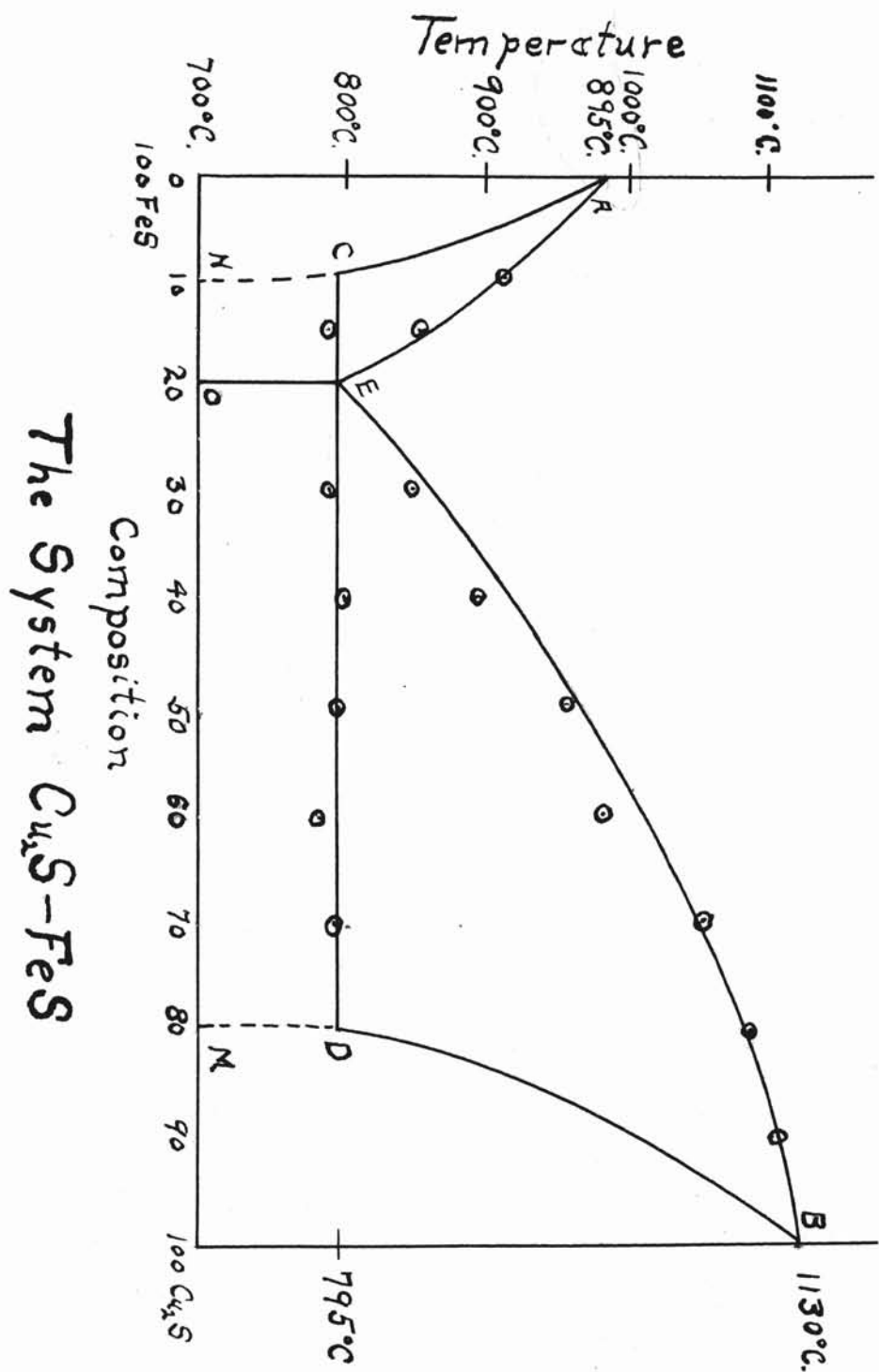
Matte	% Cu ₂ S	1st Break	2nd Break	Temperatures
#1	100	13.6	No	1130°C
#2	90	13.3	No	1100°
#3	80	13.1	No	1085°
#4	70	12.7	9.7	1050, 800°
#5	60	11.8	9.4	980, 775°
#6	50	11.5	9.7	950, 800°
#7	40	10.8	9.8	890, 810°
#8*	30	9.9	9.6	820, 790°
#9	20	9.8 or 7	Same	800°
#10	15	10.3	9.4	850, 770°
#11*	10	11.1	No	910°
#12	0	11.85	No	985°

*Note: The break for #8 was continuous but seemed to start at 9.9 and to stop at 9.6 and so those points were taken. For #11 there was no particular point, in fact there seemed to be at least half a dozen but 11.1 seemed to fit in best. For the standardization of the couple Pb at 327° was taken to correspond to 3.95 millivolts and Al at 685° to 8.12 millivolts.

1. Min.Sci.Press.,XCIII,604.

2.Fulton,"Principles of Metallurgy," 294.

3.100g. piece raised 1000cc. H₂O about 11°C.



The System $\text{Cu}_2\text{S}-\text{FeS}$

The diagram as it arranges itself is not nearly so complicated as past investigations would have it. As suggested by Hofman and Fulton there exists a simple eutectiferous series between the limits 10% Cu_2S -90% FeS and 80% Cu_2S -20% FeS outside of which the end members form solid solutions with each other.

The points check up beautifully with the exception of the composition 60 Cu_2S -40 FeS but it is self-evident that the difference is in the mixture and not in the constitution of the matte. The eutectic line points all vary considerably but it was only with difficulty that these points were determined at all.

There is no positive proof for the existence of the lines DB and AC in the positions given then. Nevertheless, the eutectic line ends as shown or at least nearly so and this fact together with the microscopic evidence to be brought forward later would seem to justify this arrangement. The continuation of the lines BD and AC is pure conjecture only but since they have to continue somewhere the assumed arrangement seems as logical as any other could be.

To sum up, therefore, the field to the right of BD limits the solid solution series of the end members just as does the field to the left of AC. The fields EDB and EAC show two phases - a solid or "mushy" phase which is the excess metal - the solid solution and a liquid phase - the gradually concentrating melt, the final product of

which will be the eutectic. Below CED this eutectic will be solid giving, consequently, two solid phases - the solid eutectic and solid excess metal. The line AEB is the so-called "liquidus" and the line ACE DB marks the so-called "solidus". The meeting point of the two lines - the point E is the so-called "eutectic" point.

The melting point of Cu_2S is found to be 1130°C and that of FeS to be 985°C . The eutectic solidifies at 795°C and is present in all mattes between the compositions 10% Cu_2S -90% FeS and 80% Cu_2S -20% FeS .

This version of the matte diagram is much simpler than any heretofore presented. It has one notable difference with other diagrams in that the eutectic line is placed at a point much lower than any other investigator places it. Nevertheless, this is the true and exact eutectic line. During the freezing of several mattes the author noticed that pockets had been formed in the top of the melt. During the freezing of another matte the thin solid coating over this pocket was broken and the author was able to witness the freezing of the last bit of melt.

This performance was repeated several times with like results and for that reason the author claims to have established the eutectic line beyond any possible doubt.

Investigation of Synthetic Mattes

The process by which unknown constituents of alloys or metal mixtures are identified is a rather vague and uncertain one. No two persons go about constituent

investigation in the same way. There are a number of avenues of research or methods of procedure but the only convincing evidence is that verified by all known methods of identification. It is possible to identify a constituent by a microchemical analysis but it seems that such an analysis alone is insufficient. Conclusions must be verified by the microscope, by etching comparisons and by every other means available.

A microscopic study of mattes reveals two main constituents with reference to color - one a buff or dirty yellow colored substance and the other a light purple or bluish colored substance. Cu_2S has, as is generally known a blue or purplish color and FeS is yellow. The natural inference that follows is correct and is verified as will later be shown, by both the pyrometer and the microchem analysis.

The specimens after being ground and polished as explained earlier in the article, were thoroughly examined with an upright mechanical stage microscope under direct reflected electric light at a magnification of from 150 to 450 times. Attempts at etching were positively unsuccessful with regular commercial mattes as is exemplified by Fig. 21c- VI. The silver-nitrate etch as suggested by many investigators¹ produced nothing but blurred unrecognizable sections. Silver-nitrate is supposed to bring out Cu_2S . It does possibly

1 T.A.I.M.E., XXXVI, 665 (1906)

but at the same time it brings out anything else that happens along. KCN is supposed to act the same as AgNO_3 . KCuCl however brings out FeS without touching the Cu_2S and although this etch works, no good picture was obtained. On the whole, with the exception of white metal, matte constituents are best brought out by relief polishing. White metal etched with FeCl_3 shows a very clear polyhedral grain structure as will be noted later. But with the exception of this one constituent, nothing is gained by etching.

As a further means of identifying the constituents microchemical analyses were made, the work being restricted of course to just the main constituents.

Cu_2S is identified somewhat as follows: 1 Color- Gray or bluish white. Sometimes "mottled" with bright colors - blue and green. With PbS it is a pale bluish white; and with cuprite Cu_2O slightly whiter. Surface.- Smooth and grained. Hardness. - 2.5-3. Chem.- HNO_3 - effervesces vigorously and etches, turning more or less blue. KCN- very rapidly blackens; rubs off to show cleavage or cracking, very fine grained.

The above mentioned tests and marks of identification were first verified with white metal- pure Cu_2S and found to be practically correct. They were then tried on the blue constituent of the Anaconda sample (Fig. 24c Plate 10) and the results settle for all time the doubt 1 Davy.- "Microstudy of Opaque Minerals".

concerning the identification of the blue constituent in mattes.

The same procedure was gone thru with respect to FeS and PbS with the same results. The buff colored constituent is FeS and the gray constituent in the so-called "lead" eutectic is PbS. These microchemical analyses were made under extreme difficulties. Only six specimens could be found which had surface susceptible to analysis. No hardness test could be made although it was attempted, that is, with regular mattes, the white metal, however, checked up splendidly.

As another means of constituent identification several authors suggested measuring the amounts of different sulphides in a given area and comparing the ratio of these results with the atomic proportion theoretically present but owing to the unevenness or coalescence of the constituents no representative ratio could be obtained.

A discussion of the constituents identified follows:

Cu - rich solution. - The first constituent to be taken up is naturally the one so generally recognized by its sky-blue color - the "Cu-rich" constituent. This constituent is the so-called "excess metal" to the right of the eutectic point and is found in all mattes to the right of this eutectic point. (See diagram page 9a)
Cu-rich solution is $\text{Cu}_2\text{S} \cdot \text{Cu-FeS} \cdot \text{Fe}$ - the FeS.Fe being

dissolved in the $\text{Cu}_2\text{S.Cu}$. $\text{Cu}_2\text{S.Cu}$ is the end member of the series on the Cu_2S side. During commercial operations e.g. smelting, the Cu_2S is carried to a temperature at which S is volatilized, thus setting free a certain amount of metallic Cu. This metallic Cu enters into solution with Cu_2S to the extent of 15%. The end member, therefore, is $\text{Cu}_2\text{S.Cu}$. This $\text{Cu}_2\text{S.Cu}$ will dissolve FeS.Fe to the extent of 20%. The "excess metal" is, therefore $\text{Cu}_2\text{S.Cu-FeS.Fe}$ or "Cu-rich" solution called by Fulton and Goodner substance "D".

Cu-rich solution ranges from a sky-blue to dark purple in color and this color becomes darker as the FeS.Fe increases. It has a smooth and uniform surface and is the softest of the constituents. It very often contains seams of metallic Cu of a lustrous Cu color. Cu-rich solution exists as such to the right of BD and in part with "Main" eutectic it exists as the "excess metal" to the left of DBM and to the right of EO.

Fe-rich Solution.- This is the buff colored substance so generally found in mattes and might be denoted by the formula $\text{FeS.Fe-Cu}_2\text{S.Cu}$. In this case the $\text{Cu}_2\text{S.Cu}$ is dissolved the FeS.Fe but the solubility is not so great as under the reversed circumstances- the extent of solubility being about 10% according to W.S. Cayple¹.

"Fe-rich" solution generally presents a brassy or buff colored appearance but as the Cu content increases
1 W.S.Cayple¹, "Ferro-Cuprous Sulphides".

(FeS dissolves Cu in all proportions up to 120% of its weight) the color assumes a rather dirty yellow appearance. It tarnishes rapidly to a variegated purple when exposed to air. Cavities and blowholes are quite frequent. It is owing to this fact that the polishing of low Cu_2S or "Fe-rich" mattes are so difficult to polish. Witness the intensely black portions of Fig. 6s Plate 4 or Fig. 28s Plate 5.

"Fe-rich" solution is common to that portion of the diagram to the left of AEO. It exists as solid solution to the left of ACN that phase being the only one present in this region. However, to the left of AEO and to the right of ACN two phases are present - the eutectic of "Fe-rich" solution and "Cu-rich" solution and also additional "Fe-rich" solution as the "excess metal".

"Pb-rich" solution.--A theoretical matte constituent--the solid solution of PbS-Pb. It never occurs as excess metal and is present only as one of the entities in the "lead" eutectic.

The "Main" Eutectic of Mattes.-- This "main" eutectic is so designated that it may be differentiated from the other matte eutectics e.g. the "lead" matte eutectic and the Ni matte eutectic.

This "main" eutectic is a conglomerate composed of interstratified plates of "Cu-rich" solution and "Fe-rich" solution. "Fe-rich" solution about 80% and "Cu-rich" solution about 20%. Low mattes or mattes of

low Cu content naturally show the most eutectic. See Fig. 9s, Plate 6.

Metallic Cu.-- Practically every matte specimen shows more or less of this constituent. It occurs usually in the "Cu-rich" solution and as before mentioned is called "**Moss Copper**". It has, naturally, a lustrous coppery color. The large island in Fig. 7s, Plate 11, is metallic Cu.

Metallic Fe.--This constituent has no notable characteristic except its conspicuous rarity. It is the whitest constituent so far observed. It occurs generally in or near the "main" eutectic. The lightest constituent in Fig. 2s, Plate 1 and 1s Plate 2, is metallic Fe.

The "Gray" Eutectic of Mattes.--This eutectic is easily distinguished from the "main" eutectic, the "gray" eutectic being much more massive than the "main" eutectic.

The "gray" eutectic is a conglomerate composed of "Pb-rich" solution (PbS with a small amount of Pb in solution) and "Cu-rich" solution in interstratified plates. It is a peculiar fact that although "leady" mattes are usually composed of all three end members - "Cu-rich" solution, "Fe-rich" solution and "Pb-rich" solution - there is no ternary eutectic formed. Some explain it by saying that the ternary eutectic is "hidden", that is, that its melting point is above that of one of the binary eutectics. Another explanation is that the "Fe-rich"

solution is never present in sufficient quantities in a "leady" matte to form its binary alloy. However, that may be, a "leady" matte will usually show a "leady" eutectic, a "main" eutectic and excess "Cu-rich" solution. The "leady" eutectic is a very good collector of metallic Cu. All of the metallic Cu in a "leady" matte is usually collected in the "leady" eutectic and held there in mechanical suspension.

Soniums.-- They occur in long thin strips or seams and have a dark greenish color. They are not so important as a constituent because their occurrence in any appreciable amount is rather rare.

This completes the list of constituents as found in mattes and it is proposed now that a discussion of the microscopic analyses of the microsections of the series of synthetic mattes be taken up. The discussion will begin with the FeS side of the diagram and continue on across towards the Cu_2S side. The set of pictures appended to this paper illustrate the manner of freezing of copper-iron and copper-lead-iron mattes, and tend to explain the constitution as found by microscopic analysis. The first set of pictures (beginning with Fig. 5s and ending with Fig. 14s) illustrate the constitution of differently proportioned mattes beginning with 0% Cu_2S and continuing on up to 100% Cu_2S which were poured in cold molds. The set of pictures immediately following Fig. 14s that is, the remainder of the pictures thru Plate 7 illustrate the constitution of the same mixtures poured, however, in hot molds.

The synthetic matte of 100% FeS shows two constituents. See Fig. 5s, Plate 1. The white areas represent FeS and the darker network a eutectic. Now the question is - why should there be more than one constituent in a 100% FeS specimen? Here is the reason: In producing FeS the melting point of pure FeS is passed by a couple hundred degrees and S is volatilized making the FeS exist really as a member of the Fe-FeS system. Also Fe_3O_4 is produced at the temperature reached; it forms a eutectic with the FeS. Theoretically 100% FeS should give a plain single phase homogeneous surface.

This eutectic of Fe_3O_4 and FeS is more strikingly visible in Fig. 19s, Plate 1. This picture illustrates the constitution of a 10% Cu_2S matte. The peculiar thing about this eutectic, however, is its striking resemblance to the "main" matte eutectic. The two, in fact, cannot be differentiated between.

Fig. 20s illustrates the constitution of a 15% Cu_2S matte and shows the darker "Fe-rich" excess metal" and the "main" matte eutectic. Fig. 2s approaches very near the eutectic point and microscopic examination shows the specimen to be practically all eutectic.

The figures of Plate 2 show merely a gradually decreasing eutectic and an increasing excess metal- "Cu-rich" solution. These figures illustrate that portion of the diagram labeled EOMD.

Fig. 11s, Plate 3, 15s Plate 4, and 14s Plate 4 illustrate the solid solution phase of the diagram, the solid solution being "Cu-rich" solution.

A comparison of the first set of pictures- those illustrating the mattes poured in cold molds- and the second set- those illustrating the hot mold mattes will show very clearly the part time plays in matte constitution.

Investigation of Commercial Mattes

As will be remembered the commercial mattes were to be studied with especial reference to structure. The structures obtained will, therefore, be the true and not theoretical ones. The specimens for this series of investigations were obtained from various copper concerns throughout the United States.

The specimens were ground, relief polished, studied microscopically and photographed. It was found that the structures associated with alloys in general are very common in mattes. Table II gives a list of the various mattes used in this investigation together with their Cu_2S contents.

Table II Commercial Mattes*

Print #	% Cu ₂ S	Producing Company
18c	46	Ariz. Copper Co.
13c	75	Garfield Smelting Co.
3Ac	88	Omaha (Good Grade)
20c	62	Chicago M.
5c	55	Butte Copper Co.
21c	45	Omaha Smelter (Poor grade)
10c	51	Old Dominion Copper Co
25c	82	Tacoma White Metal
7c	31	Duck Town Low Matte
16c	41	Tacoma Smelter
24c	46	Anacosta Copper Co.

*Note: Other commercial mattes were available but were either indential with those already taken or would not give good pictures.

Dendritic Structure.-- Slowly cooled mattes show a decided tendency towards a characteristically coarse dendritic structure. This structure shows up best in mattes having between 40 and 60% Cu_2S . The "Cu-rich" constituent originally forms as very small dendrites and the coarse structure is due to the growth of these small crystals. Figs. 21c-II and III Plate 9, illustrates this structure admirably. Fig. 21c-V is a picture of one of the big coarse dendrites so characteristic of medium high grade mattes. Four or five of these crystals would completely fill the photomicrographic ground glass camera plate.

The dendritic material or the so-called inner dendritic filling is "Cu-rich" constituent. The dendrite is surrounded usually by coalesced "Fe-rich" constituent but in rare cases by the eutectic.

Cracks and Seams.-- In mattes of 60% Cu_2S and over a light KCN etch will uncover myriads of infinitesimally small cracks. These cracks can be observed only with the aid of high magnifications and could not be photographed. Large seams (Fig:3s Plate 5 and Figs 12 and 13s Plate 7) are very common in the higher grade mattes. These seams appear to be fissures left by some extruded metal.

Widmanstätten Structure.--This structure was first observed in a commercial matte that had to be remelted in order to obtain a sizeable specimen for polishing.

See Fig. 21c-IV, Plate 9. Although quite a number of the commercial mattes showed this structure it was impossible to obtain pictures. (This was the case generally with commercial specimen - the high percentage of impurities making it impossible to photograph the structures.) Fig. 16s Plate 3, however, illustrates this structure in a very clear manner. The plates appear to be "Cu-rich" constituent and the matrix "Fe-rich" constituent. It seems possible that this structure is the result of an intensified coalescence into the grains of "Fe-rich" solution along the crystal planes.

The Polyhedral Grains of "Cu-rich" solution.-

The grain structure of "Cu-rich" solution can be brought out very clearly by etching with syrupy FeCl_3 . White metal etches even more clearly than the "Cu-rich" solution. See Figs 25c III and IV Plate 12. Rapid cooling greatly retards grain growth with results as shown by Fig. 18c Plate 8.

Eutectic Structure.-- The "main" eutectic is very uniformly distributed in synthetic mattes but rather poorly distributed in commercial mattes. The commercial mattes are, of course, very slowly cooled allowing, naturally, for much coarsening of the structure. The eutectic, if slowly cooled, seems to have a natural tendency towards coalescence. The "main" eutectic except where the tendency towards coalescence is felt, is generally finely globular (Fig. 9s Plate 6 and Fig. 21s - I Plate 8) while the "lead" eutectic is very

coarsely laminar or globular but mostly laminar.. Figs 7c-I and II show this coarse "leady" matte very clearly. The "leady" eutectic presents a very curious speckled appearance under fairly high magnification. The specks are small globules of metallic Cu held in suspension.

Both eutectics but more especially this "main" eutectic show a gradually increasing network structure--the eutectic forming the network - as the Cu_2S content decreases. This is shown very clearly by comparing Figs 9s, 10s, and 4s Plates 6 and 7.

Coalescence. --Coalescence is the separating out of the entities of the eutectic into separate distinct fields of each constituent of the eutectic. This is a very exasperating tendency and was probably the cause for Gibb and Philp so wildly missing the point. In some cases coalescence completely destroys all evidence of eutectic structure in a matte which according to all the rules and regulations should show a well developed eutectic.

One fact noticed in connection with this coalescent tendency is that the greater the amount of eutectic present the less the tendency is for that eutectic to coalesce. The higher Cu_2S content mattes show, therefore, a well-developed network structure while mattes nearer the eutectic point which should show practically all eutectic show instead what might be easily considered to be two "excess metals".

Many low grade mattes when examined microscopically show just two constituents - one the buff colored coarse looking material (designated by the author as "Fe-rich" solution) and the other the aforementioned sky blue substance referred to by the author as "Cu-rich" solution. That coalescence explains this seeming departure from theory is a fact beyond doubt because many commercial specimen showed a clearly defined eutectic in one portion of the microsection, the entities of which would gradually spread and widen out into separate fields of each constituent existing side by side. Fig. 16c-I Plate 10 and 19s Plate 1 illustrate this tendency towards coalescence.

In summarizing it seems not inappropriate to remind the reader that the ultimate purpose of this paper was to decide which of the various conceptions as to matte constitution, e.g. the sulphide dissolving compound theory, the eutectiferous series with compounds, the eutectiferous series without compounds, etc., was to be considered reliable.

There is no particular author's conception which is not at fault in one phase or another of the question in consequence of which the author offers the following:

1. The series Cu_2S -FeS is eutectiferous between limits 10% Cu_2S -90% FeS and 80% Cu_2S -20% FeS. Outside of this range there is a series of solid solutions.

2. The eutectic point was found at 20% Cu_2S -80% FeS .
3. The freezing point of Cu_2S was found to be 1130°C ; FeS - 985°C ; eutectic 795°C .
4. No evidence whatsoever of chemical compounds between the two sulphides was discovered.

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Plate 1



Fig. 5s Cu_2S -0%



Fig. 19s Cu_2S -10%



Fig. 20s Cu_2S -15%



Fig. 2s Cu_2S -20%

Plate 2



Fig. 1s $\text{Cu}_2\text{S}-25\%$



Fig. 27s $\text{Cu}_2\text{S}-30\%$



Fig. 22s $\text{Cu}_2\text{S}-35\%$



Fig. 25s $\text{Cu}_2\text{S}-40\%$

Plate 3

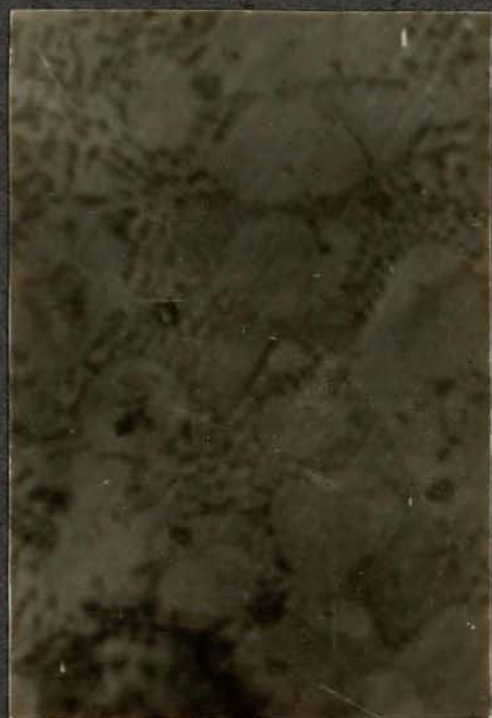


Fig. 24s Cu_2S -50%

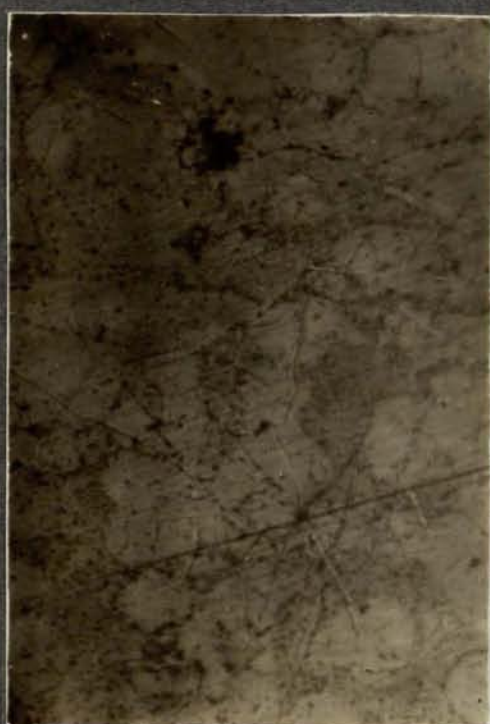


Fig. 7s Cu_2S -60%



Fig. 16s Cu_2S -70%

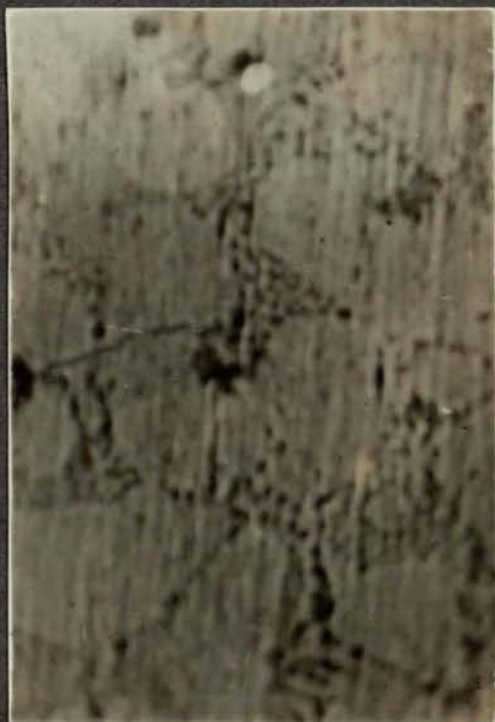


Fig. 11s Cu_2S -80%

Plate 4



Fig. 15s Cu_2S -90%



Fig. 14s Cu_2S -100%



Fig. 18s Cu_2S -0%

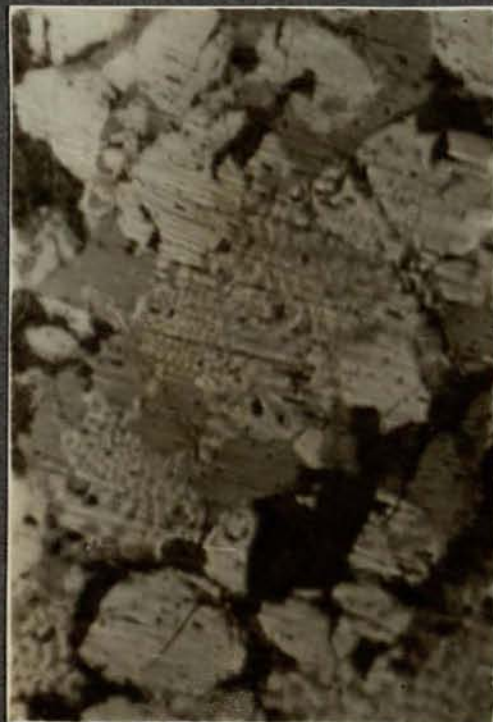


Fig. 6s Cu_2S -10%

Plate 5



Fig. 17s Cu_2S -15%



Fig. 3s Cu_2S -20%



Fig. 28s Cu_2S -25%



Fig. 26s Cu_2S -30%

Plate 6



Fig. 23s Cu_2S -35%

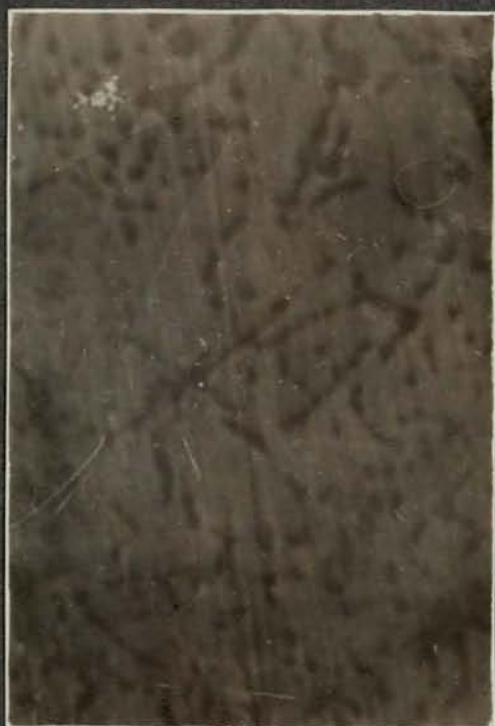


Fig. 21s Cu_2S -40%



Fig. 9s Cu_2S -50%



Fig. 10s Cu_2S -60%

Plate 7



Fig. 4s Cu_2S -70%



Fig. 8s Cu_2S -80%



Fig. 13s Cu_2S -90%



Fig. 12s Cu_2S -100%

Plate 8

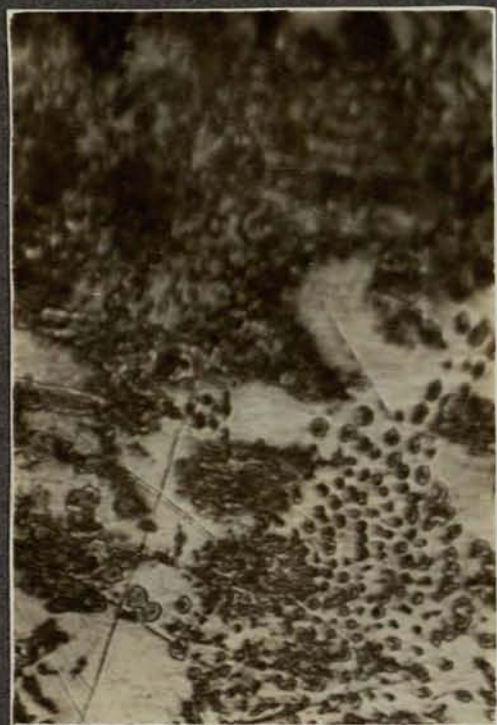


Fig. 5c Cu_2S -55%

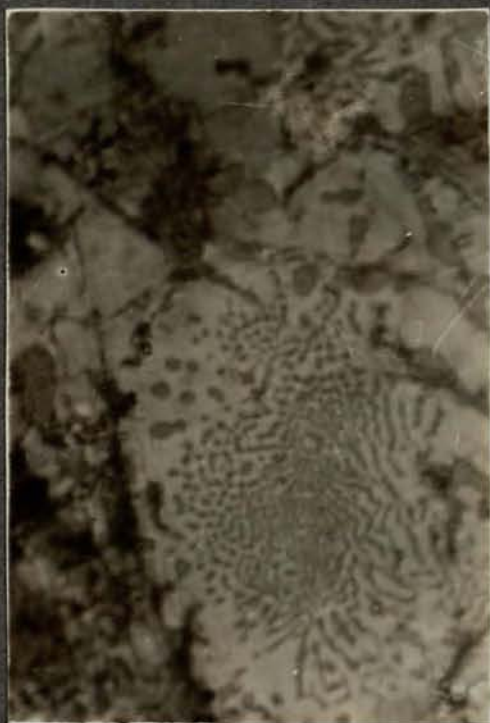


Fig. 21c-I Cu_2S -45%



Fig. 18c Cu_2S -46%



Fig. 3Ac Cu_2S -88%

Plate 9



Fig. 21c-II Cu_2S -45%

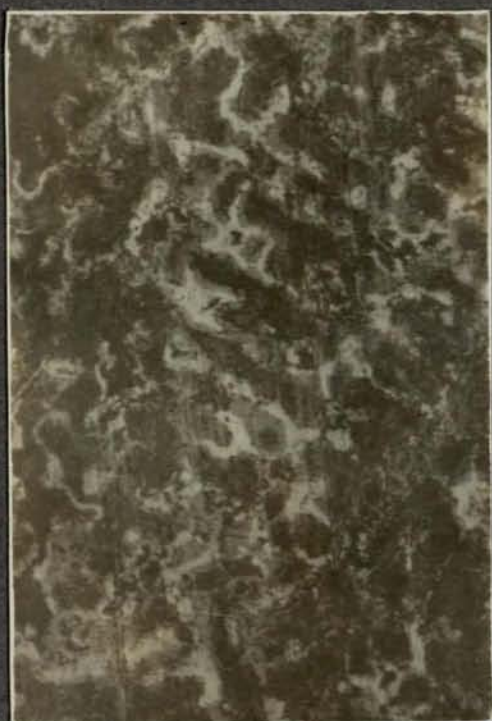


Fig. 21c-III Cu_2S -45%



Fig. 13c Cu_2S -75%



Fig. 21c-IV Cu_2S -45%

Plate 10



Fig. 10c Cu_2S -51%



Fig. 20c Cu_2S -62%



Fig. 24c Cu_2S -46%



Fig. 16c-I Cu_2S -41%

Plate II



Fig. 25c-I Cu_2S -82%



Fig. 16c-II Cu_2S -41%

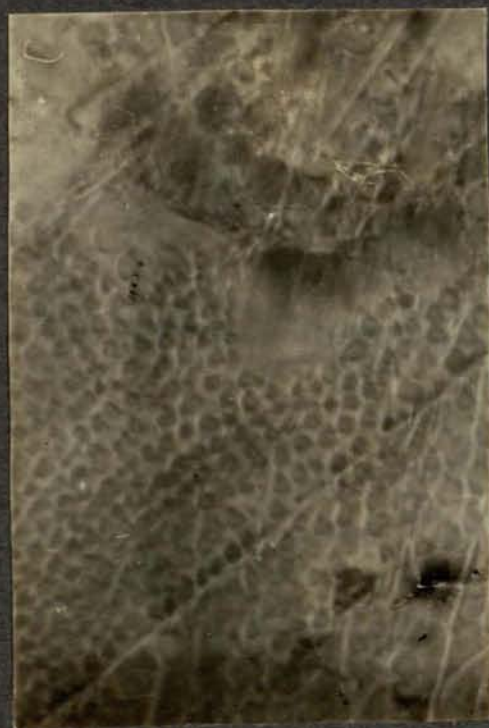


Fig. 7c-I Cu_2S -



Fig. 7c-II Cu_2S -

Plate 12



Fig. 21c-V Cu_2S -45%

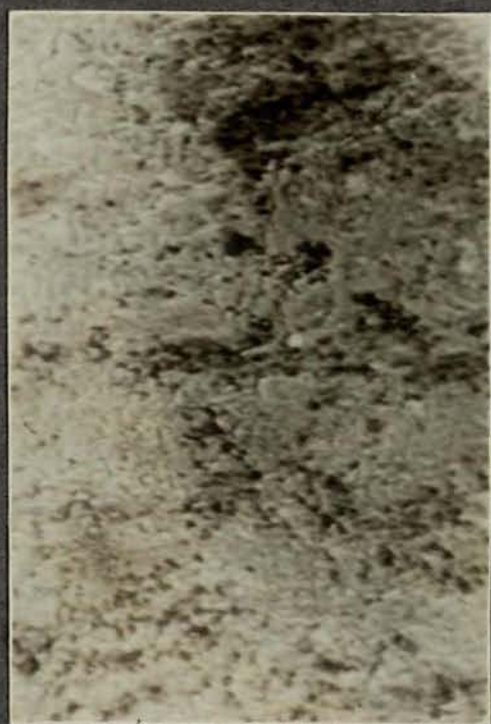


Fig. 21c-VI Cu_2S -45%

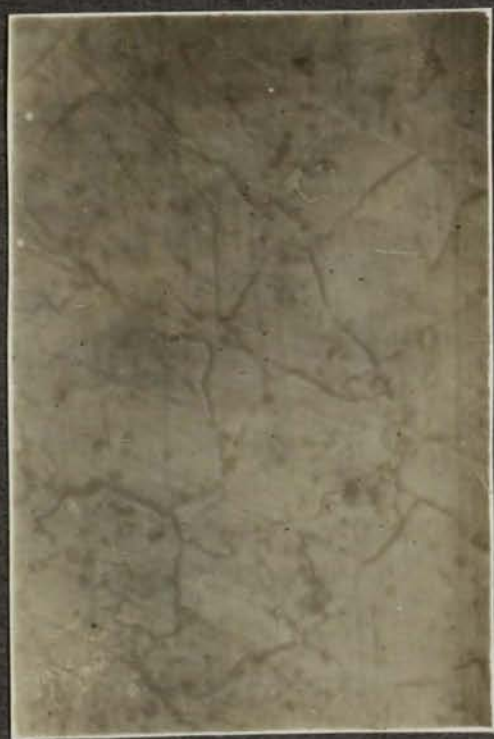


Fig. 25c-II Cu_2S -82%

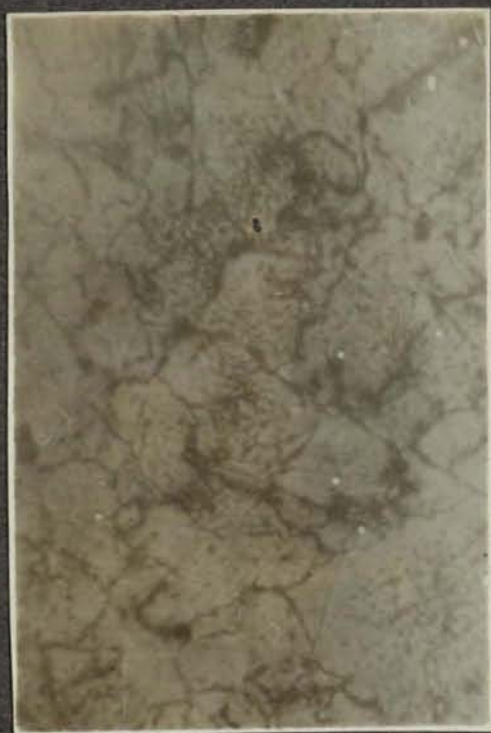


Fig. 25c-III Cu_2S -82%