FACTORS CONTROLLING THE LEAD DISTRIBUTION IN COPPER-LEAD ALLOYS USED FOR BEARING PURPOSES

BY

CHARLES HARMANY JOHNSON, JR.

S.B., Haverford College

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Signature of the Author..

Certification by the Department of Mining and Metallurgy

Professor in Charge of Research

Chairman of Departmental Committee on Graduate Students

Head of Department ....

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The author wishes to take this opportunity to express his appreciation of the interest and timely advice of Prof. C. R. Hayward, not only during this thesis, but during the whole of his two years stay at the Institute.

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I. INTRODUCTION

Copper-lead alloys have long been used for bearing purposes as they fulfil many of the requirements imposed upon a good bearing metal. These characteristics as pointed out by Dr. C. B. Dudley[1], Chemist of the Pennsylvania Railroad are:

1. It must be strong enough to withstand the load. Plain copper-lead combinations answer this requirement if there is not much "pounding" of the load. Where there is "pounding" some other metal must be added to harden the copper. For this purpose tin is almost universally used.

2. It should not heat in service. This factor depends both on the thermal conductivity and on the friction between the surfaces. As a general rule the harder the substance the less friction. The copper-lead alloys do not answer this requirement as they are both comparatively soft. However, this is not all evil as lead wears out and forms minute pockets which retain the oil.

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[1] "Bearing Metal Alloys," J. Franklin Inst., 1892, vol. 133, pp. 81;162.

If the alignment of the shaft and journal were perfect the load would ride on a film of oil and the only friction would be between a liquid film and the solid shell. However, these theoretical conditions never prevail and it is very good to have these oil pockets, especially when starting the shaft to rotate.

3. It should consist of a hard and a soft component. This again because of the lack of perfect alignment between the shaft and journal. If perfect, the shaft would be riding on the theoretical perfect oil film and the composition of the journal would be immaterial. As has been stated, the general rule is that the harder substances have lower coefficients of friction. If the journal is made entirely of the hard substance it will have a low friction loss. If the shaft moves from its initial alignment the bearing must wear to a new fit. As the hard substance will not wear easily the load is not distributed uniformly over the bearing area but is concentrated in a few small areas. Also the hard substances will tend to cut the shaft and generally the shaft is much more expensive than the bearing and should be protected. If a soft metal is used the load is uniformly distributed but the friction loss is much greater. So

in practical conditions a compromise is effected with both a hard and a soft component. The hard component with the low friction loss supports the load while the soft component can wear to give the good fit. The harder component is limited in hardness by the shaft. It is essential that the bearing constituent be softer than the shaft, otherwise wear will result on the shaft.

4. It should cast well in the foundry and machine readily in the finishing processes.

5. The loss in weight of the bearing due to abrasion should be as small as possible. This is low for copper-lead alloys as the abrasion loss depends upon the grain size of the hard component and also upon the toughness.

The difficulty in these alloys is to have the load uniformly distributed throughout the mass. Copper and lead as shown later have very small affinity for each other and the lead being much denser tends to segregate in the bottom of the casting. Many patent and secret alloys have been sold that claim to hold the lead in uniform distribution throughout the entire casting. A few of these alloys are Kelly metal, Allan metal, Stuart metal, and Ackermite.

A specimen of the latter metal was obtained and analyzed chemically and subjected to microscopic examination to determine what controlled the lead distribution. The effect of pouring temperature and the rate of solidification upon the lead segregation were also determined.

As sulfur has been used to hold the lead, the effect of varying amounts of sulfur was determined.

A sample of shale that was supposed to hold up the lead by making a "more intimate mixture between the copper and lead" was available and it was decided to determine just wherein lay the efficacy.

II. SUMMARY OF THE WORK CARRIED OUT AND THE RESULTS OBTAINED

1. Summary of the Work

For purposes of the summary the work may be divided up as follows:

1. The chemical analysis and microstructure of "Ackermite" in the original ingot. Specimens of this alloy were poured from different temperatures to see the effect of the pouring temperature on the lead distribution. The temperatures used were 1000, 1100 and 1200°C. To study the effect of the rate of solidification a 500-gram ingot (approximately) was cast in a large iron mold and a 1000-gram ingot was cast in a smaller flat iron mold.

2. A synthetic alloy comprising 70 per cent copper and 30 per cent lead was cast from the same temperatures as the alloy "Ackermite" in order to study the comparison in lead distribution in samples cooled from the same temperatures. In this series also an ingot was cast in sand in order to give a slower cooling differential.

3. The effect of varying amounts of sulfur on

the microstructure of a 70-30 copper-lead alloy was studied. In this series the pouring temperature was 1100°C. for all the specimens and they were poured only into the small flat mold. This gives a rate of cooling comparable to the slower rate in series 1 and to the middle rate in series 2. The sulfur was varied from zero to 3.12 per cent. The intermediate steps were with samples containing .30, .70, .85, 1.20, 1.70 and 1.85 per cent. sulphur The sulfur was added in the form of galena. Enough copper was added to keep the copper-lead ratio constant.

4. Two samples of an alloy composed of 70 per cent copper and 30 per cent lead were weighed out and the copper melted in two crucibles in the same furnace. One charge was melted under a charcoal cover while the other was melted under a cover composed of powdered shale. The pouring temperature was 1100°C. in both cases.

2. Summary of Results

1. The chemical analysis showed that "Ackermite" had the following composition:

Copper	68.2	per cent
Lead	30.8	" "
Tin	1.25	" "
Sulfur	.79	" "

This is one of the alloys that employs sulfur to hold up the lead as the sulfur could not be present to this amount as an impurity. The microstructure shows the lead uniformly distributed throughout the section. In the lead areas are seen blue spots that are shown to be copper sulfide particles. They appear only when sulfur is added and they could not be lead sulfide as copper sulfide has the higher heat of formation and hence would be the stable form for a sulfide.

The pouring temperature does not have an appreciable effect on the lead distribution. On the other hand pouring into the small mold gives a much smaller grain size than pouring into the large mold. The reason that the pouring temperature did not affect the grain size was thought to be due to the fact that such a small quantity was cast. The difference in temperature between 1000 and 1200 degrees would not carry enough difference in superheat to appreciably change the interval of solidification.

The correct pouring temperature was determined by making a cooling curve of the alloy. The liquidus was found to be 935°C. The alloy should be cast from as near this temperature as it is possible to make it fill the mold.

2. Here again the different temperatures did not appreciably affect the distribution. The different rates of cooling did make a great difference in the grain size of the copper.

3. The addition of sulfur was found to uniformly decrease the size of the copper dendrite. The appearance of the alloy is greatly changed by the addition of even a small fraction of a per cent of sulfur. When no sulfur is present the lead is in the form of globules held in a continuous copper matrix. With even a small percentage of sulfur the lead is the continuous matrix and the copper is present in dendritic form.

4. The shale apparently had no effect on the distribution of lead.

III. PREVIOUS WORK ON THE SUBJECT

There is very little in the literature of metallurgy that bears directly on the distribution of lead in copper-lead alloys. The most common statement that has been encountered is that it is impossible to produce by ordinary foundry methods merchantable castings of a medium or large size. Also the statement has often been seen that sulfur is added to these alloys to hold up the lead.

The difficulties that occur in making these castings are caused by (1) segregation of the lead in pools, mainly in the bottom of the casting, and (2) the appearance of globules of lead on the surface of the casting known as "lead sweat." The first of these troubles is due to the low degree of affinity that copper and lead have for each other both in the liquid and in the solid state. This factor is shown very clearly in the equilibrium diagram for copper and lead. The other difficulty is caused probably by the phenomena of inverse segregation of which "sweating" is an exaggerated example.

The constitution of the copper-lead alloy series has been investigated by Roberts-Austen, Heycock and Neville, and Friedrich and Leroux . In Fig. 1, page 11, is shown the diagram as worked out by Friedrich and Leroux[1] and modified by Waehlert[2] in the region of the two conjugate solutions. Copper has a solid solubility for lead amounting to between two and three per cent lead. This solubility line has never been accurately determined.

From the diagram it is seen that when any alloy composed of more than 69 per cent copper is being cooled from the liquid phase copper is precipitated out when the temperature reaches the line AB and the melt changes in composition along the liquidus AB. When the temperature of 957°C. is reached the melt is composed of 60 per cent copper. At this constant temperature the copper-rich solution precipitates copper and the melt changes in composition to the point represented by D which has 26 per cent copper. Copper is then precipitated out while the melt changes in composition along the curve DE to the eutectic temperature of 325°C. The eutectic composition is six one-hundredths of one per cent.

1. Friedrich and Leroux, Metallurgie, 1907, vol.IV, p.299.
2. Waehlert, Metall und Erz, 1913, vol.X, p.578.

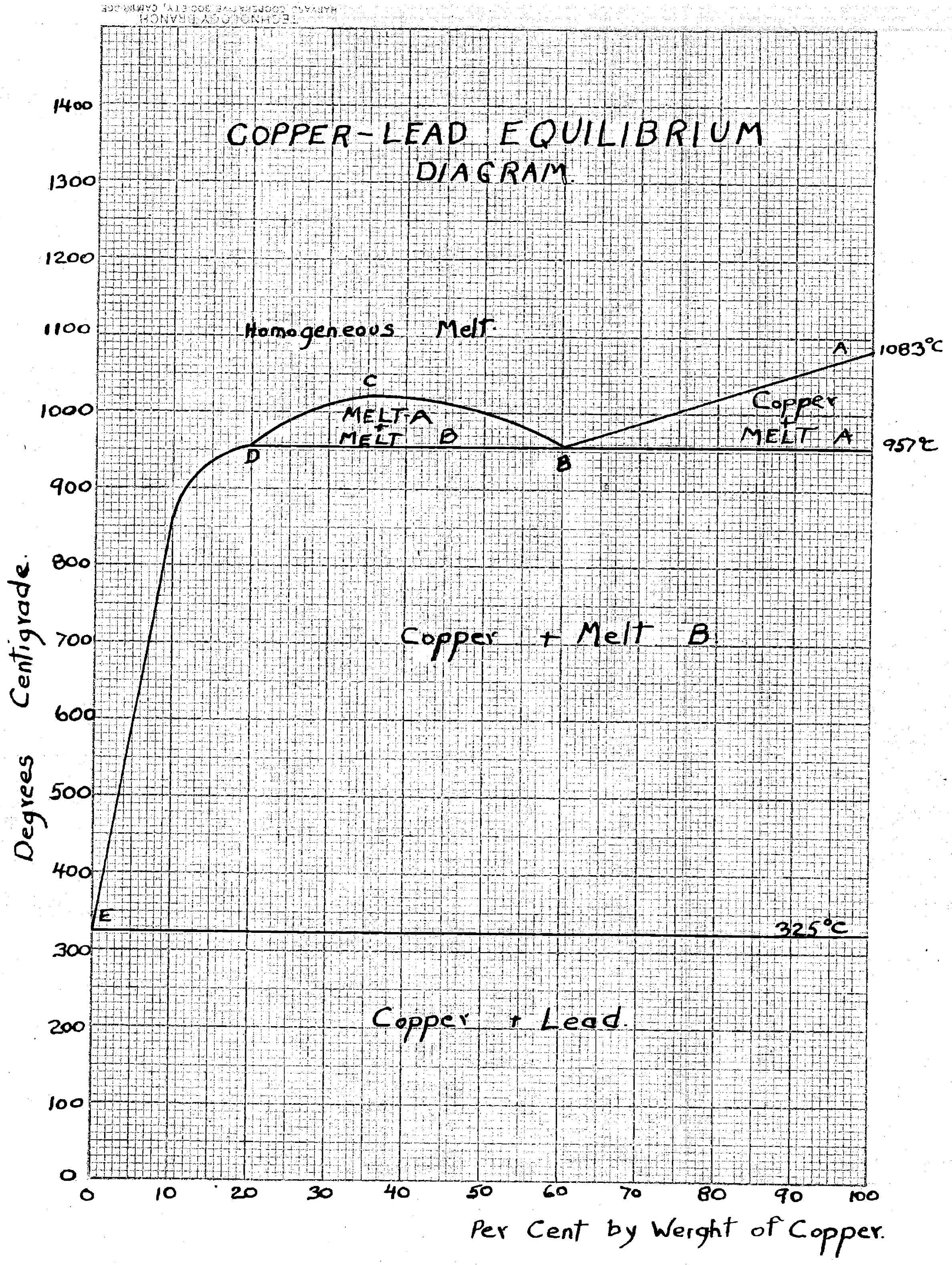
COPPER-LEAD EQUILIBRIUM DIAGRAM.
Homogeneous Melt
C
A
1083°C
MELT A + MELT B
Copper + MELT A
D
B
957°C
Copper + Melt B
E
325°C
Copper + Lead
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
Degrees Centigrade.
0
10
20
30
40
50
60
70
80
90
100
Per Cent by Weight of Copper.

Fig. 1.

With alloys between 20 and 60 per cent copper the changes are only slightly different. When the alloy cools from the field of the homogeneous melt and the temperature falls to the curve BCD the melt breaks up into two conjugate solutions, one whose composition falls along the line CB and the other along the curve CD. This occurs while everything is in the liquid state. When the temperature has fallen to 957°C. the diagram indicates that there is equilibrium between three phases, i.e., the two liquid solutions and copper. From the phase rule the system is invariant, that is the temperature must remain constant until one of the phases has been removed. The liquid solution B precipitates copper until it has changed its composition to D. Then there are only two phases and the temperature can vary. From this point on the cooling is as described for the first case of the high copper alloy.

One way to prevent lead segregation is to have a skeleton network of copper quickly form throughout the mass and to lock the lead up into small compartments. If the breakdown from the copper-rich solution (B) to the lead-rich solution (D) is rapid then the copper precipitated from the copper-rich solution will form quickly and will trap the lead. By the time the point D is reached there will be enough solid copper to prevent any segregation of the lead. So then rapid cooling through the temperature region of 957°C. would prevent lead segregation.

The "lead sweat" is an example of inverse segregation. In the cooling according to the equilibrium diagram there is a gradual enrichment of the lowest melting component toward the portion of the melt that solidified last. It has been observed that on copper, brass, leaded brass and bronze castings there is an enrichment of the lowest melting component toward the region that solidified first. In extreme cases this enrichment takes the form of exudations or "sweat."

Bassett and Bradley[1] in the examination of exudations that occur on the surface of copper castings found that these protuberances consisted almost entirely of the eutectic copper-copper oxide. The oxygen content of the whole casting was under .07 per cent, which is very far from the eutectic composition.

Price and Phillips[2] in the study of exudations on brass and bronze castings found the same enrichment

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[1] A.I.M.M.E., vol. 73, 1926, p.700

[2] A.I.M.M.E., Pamphlet No. 1586-E, Oct., 1926.

of the low melting component in the surface protuberance. On admiralty brass chemical analysis showed that the average analysis of the whole ingot was: copper 70.21, tin 1.21, zinc 28.58 per cent. The exudation showed 66.66 per cent copper, 4.02 per cent tin, 29.32 per cent zinc. Microscopic examination revealed a clear line of demarcation between the two and showed that there was more delta **eutectoid** in the exudation. It seemed as though they appeared after the surface had become solid. They found the same result in the examination of a bronze. In the examination of leaded brass they found that the lead had been rejected to the exudation.

R. Genders[1] in a refined research not on the exudations that occur on castings but on the progressive analysis of different points of an ingot of bronze showed that the same effect was present. According to his theory the exudations are an extreme example. He showed that the mechanism of inverse segregation involved three essential factors. They are:

1. A range of temperature between the liquidus and solidus of the alloy
2. The presence of dissolved gases

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[1] "The Mechanism of Inverse Segregation in Alloys," J. Inst. Metals, Advance Copy No. 423, March 10,1927.

3. An initially rapid rate of cooling, decreasing before complete solidification to below the critical rate necessary to retain the alloy as a supersaturated metal-gas solution.

Briefly the theory outlined by Genders is that solidification of a mass of liquid alloy in contact with a mold commences with the formation of crystal nuclei having various orientation. During solidification those nuclei grow preferentially whose principal axis is normal to the mold. In an alloy having a range of solidification the composition varies from the core to the outside of the crystal according to the equilibrium diagram. This is the normal segregation and the boundaries of the dendrites consist of low melting alloy. In an alloy with a small solidification range the difference in composition between the core and boundary is small. If the alloy contains a gaseous constituent it is rejected to the molten alloy as the solubility in the solid metal is small. Any gas may escape as long as the interior of the mold is liquid but near the end of solidification a gas pressure is set up. The subsequent behavior will depend upon the conditions existing at this time. If the volume of gas evolved is large and the range of solidification long then the pressure set up may be great enough to force some of the low melting alloy through channels between the dendrites and out to the surface. This gives the phenomenon of "sweat." On the other hand with a pure metal and small gas volume there is no weak, low melting wall and the result may be a distortion or the production of blisters. Between these two extremes lie the ordinary examples of inverse segregation.

The theory set forth by Price and Phillips to explain inverse segregation is that an envelop of solid metal forms. Due to contraction a pressure is set up on the inner molten metal. This pressure finally ruptures the crystal boundary of the envelop and some of the inner alloy squirts through the envelop. The envelop is immediately welded and the process can be repeated.

Another theory to explain inverse segregation is that of Benedicks[1] on the hot wall. This is based on the Ludwig-Soret effect. It has been found in chemistry that in the case of solutions of salts if a temperature gradient is established a corresponding concentration gradient will be set up. The concentration increases from the hot to the cold end.

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1. A.I.M.M.E., 1925, vol. 71, p.597, "Action of the Hot Wall."

If this applied to metals and occurred in a short interval of time it would be an explanation of inverse segregation. In the case of salts it takes a long period of hours for equilibrium to be established or even a noticeable difference. It is hardly possible that the concentration gradient could be established in the short interval of solidification.

IV. PLAN OF WORK

The experimental method decided upon consisted in melting about 2000 grams of the alloy in a graphite crucible placed in a furnace designated as American Gas Furnace Co. Heat Treatment Oven No. 1. As a cover to prevent oxidation charcoal was used. In the first runs powdered charcoal was used. As this was found to burn off too easily and would carry more or less air due to its form, pea charcoal was substituted. The copper to be melted was put into the furnace at a temperature of 1125°C. and was melted down rapidly. When thoroughly molten any lead to be added was stirred in. The temperature of the furnace was adjusted to the final pouring temperature and when the crucible reached that temperature as shown by the optical pyrometer it was held there for fifteen minutes. The crucible was then taken out and contents stirred with a graphite rod. The metal was then poured into molds. At first both sand and iron molds were used in order to study the difference in the rate of cooling. The ingots obtained by casting in sand were full of blowholes and the surface covered with knobs. This was thought to be due to the difficulty of getting such a small volume of sand at the proper "temper." For this reason the sand castings were not used in the later furnace runs. For these the melt was cast into flat iron molds. The ingots weighed about 1000 grams.

V. REPORT OF THE WORK

A transverse section was cut from one of the ingots and this was cut in half. One-half was polished and etched and examined microscopically while the other half was fractured and the fracture examined.

The section to be polished was smoothed on an endless belt and was then put through 1G, 0, and 00 grades of sandpaper and was then polished on the wheels. On the first two wheels 500-mesh carborundum was used. The first wheel was covered with canvas and the second with broadcloth. The specimens were washed and then put on the third wheel which was covered with broadcloth. The polishing compound was alumina that had been levigated for two hours. When the scratches from the second wheel had been removed the specimen was again washed and put on the final wheel. This was also covered with broadcloth. The polishing compound was alumina that had been levigated for twenty-four hours. This polishing solution also contained soap as this gives a better polish. The specimen was held very lightly to this wheel and was rotated so that the lead would not "seize" and be pulled out.

The sections were then etched with ammonium peroxide made by mixing equal volumes of ammonium hydroxide and hydrogen peroxide (3 per cent strength).

The etched specimens were examined microscopically and the structure photographed. For photographing, the same portion of the ingot should be used for all specimens. It was decided to use the central portion of each ingot.

For negative material Wratten and Wrainwright "M" panchromatic plates were used. The exposure was adjusted so that the plate developed up to the required degree in two minutes in the developing solution. Sensitometric curves had been run on the negative material and the developing solution and it had been found that two minutes was the correct developing time for the combination.

A transverse section was sawed from the ingot of "Ackermite" for microscopic examination. The saw filings were caught on a paper and were saved for chemical analysis. A sample was taken from the filings for analysis. Each analysis was run in triplicate and the alloy was analyzed for copper, lead, tin, iron and sulfur. The copper and lead were determined volumetrically by the iodide and molybdate method. Tin was determined by filtering off the residue after dissolving in nitric acid and igniting and weighing the white stannic oxide. Iron was determined by neutralizing the ferric hydroxide. Sulfur was found by igniting the alloy with a flux of sodium carbonate and potassium nitrate and then leaching and adding barium chloride and allowing to stand over night. Then the barium sulfate was filtered and dried and weighed. A blank was run to determine the sulfur in the chemicals used. The analysis showed

Copper	68.2	per cent
Lead	30.9	" "
Tin	1.2	" "
Sulfur	.8	" "
Iron	Trace	

The micro-examination of the different alloys may be divided into six parts:-

1. The examination of the original "Ackermite"
2. The examination of remelted "Ackermite"

3. The examination of a 70-30 copper-lead alloy
4. The effect of sulfur on the microstructure
5. The examination of an alloy produced by melting under shale
6. Inverse segregation in copper-lead alloy

1. The Examination of the Original "Ackermite"

Four sections were cut from the original ingot. The sections were chosen so that they were the perimeter of the half section and hence would show a representative condition of the whole ingot. The sections were polished and etched as has been described. Under the microscope the structure was seen to consist of lead globules in a copper-rich matrix. The lead distribution was very uniform throughout. In the lead areas were seen bluish particles that were shown to be copper sulfide. Also in the lead areas there were copper particles and dendrites. These probably were deposited during the breakdown of the lead-rich solution. The lead areas had a structure resembling a eutectic and this also was caused by the deposition of copper from the lead-rich solution. Plate 1, page 23, shows the uniform distribution of the lead throughout the mass. Plates 2 to 4, pages 23 and 24, show the structure of the lead areas. In these plates the white is copper or a copper-rich solid solution, the gray is the copper sulfide and the background is the lead area.

Photographs of the Structure of **Ackermite.**

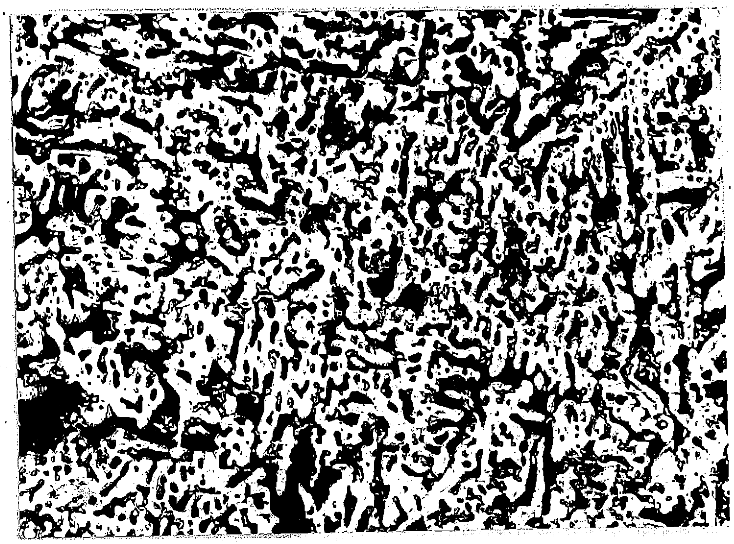

Plate 1. Showing the uniform distribution of the lead throughout the copper. The grey particles are copper sulfide. X 100.

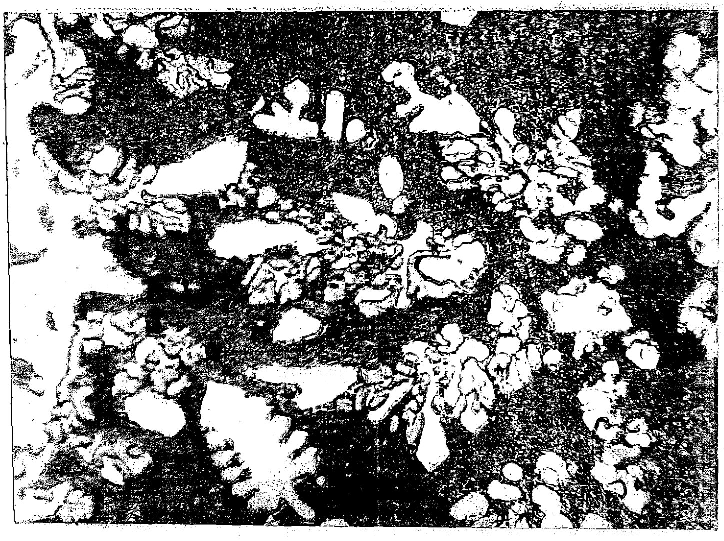

Plate 2. A lead area in the original ingot. The copper dendrites are formed during the breakdown of the lead rich solution. X 250.

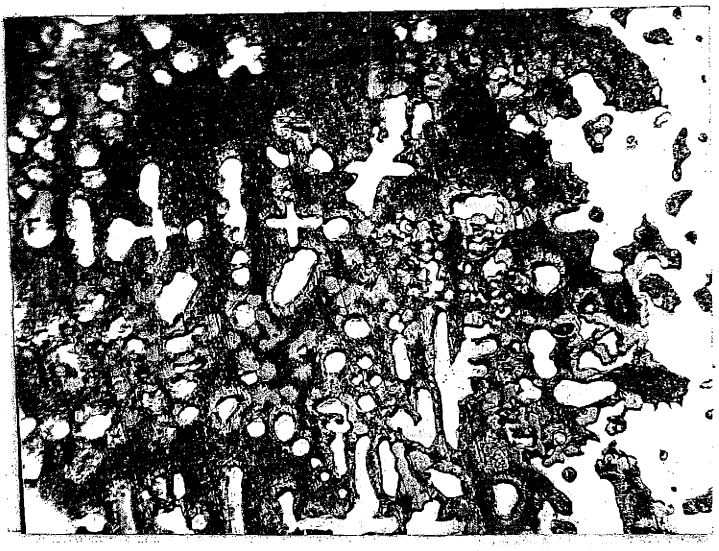

Plate 3.
Another lead segregation in the original alloy.
X 250.

Photographs of the Structure of Ackermite.

Plate 4. Ackermite at a higher magnification. The grey particles present in the dark lead areas are copper sulfide. X 1100.

2. The Examination of Remelted "Ackermite"

The alloy was remelted at temperatures of 1000, 1100 and 1175°C. successively. A small part, 500 grams, was cast in a large ingot mold, while the larger part, about 1500 grams, was cast in a flat iron mold. The sections were cut from the middle portion of each ingot. On examination it was found that the higher temperatures had very little effect on the lead distribution, while there was a marked difference in the structure between the small amount of metal and the larger ingot. The structure of the larger ingot is shown by Plates 5 to 7, page 26, each from a different temperature, while the structure of the smaller ingot is shown in Plate 8, page 27. This structure is uniform throughout the three specimens.

Microstructure of Remelted Ackermite.

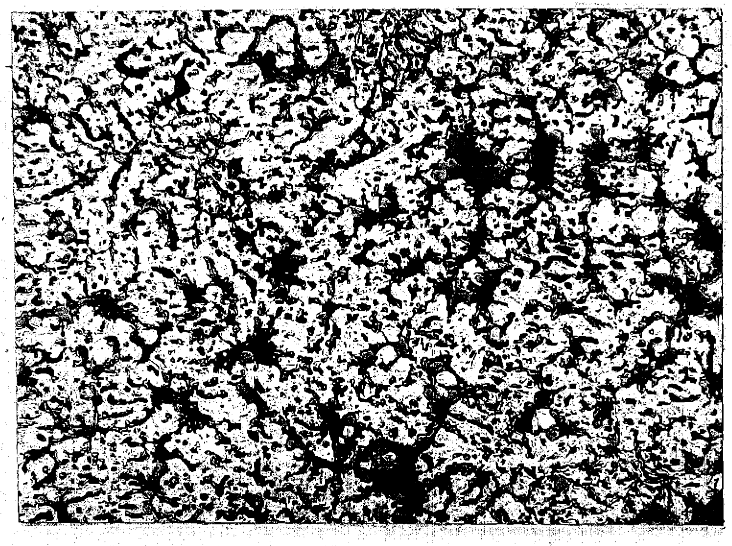

Plate 5. Poured from a temperature of 1000° C. in small mould.
X 100.

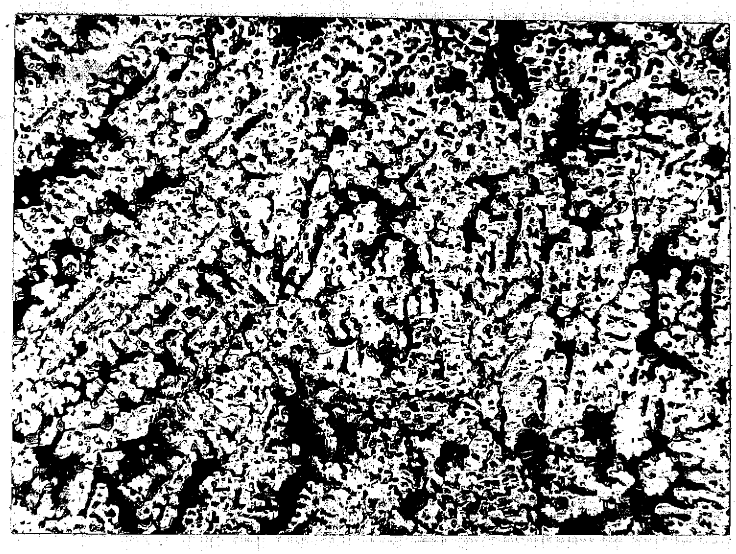

Plate 6. Poured from a temperature of 1100° C. into a small mould.
X 100.

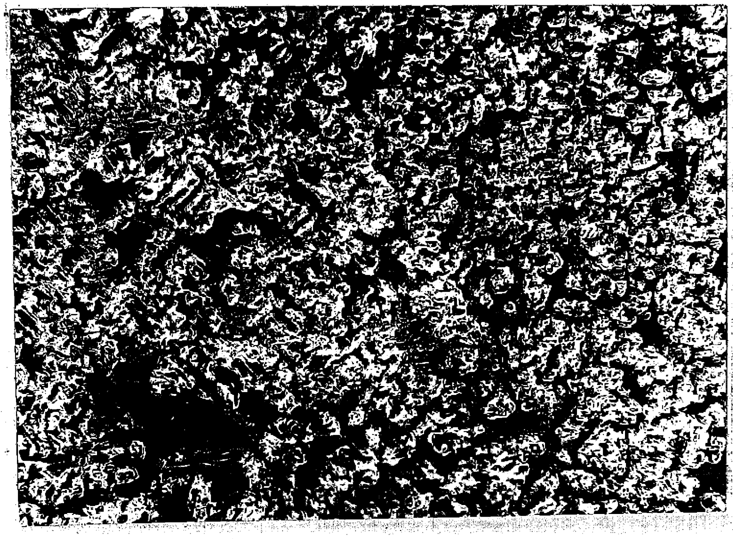

Plate 7. Poured from a temperature of 1175°C. into a small mould.
X 100.

Microstructure of Remelted Ackermite.

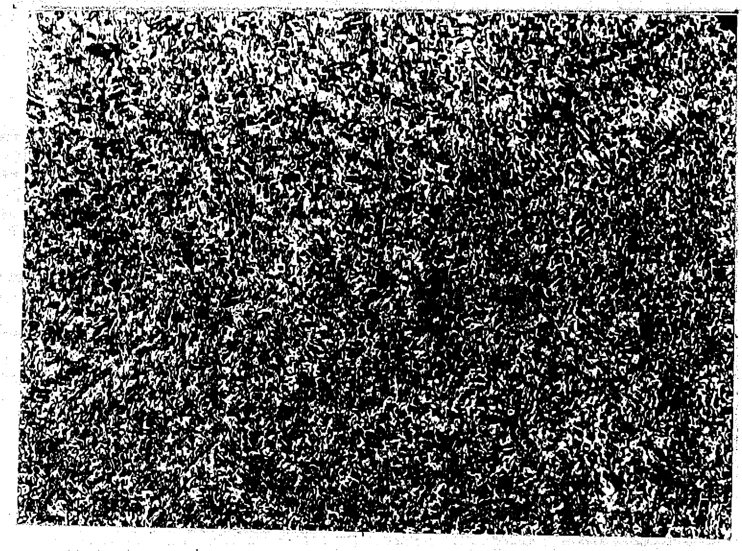

Plate 8. Poured from a temperature of 1100° C. into a large mould. X 100.

3. The Examination of a 70-30 Copper-Lead Alloy

The copper-lead alloy was prepared in the manner described and then was remelted at temperatures of 1000, 1100 and 1175°C. successively. The large and small ingots were cast as before, but this time an ingot was also cast in sand. This was done by remelting the large ingot cast in iron molds. Here again very little difference was found in the ingots cast from different temperatures under like conditions. Again marked difference was seen in the alloys cast in the iron molds and the sand mold. Plates 9 to 11, page 29, show the structure of the small ingot cast in sand. The lead distribution is quite uniform and is very good. In these alloys there were no blue particles. This is a good indication that they were sulfide, as the analysis of this alloy differed from "Ackermite" only in the matter of sulfur. Plates 12 to 14, page 30, show the structure of the larger ingot cast in the iron mold. Here again the distribution is very uniform and of good grade. Plates 15 to 17, page 31, show the structure of the ingots cast in sand mold. The very much larger size

Photographs of the Structure of Copper-lead Alloys.

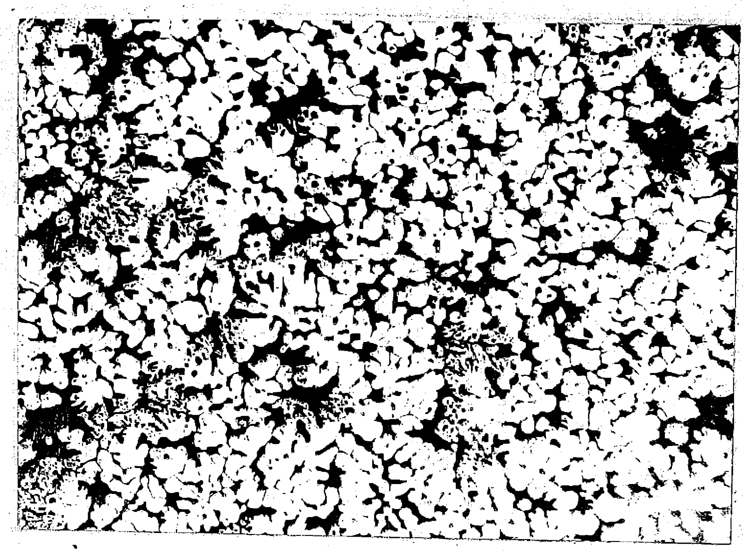

Plate 9. Alloy cast at a temperature of 1000°C. into a small ingot in an iron mould.
X 100.

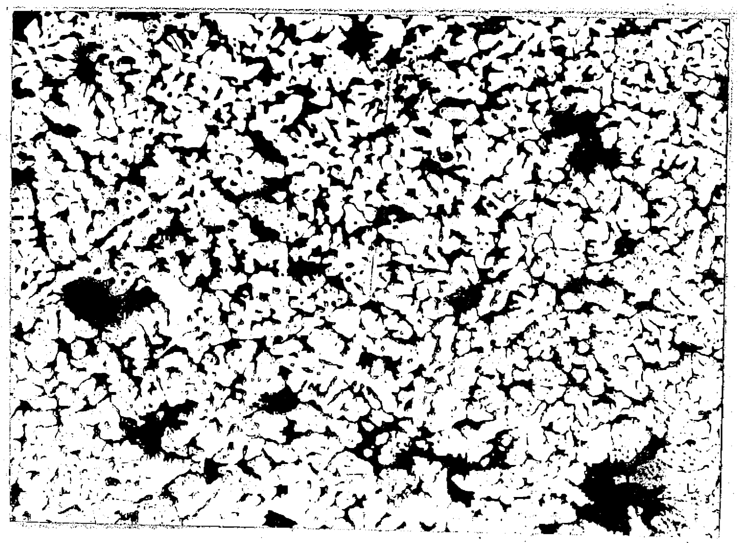

Plate 10. Alloy cast at a temperature of 1100°C. into a small ingot in an iron mould.
X 100.

Plate 11. Alloy cast at a temperature of 1175°C. into a small ingot in an iron mould.
X 100.

Photographs of the Structure of Copper-lead Alloys.

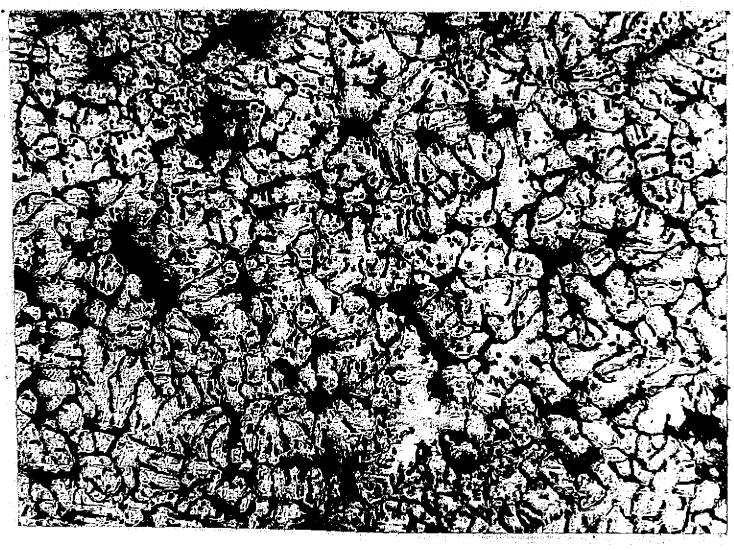

Plate 12. 70-30 copper-lead alloy cast at a temperature of $1000^{\circ}C$. into a large ingot in an iron mould.
X 100.

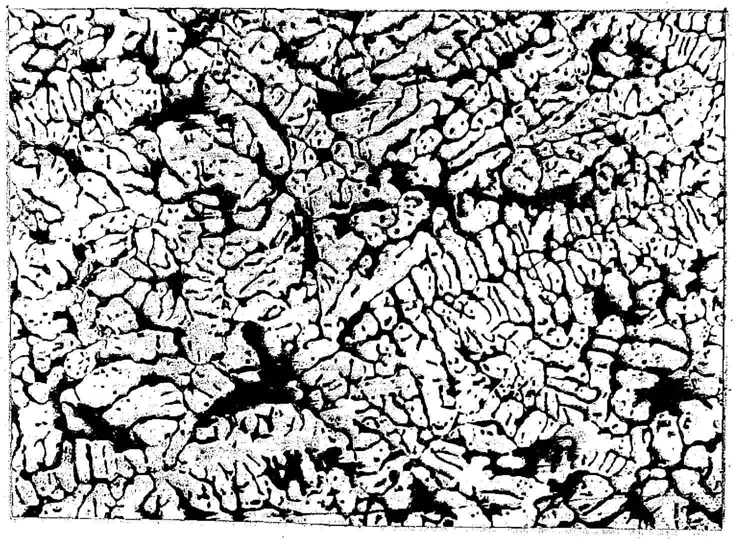

Plate 13. 70-30 copper-lead alloy cast at a temperature of $1100^{\circ}C$. into a large ingot in an iron mould.
X 100.

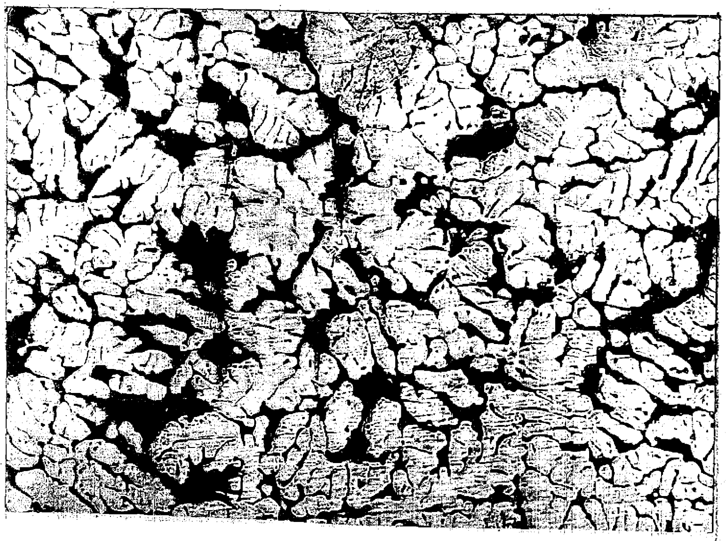

Plate 14. 70-30 copper-lead alloy cast at a temperature of $1175^{\circ}C$. into a large ingot in an iron mould.
X100.

Photographs of the Structure of Copper-lead Alloy.

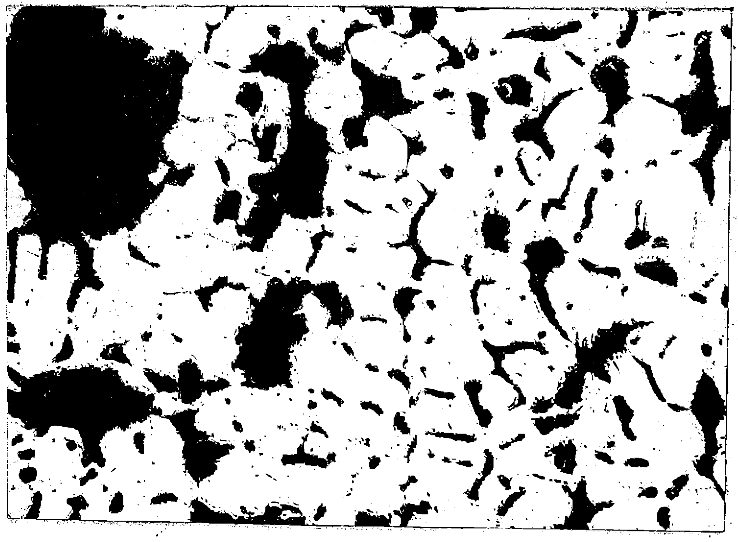

Plate 15. 70-30 copper-lead alloy poured at a temperature of 1000°C. into a sand mould. X 100.

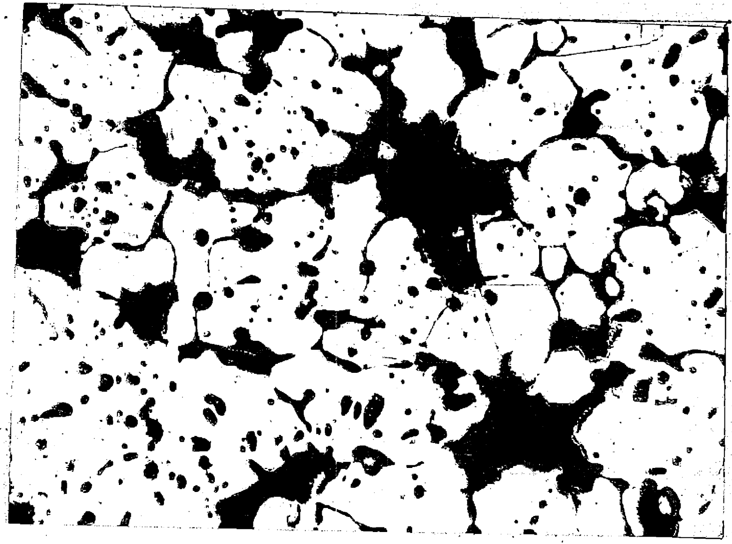

Plate 16. 70-30 copper-lead alloy poured at a temperature of 1100°C. into a sand mould. X 100.

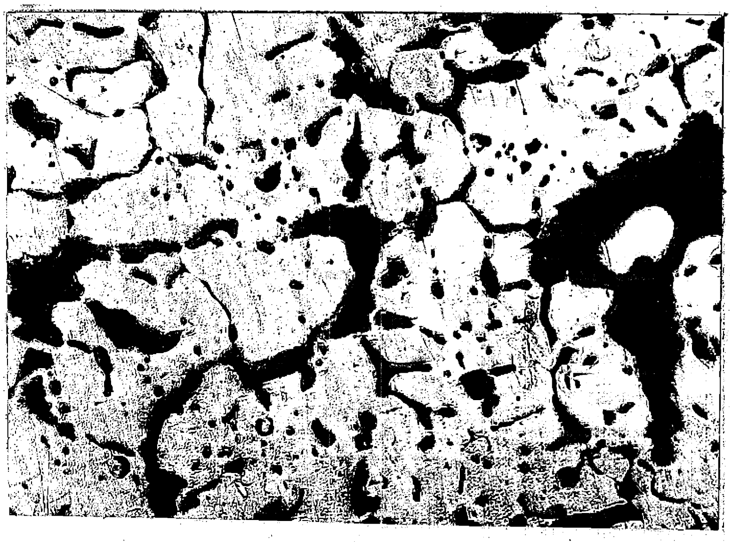

Plate 17. 70-30 copper-lead alloy poured at a temperature of 1175°C. into a sand mould. X 100.

of the copper dendrite and the segregation of the lead into pools is very noticeable. All these ingots show exudations on the top surface. That these were due to casting in sand was shown by remelting one of the ingots and casting in an iron mold. The surface of this ingot was perfectly smooth and showed no exudations.

In the sand ingots the surface appeared to become solid and glazed. Then what appeared to be drops of lead oozed out from the top surface and became solid.

Plate 18, page 33, shows the structure of the large ingot cast in the iron mold from 1100°C. at a much higher magnification. The copper particles can be distinguished in the dark lead matrix. The interesting structure of this photograph, however, is in the many lines seen in one copper dendrite. The author believes that they are evidences of what H. B. Pulsifer[1] calls granulations. According to Pulsifer granulations are the smallest of three orders of particles resolvable under the microscope. The largest particle is the dendrite, next comes the grain of the worked metal, and last the granulation. They can be shown much better by dipping in concentrated nitric acid for a moment after

[1] "Microstructure of Copper," A.I.M.M.E., vol. 73, 1926, p.707.

Photographs of the Structure of Copper-lead Alloy.

Plate 18. 70-30 copper-lead alloy at a higher magnification. The many lines in the large dendrite are granulations. X 1100.

an ammoniacal peroxide etch.

By comparing this series of melts with the corresponding ones of the remelted "Ackermite" the great difference in the size of the copper dendrite and the difference in lead distribution can be seen.

4. The Effect of Sulphur on the Microstructure of Copper-Lead Alloys

In this series sulfur was added to a 70-30 copper-lead alloy in the form of galena. Enough copper was added to keep the lead-copper ratio constant. All the alloys were poured at 1100°C. and were poured into a flat iron mold. The alloys prepared for this series contained respectively, 0 sulfur,.3 per cent sulfur, .8 per cent sulfur, 1.2 per cent sulfur, 1.8 per cent sulfur and 3.1 per cent sulfur. This series at 100 diameters magnification is shown in Plates 19 to 24, pages 36 and 37. The same series at 250 diameters is shown in Plates 25 to 30, pages 38 and 39. It is seen that sulfur has a very great effect upon the size of the copper dendrite. As sulfur is added the size of the copper dendrite decreases. The amount of the blue constituent increases with increased sulfur proving that it is a sulfide. From the heats of formation of copper sulfide and lead sulfide it is known that copper sulfide is the stable form and so the lead sulfide would change over to copper sulfide. In the two alloys highest in sulfur the excess sulfide has formed into round globules in many cases, and in the highest in one place has formed a long

Photographs of the Effect of Sulfur on the Lead Distribution

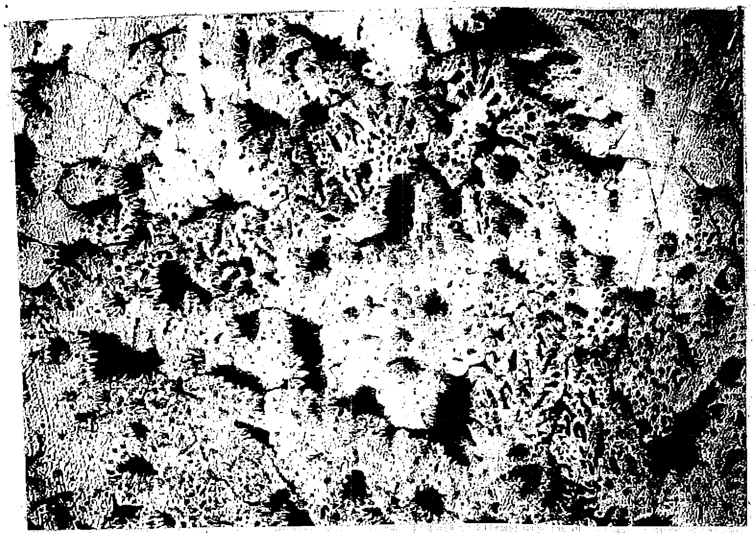

Plate 19. Alloy with no sulfur poured at a temperature of 1100°C. The copper is the continuous matrix and the lead forms in more or less rounded areas. X100.

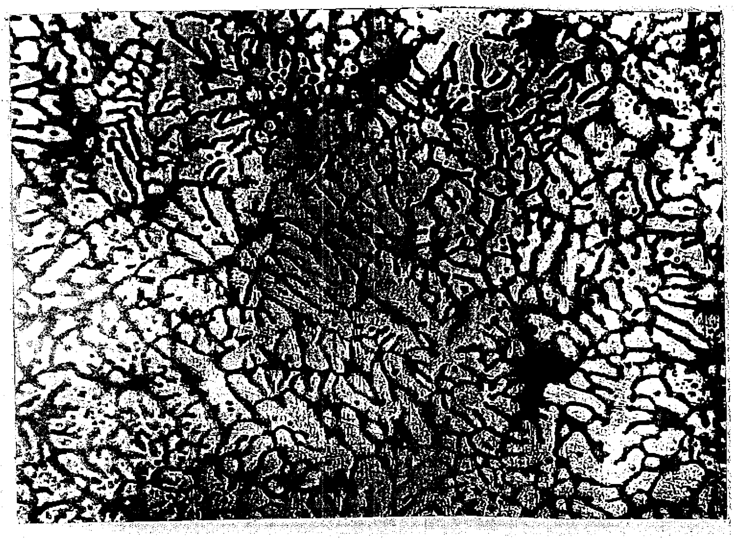

Plate 20. Alloy containing .3 per cent sulfur. The lead is the continuous matrix and the copper forms dendrites. No grey sulfide particles are seen. X 100.

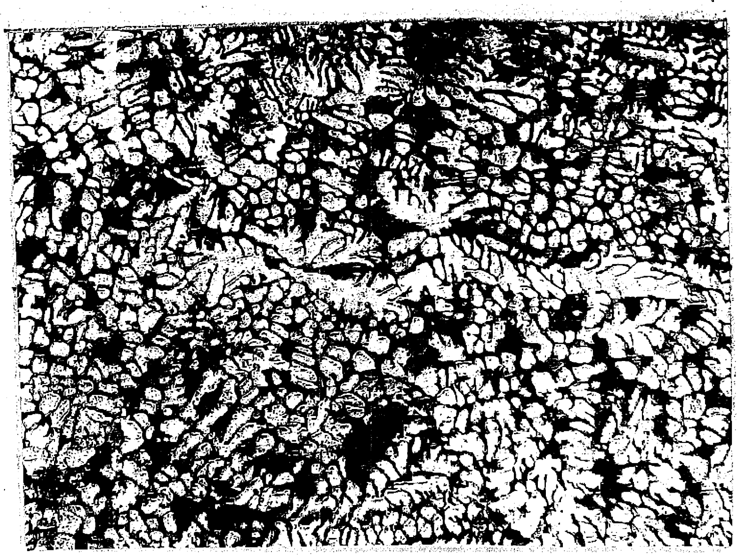

Plate 21. Alloy containing .8 per cent sulfur. The copper dendrites are smaller and particles of sulfide are seen. X 100.

Photographs of the Effect of Sulfur on the Lead Distribution.

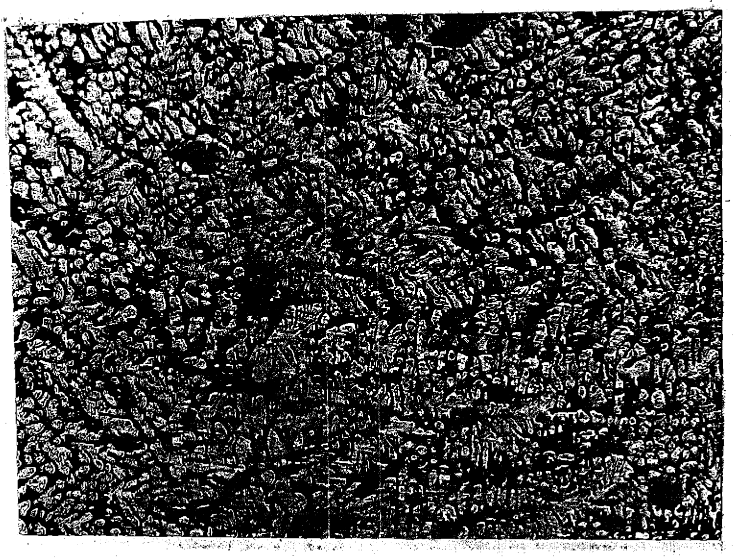

Plate 22. Alloy containing 1.2 per cent sulfur. Dendritic structure of the copper is smaller. X 100.

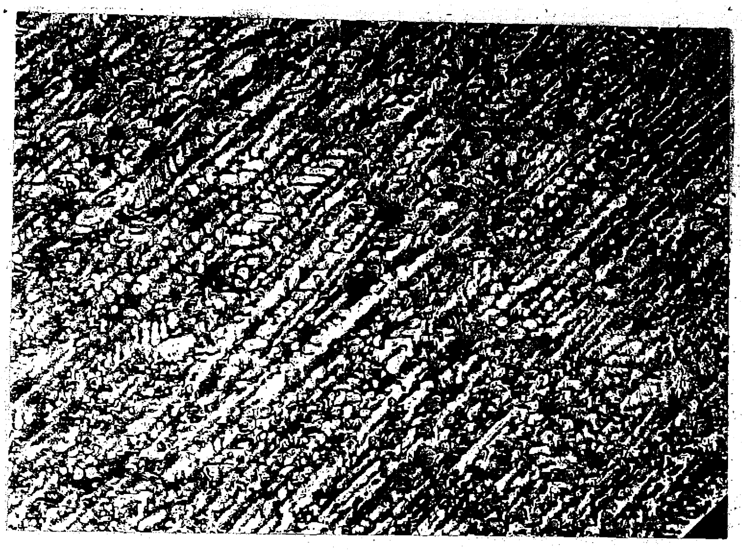

Plate 23. Alloy containing 1.8 per cent sulfur. Smaller structure and more sulfide. In this ingot the copper formed long dendrites elongating what is roughly the equi-temperature surface. X 100.

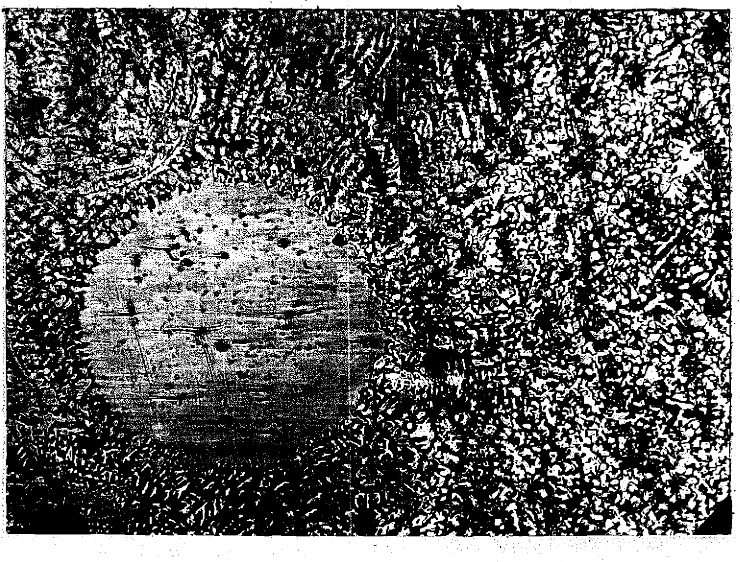

Plate 24. Alloy containing 3.1 per cent sulfur The excess globules of sulfide are seen. The dendrites are much smaller than in the preceding alloy. X 100.

Photographs of the Effect of Sulfur on the Lead Distribution.

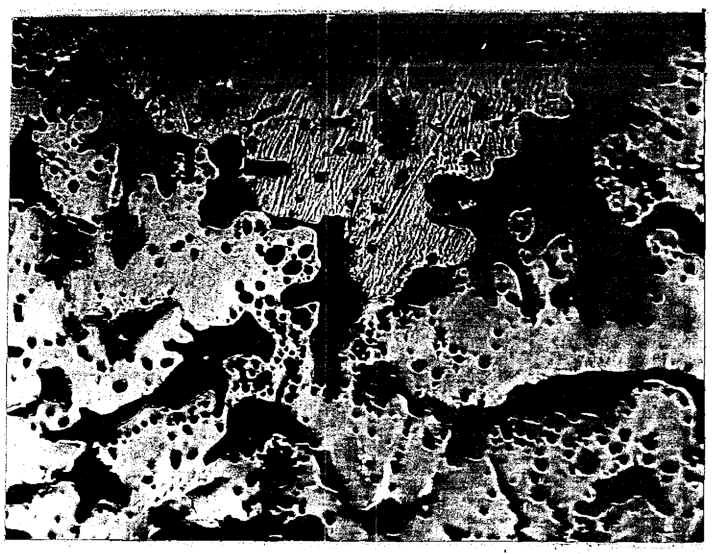

Plate 25. Alloy containing no sulfur. Granulations can be seen in one dendrite.
X 250.

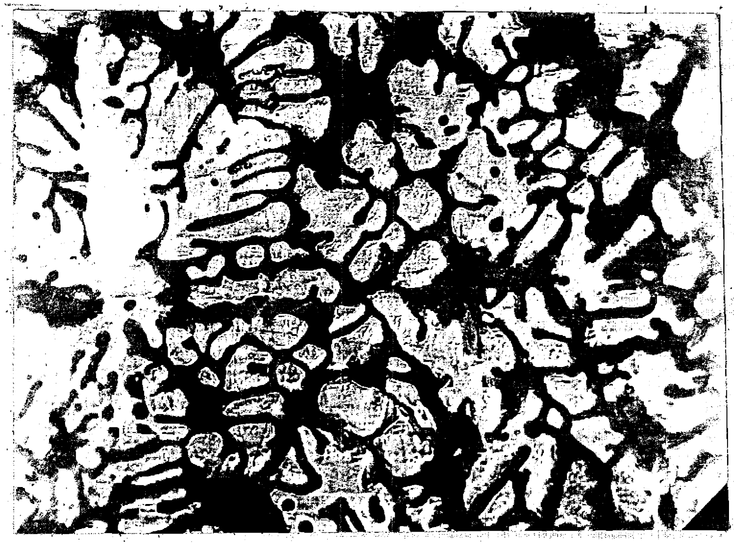

Plate 26. Alloy containing .3 per cent sulfur. No sulfide can be seen.
X 250.

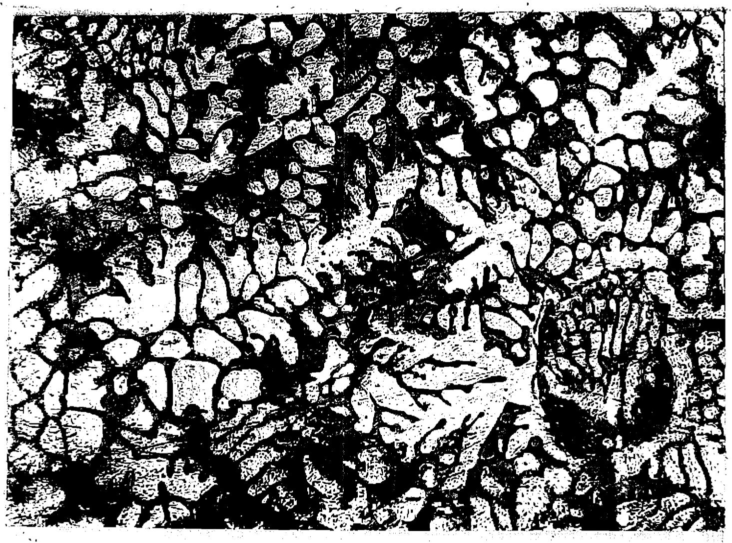

Plate 27. Alloy containing .8 percent sulfur. Smaller copper dendrites and better lead distribution.
X 250.

Photographs of the Effect of Sulfur on the Lead Distribution.

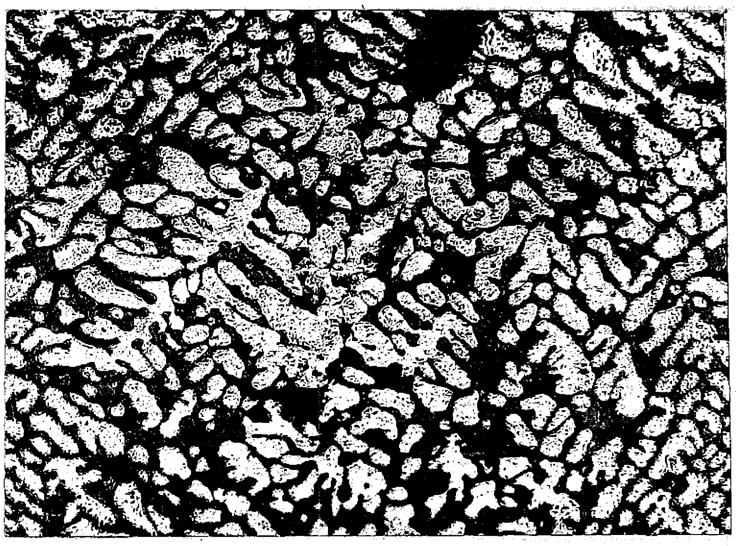

Plate 28. Alloy containing 1.2 per cent sulfur. Increasing amount of sulfide and smaller size.
X 210.

Plate 29. Alloy containing 1.8 percent sulfur.
X 250.

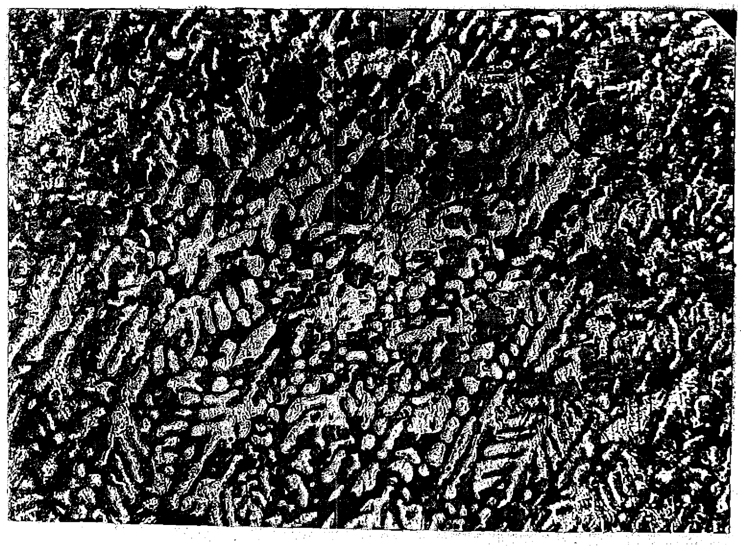

Plate 30. Alloy containing 3.1 per cent sulfur.
X 250.

streak that is visible to the naked eye. The structure shown by the microscope indicates that the .8 per cent sulfur alloy gave the structure best suited for bearing purposes. Higher sulfur content gave an excessive amount of copper sulfide and in two ingots the copper assumed long dendritic forms that would not stand the wear as well as equi-axed grains. In the .3 per cent sulfur alloy none of the sulfide particles can be seen in the lead areas where the sulfide is always present. This indicates that the sulfide is soluble to a slight extent in either the copper or the lead. Plate 31, page 41, shows the alloy containing 1.8 per cent sulfur at a very much higher magnification. Plate 31, page 41, shows the alloy containing 1.8 per cent sulfur at a much higher magnification.

Plates 32 and 33, page 41, show the effect of the addition of a small amount of sulfur. Plate 32 shows the alloy with no sulfur. Here the lead forms globules and the copper seems to form the continuous matrix. With .3 per cent sulfur the structure is radically changed. Here the lead forms the continuous matrix and the copper forms dendrites. This is the typical structure for all the alloys that contain sulfur. The structure shown in Plate 32 does not occur throughout all portions of the lead-copper. In some places the copper

Photographs of the Effect of Sulfur on the Lead Distribution.

Plate 31. Alloy containing 1.8 per cent sulfur at a higher magnification. Shows the dark copper sulfide particles in the lead areas. X 2000.

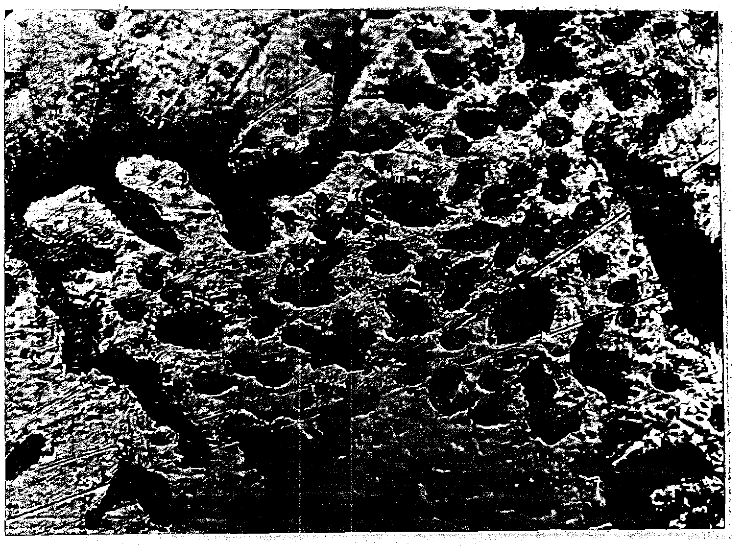

Plate 32. Alloy with no sulfur at a higher magnification. This photograph shows the copper forming the continuous matrix and the lead forms globules. X 500.

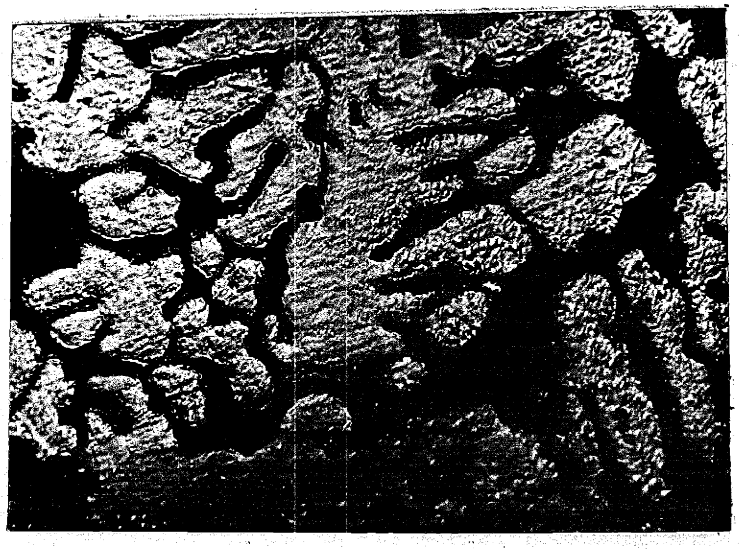

Plate 33. Alloy containing .3 per cent sulfur. The lead now forms the continuous phase and the copper forms dendrites. A few dark particles of copper sulfide can be seen in the lead. X 500.

forms in dendrites. This structure however only occurs in the alloy with no sulfur.

This changing of the continuous phase has its counterpart in liquid emulsions and is a surface tension phenomenon. When two non-miscible liquids are shaken together they may form an emulsion. One liquid called the internal or discontinuous phase forms drops within the external or continuous phase. One of the conditions of stability is that the drops shall be enveloped in a film strong enough to prevent their evalescence. In order to do that the interfacial tension between the phases is lowered by the addition of an emulsifier. If the size of the interfacial tension is changed, that is if the surface tension of the drops is lowered to below that of the envelop by the emulsifier, then the drops form the continuous phase and the envelop then forms the drops.

This explanation would account for the known fact that sulfur has a weakening effect on the alloy. With sulfur present the alloy would only be slightly stronger than pure lead. With no sulfur the strength would approach that of the copper matrix.

Another factor in the effect of sulfur might be due to the fact that the copper sulfide is in the lead areas. The copper sulfide has a much lower specific gravity and hence would tend to float the heavy lead. That this factor does not have an appreciable effect is shown by the fact that .8 per cent sulfur, which is the common alloy, reduces the average specific gravity of the lead areas from 11.37 to 10.75 while the copper matrix is 8.93.

5. Structure of Alloy Prepared by Melting Copper-Lead Alloy under a Cover of Shale

The shale used is found in the state of Utah and is supposed to control lead distribution by "making a more intimate mixture between the copper and lead." In one crucible the copper was melted down under a cover of charcoal while in a second crucible the copper was melted down under a cover of this shale that had been powdered. When molten, the lead was added and the temperature adjusted to 1100°C. and then the contents stirred and poured into similar iron molds. Sections were cut out from the middle of each ingot in the usual manner and polished and etched. The specimen melted under the shale showed long patches of lead before even being put under the microscope. In this respect it was the worst specimen that was cast. However, under the microscope the general structure of specimen, except for the lead areas, was fairly good. The structure is shown in Plate 34, page 45. The corresponding structure of the alloy melted under charcoal is shown in Plate 35, page 45. Plate 36, page 46, shows a curious crystallization figure that occurred in a lead area in the alloy melted under the shale. Plate 37, page 46, shows the same figure at a higher magnification.

Comparison of the Shale with the Charcoal as Covers.

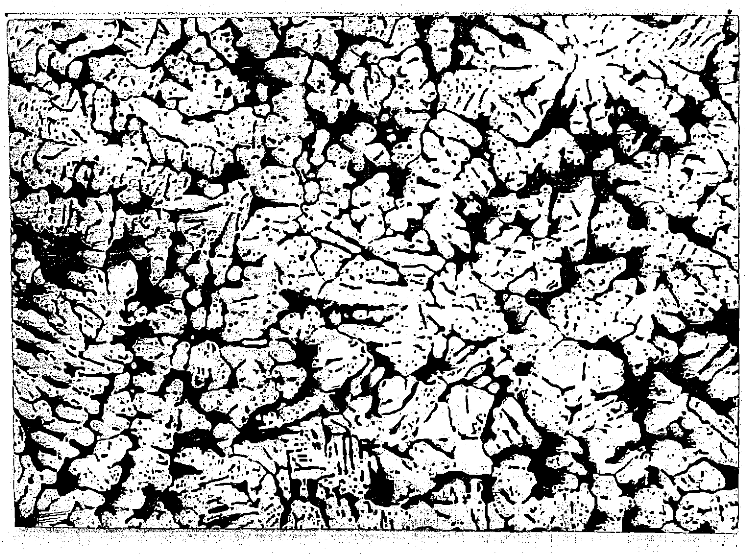

Plate 34. 70-30 copper lead alloy melted under a cover of powdered shale and poured at 1100°C. into an iron mould. No particles of sulfide can be observed. X 100.

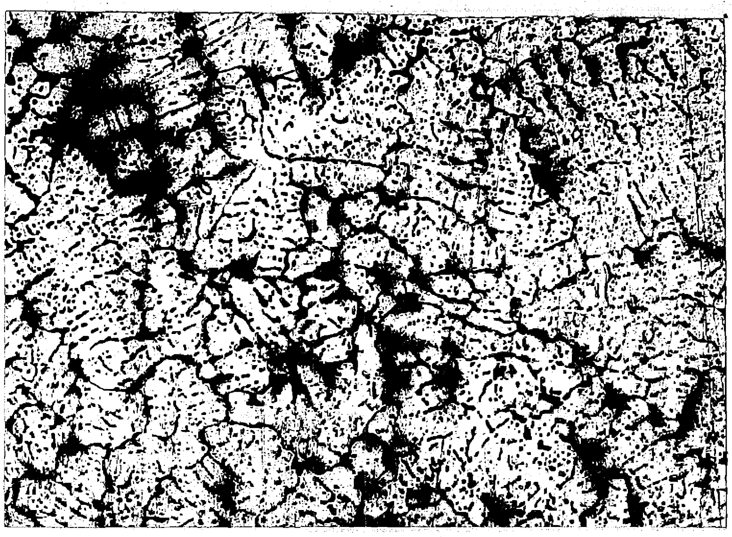

Plate 35. 70-30 copper lead alloy melted under a cover of charcoal and poured at 1100°C. into and iron mould. The lead distribution in this is just as uniform as in the alloy melted under shale. X 100.

Comparison of the Shale with the Charcoal as Covers.

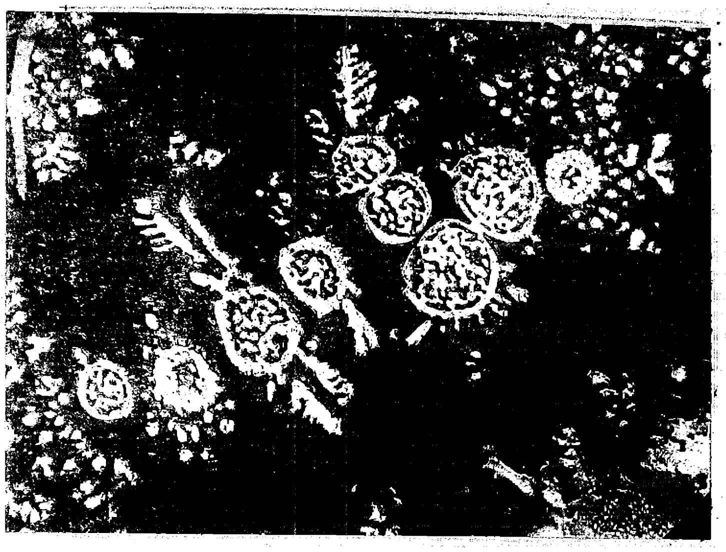

Plate 36. Curious crystallization figure found in a lead segregation in the alloy melted under the shale cover. X 100.

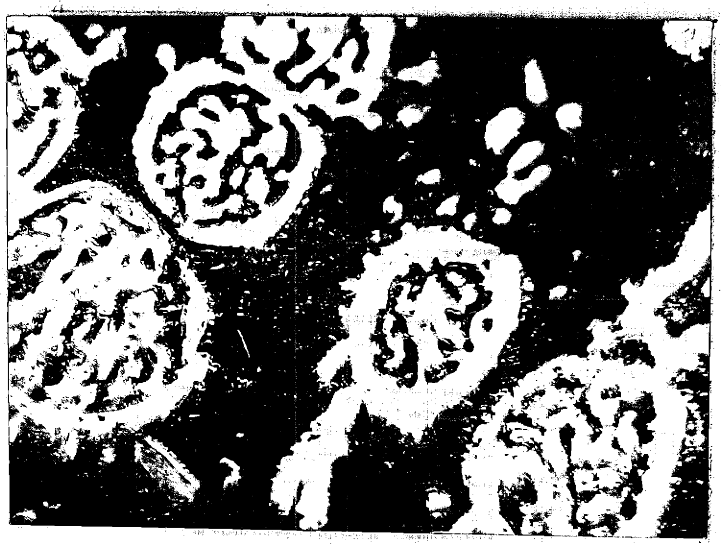

Plate 37. Same crystallization as plate 36. at a higher magnification. X 750.

6. Inverse Segregation in the Copper-Lead Alloy

The ingots that were cast in sand showed the exudations on the surface. It was found in the three ingots cast in sand that at the base of nearly every exudation there was a layer of lead. There did not seem to be an appreciably different amount of lead on one side or the other of this layer, but there was a marked difference in the size of the copper dendrite. It was very much smaller on the surface side of the lead layer. Examination of this lead layer showed that in several cases it was full of channels. These might have been caused by gases forcing the exudation out. Plate 38, page 48, shows the internal structure of the ingot cast from 1100°C. Plate 39, page 48, shows the marked difference in the copper dendrite in the exudation. Plate 40, page 48, shows the structure of the lead layer, and the connecting channels can be plainly seen.

Inverse Segregation in Copper-lead Alloys.

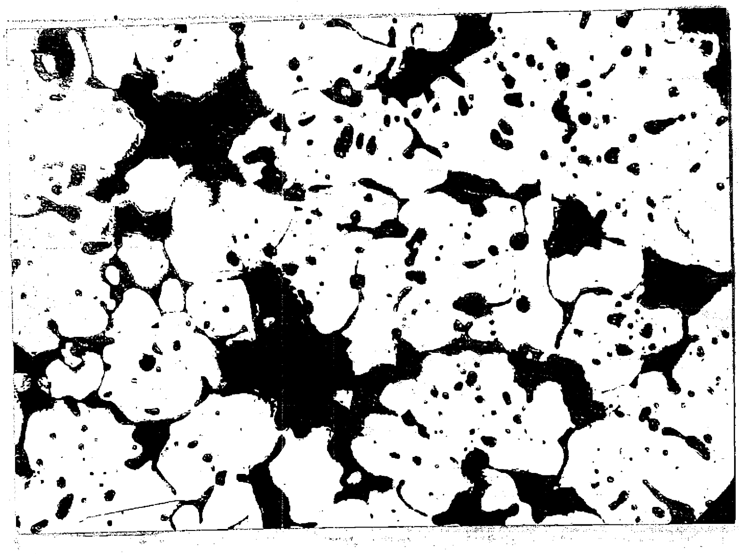

Plate 38. Showing the structure of the internal side of the lead layer in an ingot that showed exudations. X 100.

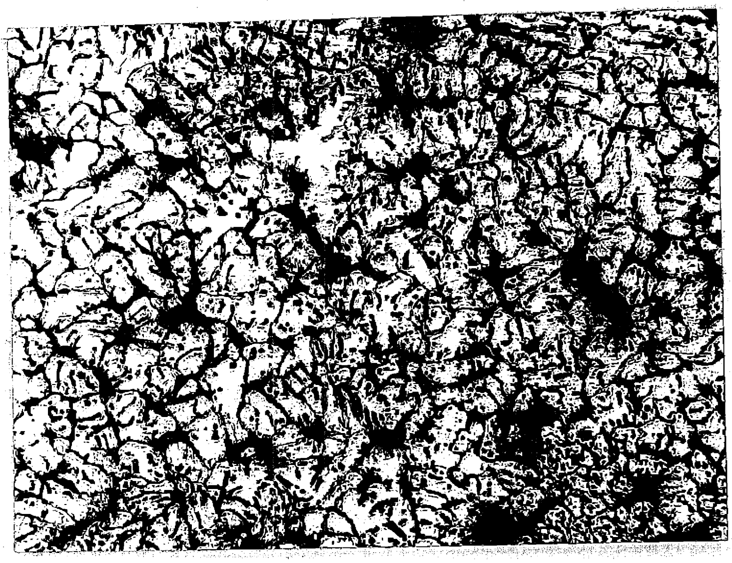

Plate 39. Showing the structure on the external side of the lead layer. X 100.

Plate 40. This shows the structure of the lead layer. The connecting dark channels are probably caused by evolved gas. Copper can be seen along one channel as if remnants of the copper rich solution had been left in the progress of the remainder to the surface. X 100.

The microstructure of "Ackermite" did not show the proper casting temperature as the difference between 1000 and 1175°C. for such a small quantity of alloy as was used made no difference in the rate of solidification. Heat was abstracted just as fast from the hot metal as from the cool. The liquidus was determined by melting a sample of 100 grams of the alloy under charcoal and inserting a calibrated thermocouple and attaching it to a recording pyrometer and obtaining the cooling curve of the alloy. The liquidus was shown to be 935°C.

VI. CONCLUSIONS

1. The lead distribution in "Ackermite" is effected by means of sulfur. The copper sulfide particles are completely within the lead areas.

2. The proper pouring temperatures of"Ackermite" depend upon the size of the casting.The liquidus lies in 975°C. The alloy should be poured from above this temperature and only enough above it to have the metal run into the mold and completely fill it. For a small casting the temperature would have to be higher than for a large casting.

3. Sulfur has a marked effect on the lead distribution throughout the alloy. The size of the copper dendrite is decreased by increasing amounts of sulfur.

4. The rate of solidification has a great effect on the lead distribution. For rapidly cooled metal the size of the copper dendrite is very much smaller.

5. The oil shale apparently has no effect on the lead distribution.

VII. SUGGESTIONS FOR FURTHER WORK

The author suggests that it might be desirable to do further work in the following lines:-

1. Study of the causes and prevention of "lead sweat." The author believes that it would have to be carried out with larger ingots as in only a few cases did "lead sweat" occur in the ingots used. If due to gases evolved at solidification, the small amount of gas evolved in the size of ingots used in the present work probably would not be large enough to create sufficient pressure to cause "sweating."

2. Study of the effect of sulfur on the copper-lead series. It might be profitable to observe the effects of a small amount of sulfur and determine the solid solubility limits.

3. Study of the change in mechanical properties with changing amounts of sulfur to determine which from the mechanical standpoint is the best.

4. Study of the effect of tin in the lead distribution. Tin is supposed to hold up lead and the exact mechanism is not clear. It is known, however, from the Ajax plastic bronze patent that the tin should not exceed 9 per cent of the amount of copper present. With

greater amounts the delta eutectoid forms and increases the solidification interval. It can not be seen how smaller amounts would aid in the lead distribution as a copper-tin matrix would have a larger freezing range than a pure copper matrix. Whether or not for equal amounts the solidification time would be longer or not is not known.

5. It might be profitable to experiment further with the shale. The tests carried out on the shale were by no means complete and the shale might easily control the lead segregation. It might be well to analyze the shale. If analysis reveals sulfate it is quite certain that the shale will be beneficial. Often in the foundry instead of adding sulfur in the form of sticks or galena it is added by stirring in a sulfate. For this gypsum is usually used. However, probably various other metal sulfates would do just as well.

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