July 6, 1948. W. A. BROWN ET AL 2,444,424

STEEL METALLURGY

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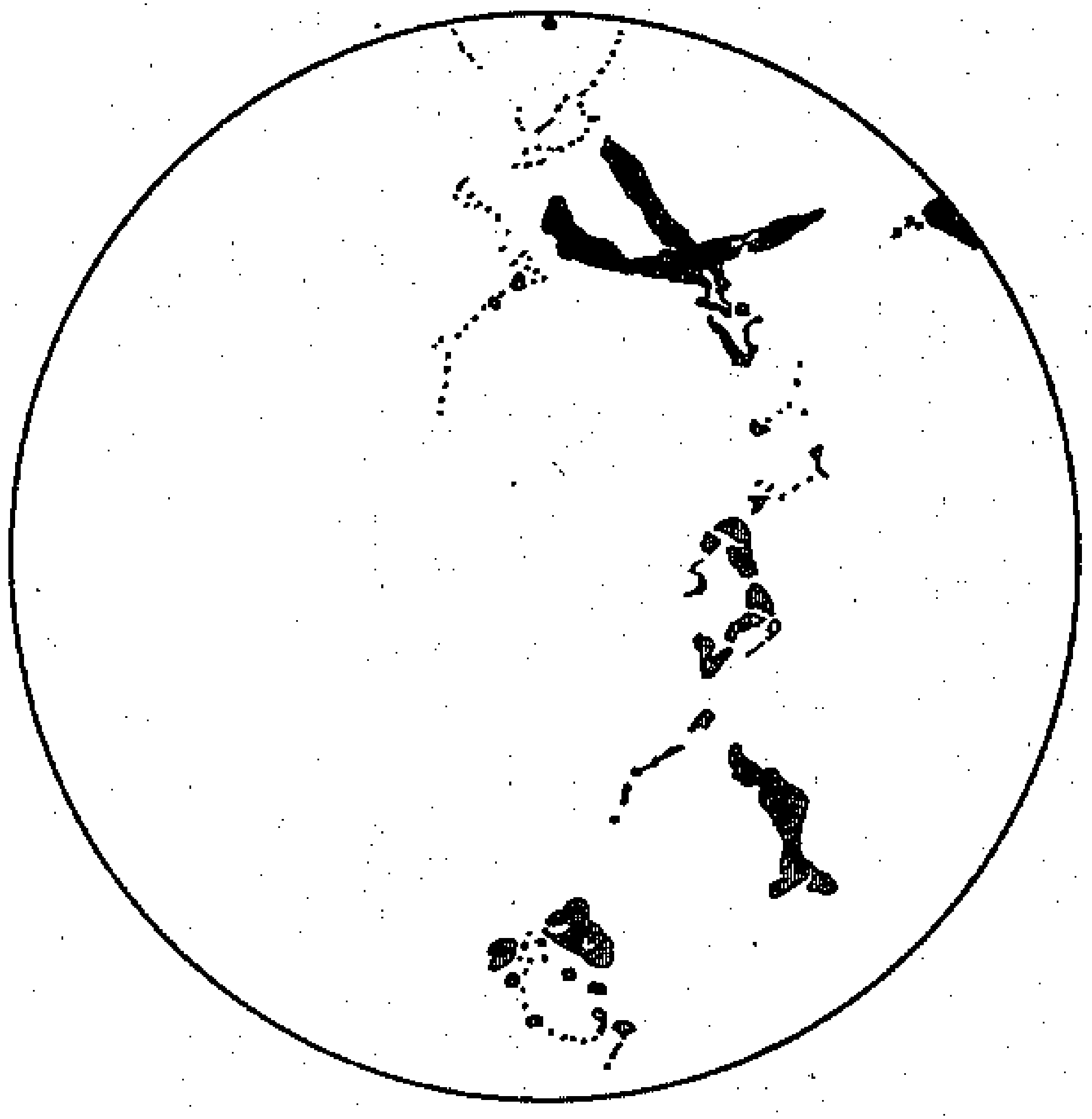

Figure 1

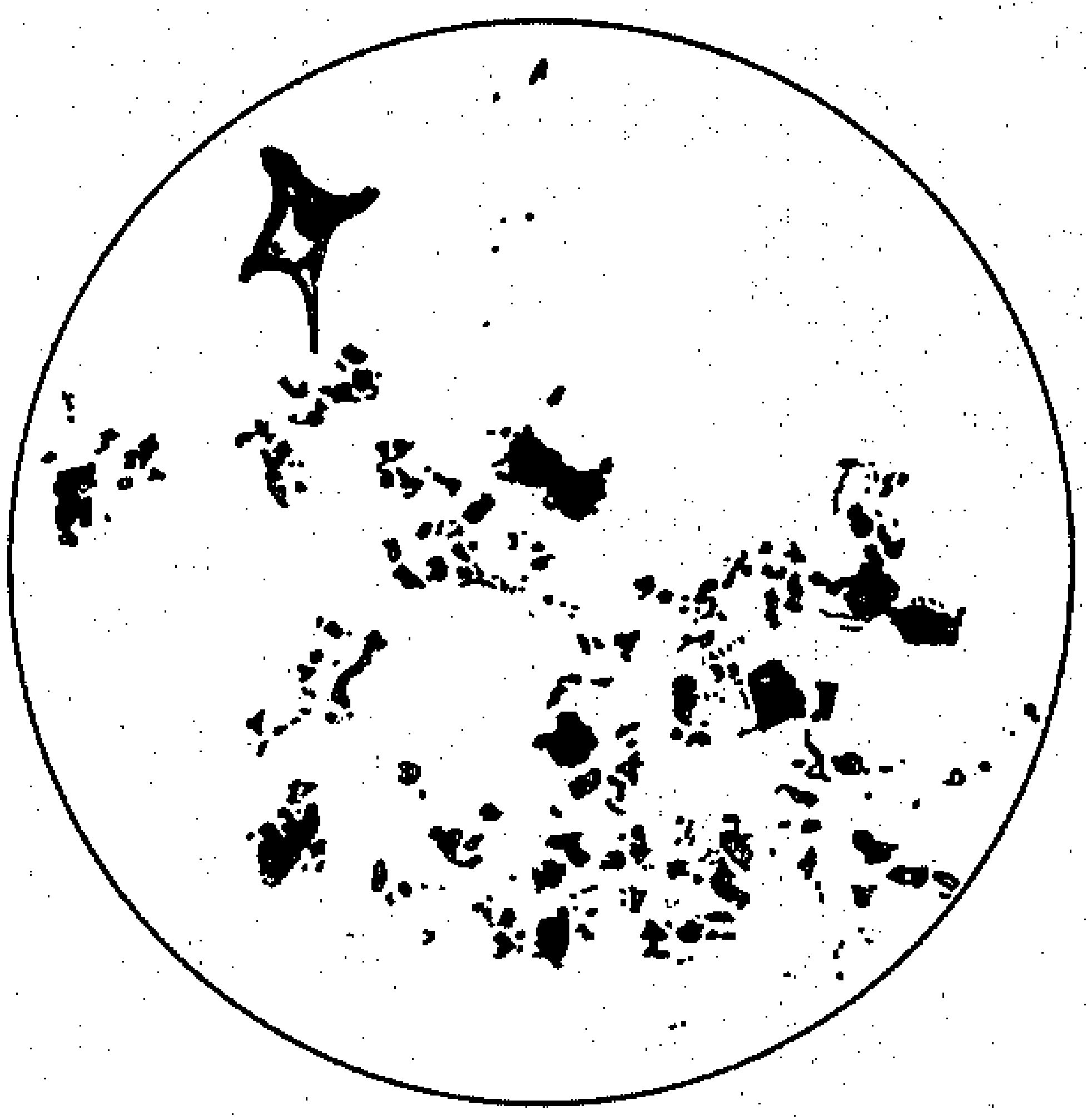

Figure 2

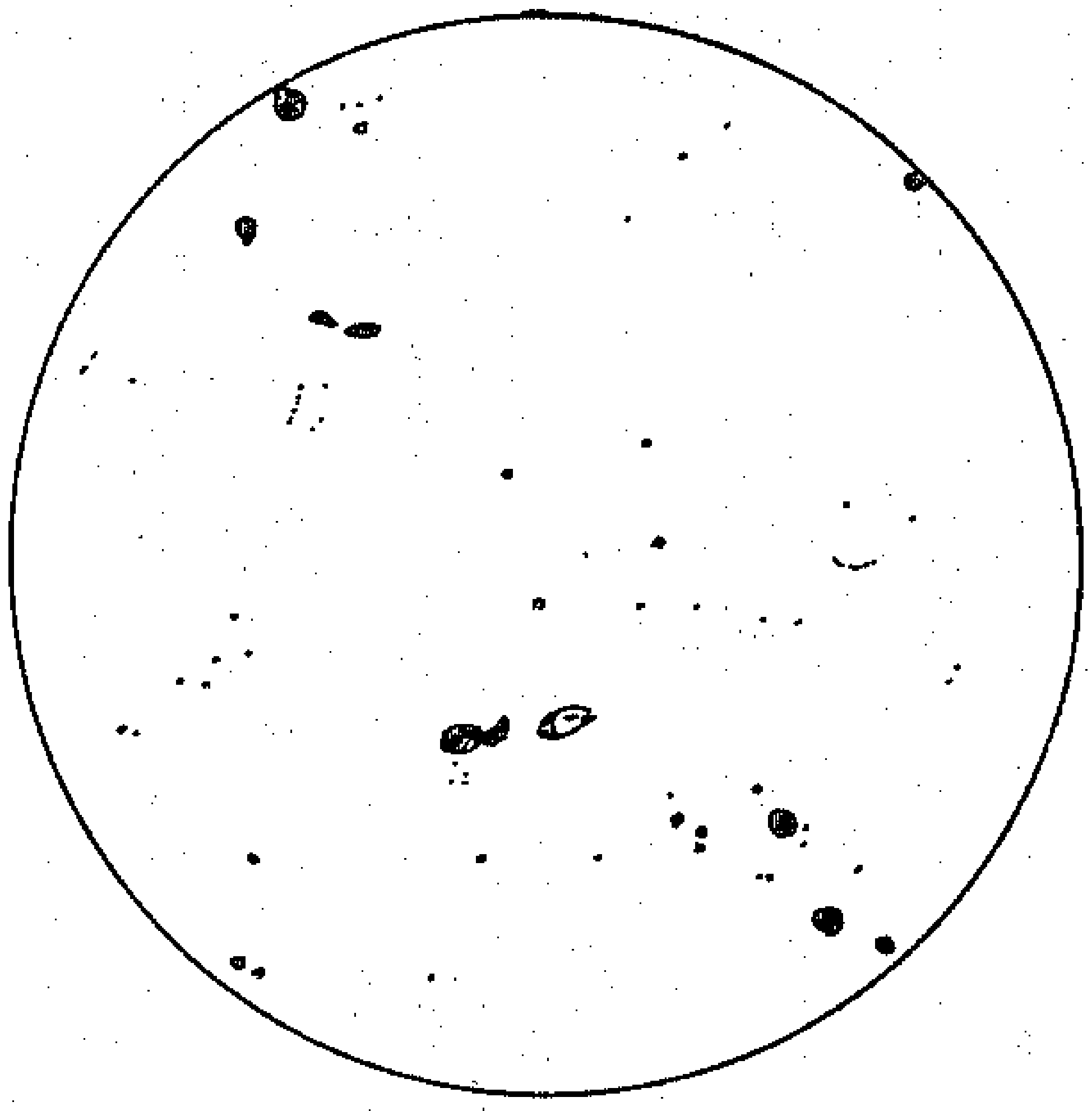

Figure 3

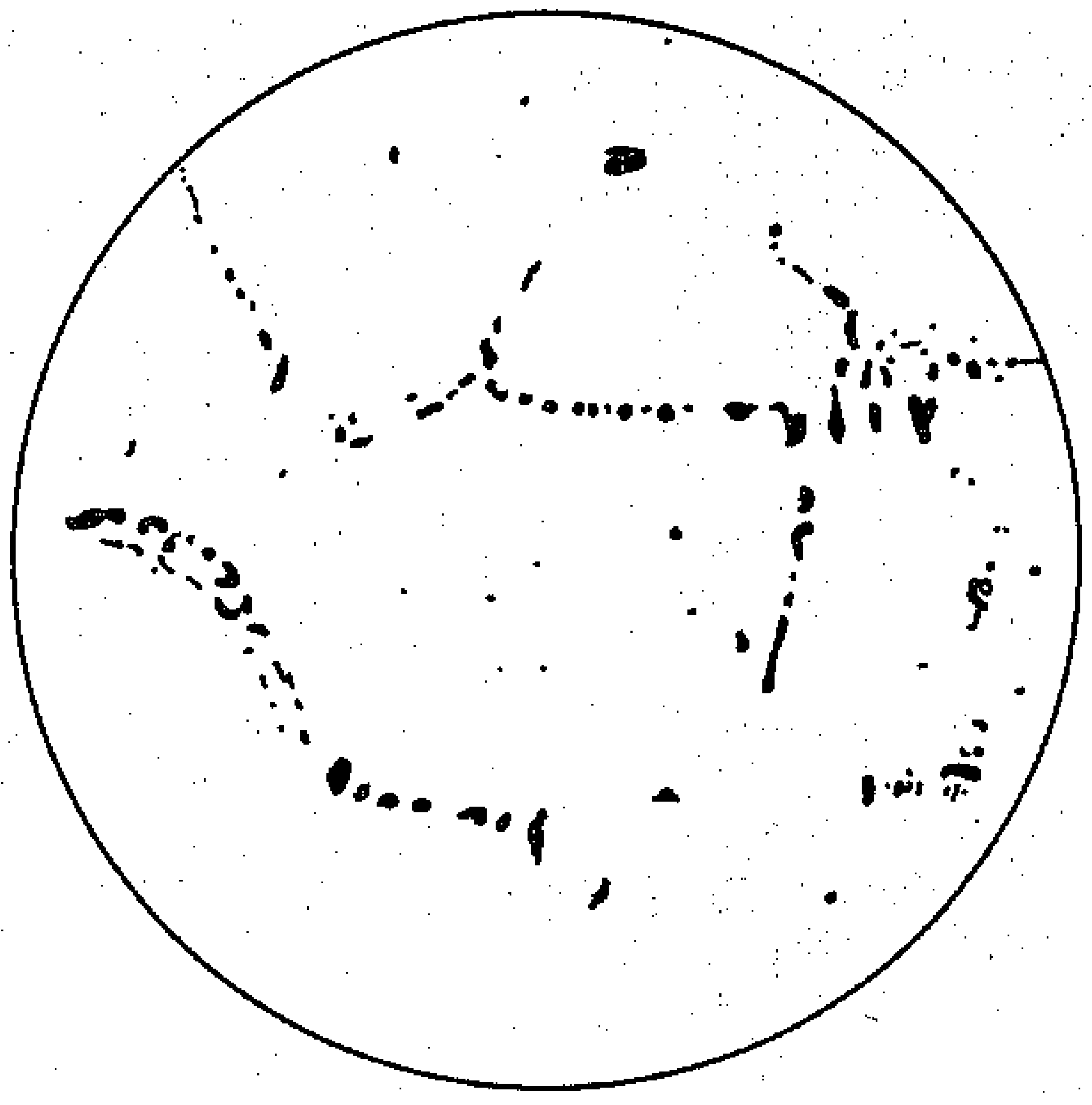

Figure 4

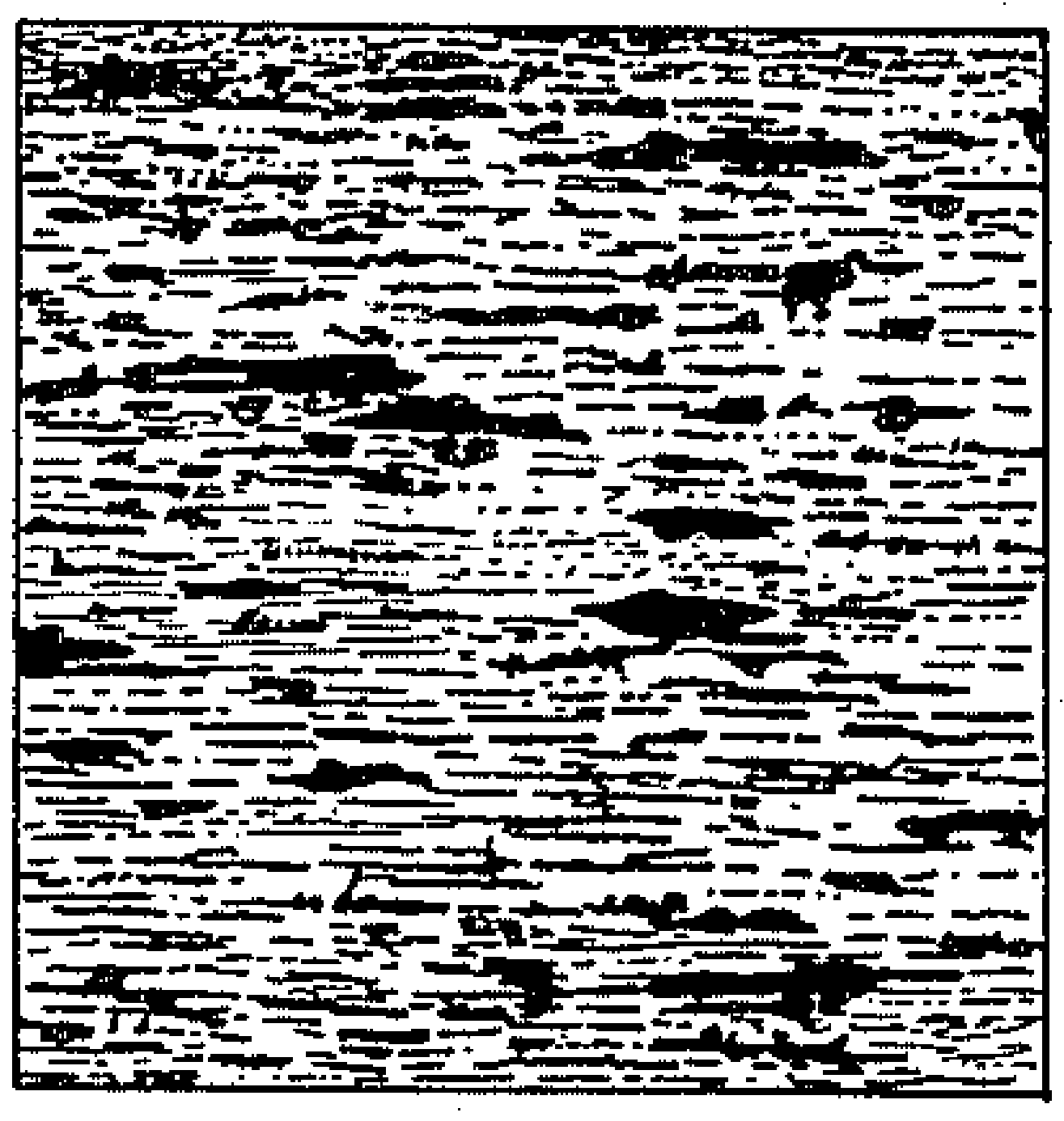

Figure 6

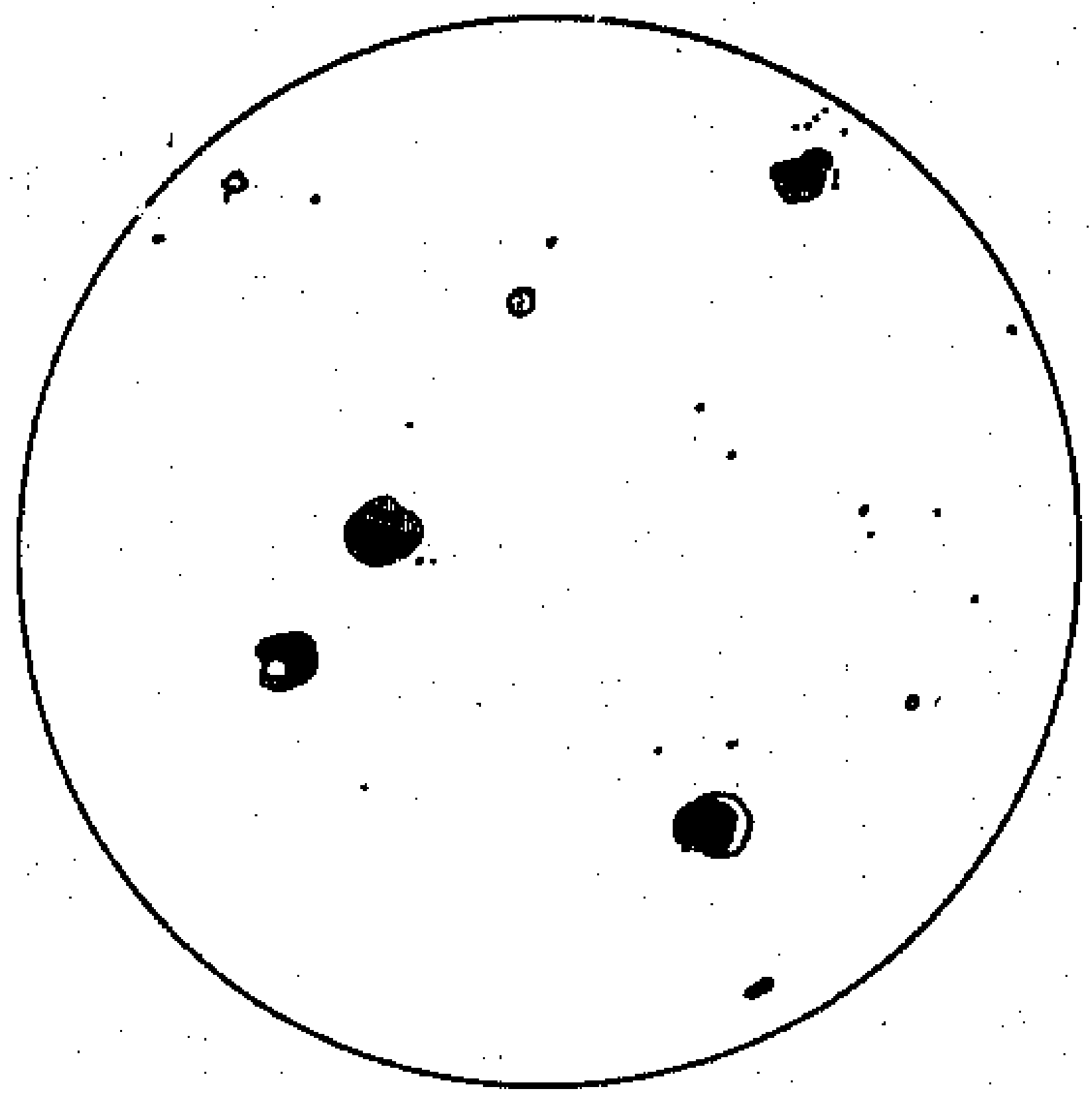

Figure 5

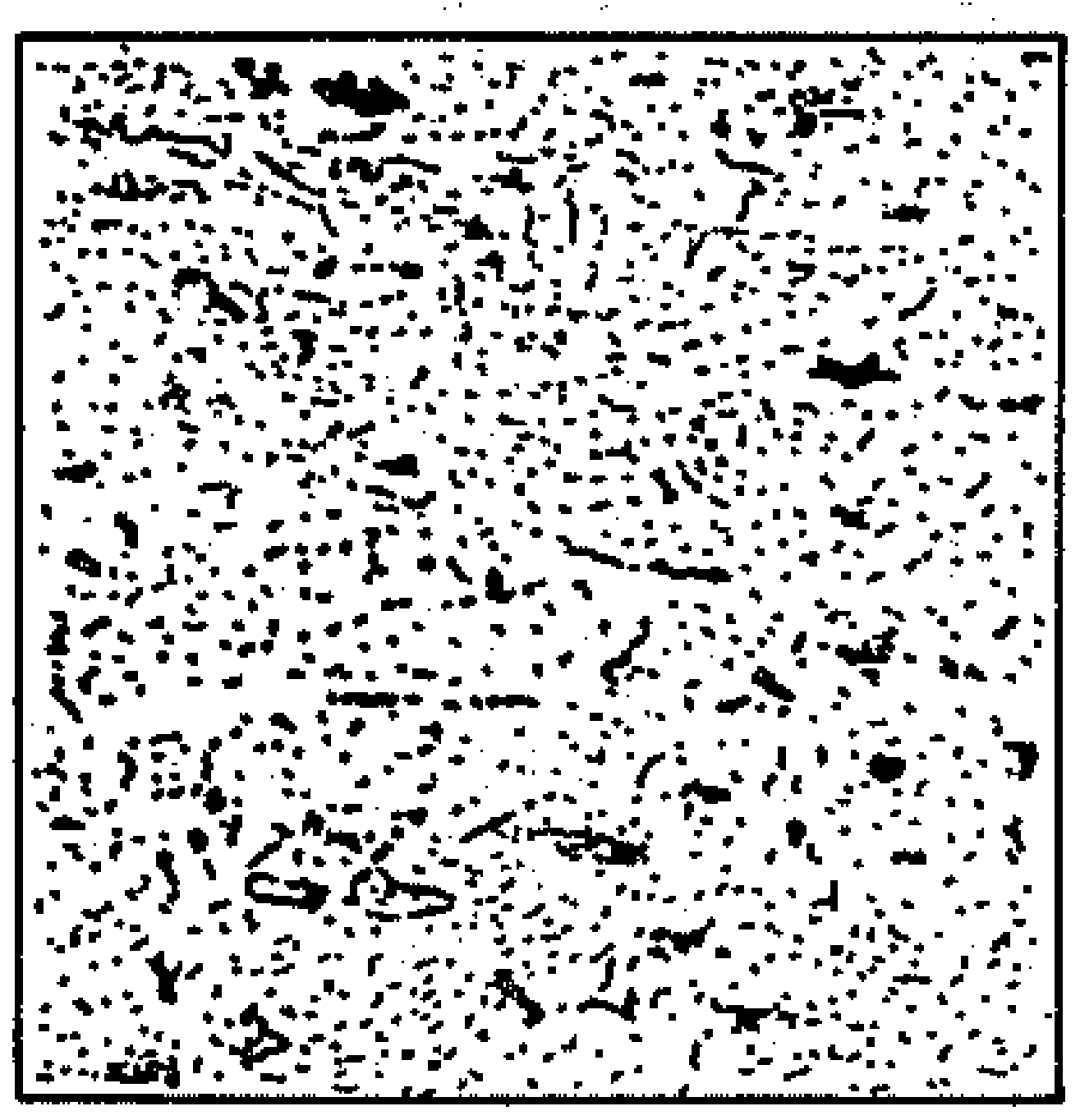

Figure 7

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STEEL METALLURGY

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10 Claims. (Cl. 75—58)

This invention relates to the production of steel. It particularly relates to the production of steel for ingots or castings in which it is very important to produce sound metal with the greatest possible freedom from gas bubbles or holes in the metal and from deleterious inclusions.

It is an object of the present invention to provide a process for the final deoxidation of steel which will result in the production of sound, clean ingots or castings having improved microstructure and physical properties. Other objects of the present invention are to increase the ductility of deoxidized steels and to reduce the tendency in such steels for the segregation of inclusions, particularly oxide and sulfide inclusions. A still further object of the present invention is to produce a steel which has an increased hardenability and creep strength. Additional objects of the present invention will be perceived from the following specification. These desired objects are obtained by a process which involves the use of granular silicon carbide in the manner hereinafter set forth for controlled final deoxidation of the steel.

In the ordinary processes of making steel a ferrous base mixture is treated in such a manner as to oxidize and remove the undesired elements present. These elements vary with the composition of the charge used. The more common elements which are removed by oxidation are carbon, silicon, and manganese. With the exception of the carbon (the carbon monoxide formed by its oxidation passing off as a gas) these elements are converted into fusible oxides which for the most part rise through the steel and become part of the slag which floats on the surface of the metal. Sulfur and phosphorus, also occurring as impurities, may be partially removed into the slag as sulfides and phosphates when a basic slag is employed.

It has been customary to add various substances such as aluminum, calcium silicide, titanium and other deoxidizing agents to remove the oxides that are mechanically entrapped and in solution in the steel after it has left the furnace. It has been discovered that the use of granular silicon carbide as a final deoxidizer in accordance with the process of the present invention removes almost completely the last traces of oxides and oxygen that still remain in solution in the steel, and at the same time breaks up the mechanically entrapped oxides, destroying their continuity and dispersing them uniformly throughout the mix. In this way there is produced a steel of exceptionally good quality, possessing physical properties and structure superior to those ordinarily obtained.

In order to obtain the herein disclosed benefits which may be derived from the deoxidation of steel with silicon carbide, it is essential that silicon carbide be added to the steel in the ladle in accordance with the process now to be disclosed and under the conditions specified herein. Additions of silicon carbide which are not made in accordance with this method and under these conditions will invariably produce results which are erratic or ineffective. Indeed, such additions are almost invariably actually detrimental to the quality of the steel since they result in the production of steel which is of lower quality than steel to which silicon carbide has not been added.

The first problem in the application of silicon carbide to steel is that of obtaining complete dispersion of the silicon carbide particles throughout the mass of molten steel in the ladle. The layer of slag which lies over the steel bath, the high surface tension of the molten steel, and its high specific gravity as compared to that of silicon carbide, all combine to make it impossible to disperse the silicon carbide particles throughout the molten steel bath unless the addition is made in the manner hereinafter described.

The second problem which remains even after complete dispersion of the silicon carbide has been obtained, is that of obtaining satisfactory reaction of the silicon carbide with the impurities in the molten steel. The solution of this problem requires the taking of certain precautions and careful regulation. Such precautions and regulation are concerned with the mesh size of the silicon carbide used, the size and temperature of the steel bath in which deoxidation takes place, and the period during which the molten steel must be held in the ladle before starting to pour it into molds.

It is essential that silicon carbide of comparatively small particle size be used and that the ladle of steel be held much longer than is now commercial practice in order to produce the results desired. It has been found that the beneficial results which are obtained by holding the steel in the ladle for a longer period before pouring far outweigh the usual objections to following this practice, especially since these beneficial results can be obtained only in this way. Furthermore, it has been found that the exothermic action of the silicon carbide in deoxidizing the steel substantially offsets the usual objection that excessive temperature reduction results when the ladle of steel is held for the period of time called for by the process of the present invention. The required holding time must be determined, as discussed hereinafter in more detail, in relation to the size and temperature of the steel bath and the grain size of the silicon carbide employed.

The details of the process by which it is possible consistently to secure successful results in the deoxidation of steel with silicon carbide are as follows.

A. The silicon carbide must be added to the steel pouring into the ladle. The addition should be made between the time when the ladle bottom is just covered with metal and the time when the ladle becomes one-fourth filled with molten steel. It is necessary that the silicon carbide be enclosed in containers which will disintegrate in the molten steel but which do not disintegrate until they have been forced, by the stream of steel entering the ladle, beneath the surface of the metal in the ladle. Although other containers may be used, it has been found that a convenient and very satisfactory container is a four-ply paper bag. The bags or other containers of silicon carbide are thrown into the ladle directly at the base of the entering stream of steel. The molten stream thus acts as a mechanical plunger which forces the packages of silicon carbide beneath the surface of the bath, whereupon the container disintegrates and the fine particles of silicon carbide are distributed throughout the bath by the turbulence there existing. Thereafter the silicon carbide particles slowly rise through the molten steel, their rise being retarded by their fine particle size and by the inherent high viscosity of the molten steel.

B. After the ladle is filled, it is necessary to hold it for a more or less prolonged period in order to allow sufficient time for the silicon carbide molecules to dissociate and react with the impurities of the steel.

These reactions, by removing the oxides in the steel, increase its fluidity. There is also an evolution of heat because the reactions of the silicon carbide with the oxides are exothermic. As a consequence of these circumstances, more time may be allowed, without undue loss of fluidity, for the inclusions which occur in the molten steel, or which are formed therein as a result of the deoxidizing reactions, to coalesce and rise through the bath of steel into the covering slag. With the steel at a temperature of 2900° F. when tapped from the furnace and with silicon carbide of comparatively small size (factors discussed in the following two paragraphs) the steel should be held in the ladle for at least 15 minutes.

C. It is necessary for the steel to have a temperature of at least 2900° F. when it is tapped from the furnace although higher tapping temperatures may be employed.

D. Rather finely-divided silicon carbide must be used as a ladle addition for the deoxidation of steel since if coarse particles are used they do not completely react in the ladle and will consequently cause pores or gas bubbles to appear in the castings or ingots. With a tapping temperature of 2900° F. and with the steel being held in the ladle for 15 minutes, it is preferred to use silicon carbide of particle size such that it will pass through a standard screen having 50 mesh openings per linear inch; and silicon carbide of such fineness is meant when "50 mesh silicon carbide" is referred to hereinafter in the specification and claims. Although there is no advantage to the use of coarser silicon carbide it is possible under the above-mentioned conditions to use silicon carbide substantially no particles of which are held on a standard screen having 36 mesh per linear inch; and silicon carbide of such fineness is meant when "36 mesh silicon carbide" is referred to hereinafter in the specification and claims. If silicon carbide having any substantial proportion of its particles coarser than 36 mesh is used it has been found that almost invariably after the steel has been poured into the ingots or molds the unreacted coarse particles of silicon carbide remaining in the steel will react. The resulting reaction products—silica (SiO_2) and carbon monoxide (CO)—being unable to escape from the steel in the ingot or mold because of the lowered viscosity resulting from loss of heat remain entrapped and produce a dirty, gaseous product unfit for commercial use.

By following the method above set forth and conforming to the conditions specified, and only by so doing, steel may be produced which is much cleaner, freer of gases and inclusions, and considerably superior in physical properties to the steels now produced by presently known processes of deoxidation.

In the accompanying drawings, Figures 1–5, inclusive, illustrate the appearance of photomicrographs of polished sections of steel. Figures 3 and 5 show sections of steel specimens made in accordance with the process of the present invention and Figures 1, 2 and 4 show sections of steel specimens which have not been so made.

Figures 6 and 7 are reproductions of sulfur contact prints of steel, Figure 6 being taken on a steel made without deoxidation by silicon carbide and Figure 7 being taken on a steel of the same analysis which has been deoxidized with silicon carbide in accordance with the process of the present invention.

The effect of the deoxidation by silicon carbide in accordance with the process of the present invention on the physical properties of steel may be seen from the following example:

Example I

To a steel having a carbon content of .27% and a silicon content of .41% there was added as a deoxidizer, in making one casting, 3 pounds of aluminum per ton of steel to the ladle, and, in making another casting, silicon carbide as a deoxidizer was added to the ladle, in accordance with the process of the present invention, in the proportion of 4 pounds per ton of steel. The following table shows the effect upon the yield point and ultimate strength of the steel resulting from the use of the different deoxidizers as compared to steel with no deoxidizer.

	Yield Point	Ultimate Strength
	P. s. i.	*P. s. i.*
No deoxidizer	54,700	87,000
Al deoxidizer	47,400	80,150
SiC deoxidizer	60,950	94,600

It will be seen from the results of these tests that both the yield point and the ultimate strength of the steel deoxidized with silicon carbide have been materially increased above those of the aluminum deoxidized steel as well as the steel without a deoxidizer. All of the specimens were tested after being cooled in air from 1700° F.

Another example which indicates the nature of the improvement in physical properties of a steel resulting from the use of silicon carbide as a deoxidizer in accordance with the process of the present invention is as follows:

Example II

	Carbon	Silicon	Yield Point	Ultimate Strength	Elongation	Reduction in Area
	Per cent	*Per cent*	*P. s. i.*	*P. s. i.*	*Per cent*[1]	*Per cent*
No deoxidizer	0.29	0.39	51,000	80,000	16.5	35.0
			51,150	80,150	17.0	33.8
SiC deoxidizer	0.29	0.41	55,800	84,000	29.0	47.2
			56,000	84,500	30.0	49.5

[1] In 2 in.

It will be noted that the steel in which no deoxidizer was used and the one in which silicon carbide, in the proportion of four pounds per ton of steel, was used in accordance with the process of the present invention are almost identical so far as carbon and silicon content are concerned. It will be noted further that not only is the strength increased as shown by the increased yield point and ultimate strength figures, but that the elongation and reduction in area are also greatly increased by deoxidation with silicon carbide. It is evident that the steel of the silicon carbide deoxidized specimens will have a much greater ductility than will that of the specimens which were not deoxidized with silicon carbide. The specimens tested in this example were air cooled after heating for 2 hours at 1700° F., reheated for 2 hours at 1460° F. and again air cooled.

The employment of granular silicon carbide, in accordance with the process of the present invention, as a deoxidizer for steel is also advantageous in other ways. The fluidity of the steel bath is very materially increased as a result of the deoxidizing reactions with silicon carbide both because of their effect in decreasing the oxide or gas content of the steel and also because of the considerable heat evolved as a result of the exothermic nature of these reactions. This increased fluidity is beneficial since it improves the castability of the steel and since it permits slag inclusions and gas bubbles in the steel to rise more readily to the surface. For this reason steel which has been deoxidized with silicon carbide in accordance with the process of the present invention is very clean and has fewer detrimental inclusions.

Moreover, the chemical reactions between the silicon carbide and the inclusion-forming impurities in the molten steel alter the chemical composition of the impurities and thus change their solubility in the steel. Accordingly, even such impurities as are not removed from the molten steel are likely to be precipitated early during the solidification of the steel. They thus occur in the form of the more desirable random globules instead of the undesirable segregations which are produced when impurities are precipitated late in the solidification. It should also be remembered that both the silicon and carbon which form silicon carbide are normal ingredients of steel and therefore add no undesired foreign elements to the steel.

Other deoxidizers do not have the advantages, mentioned in the preceding paragraphs, that are found in the use of silicon carbide in accordance with the process of the present invention. Thus, for example, when aluminum is used as a deoxidizing agent, residual aluminum oxide and aluminum sulfide are found in the resultant steel. Not infrequently these impurities are found so distributed or segregated as to render the steel unsuitable for use. One of the disadvantages of such inclusions is their effect in materially reducing the ductility of the steel.

The following example shows that improvement in the physical properties, including the ductility, of steel may be obtained by deoxidation with silicon carbide in accordance with the process of the present invention, not only in the direction of the grain of the steel but also across the grain of the steel. The latter is of particular importance in the case of forgings and other highly-worked steel products or articles.

Example III

Deoxidizer	Direction of Specimen	Yield Point	Ultimate Strength	Elongation	Reduction in Area
		P. s. i.	*P. s. i.*	*Per cent*[1]	*Per cent*
None	Across grain	57,700	67,400	3.0	3.6
Do	With grain	61,500	90,000	26.8	58.6
SiC	Across grain	61,060	80,900	14.5	18.2
Do	With grain	69,900	88,000	29.0	61.6

[1] In 2 in.

The specimens for which test results are shown in this example were taken from steel forgings showing, by analysis, 0.32% carbon and 0.30% carbon. The specimens were water quenched and drawn. In the specimens of steel deoxidized by silicon carbide, the silicon carbide was added to the steel in the ladle, according to the process of the present invention, in the proportion of 4 pounds of silicon carbide per ton of steel. The test results given above show a remarkable increase in the elongation and reduction in area figures for the specimens taken across the grain of the steel deoxidized with silicon carbide. It will be evident that the overall improvement in the silicon carbide deoxidized steel so far as ductibility is concerned is very great.

In another series of tests run with varying percentages of silicon carbide as a deoxidizer in accordance with the process of the present invention it was further found that even comparatively small amounts of silicon carbide are effective in improving the quality of the steel. These tests are shown in the following example:

Example IV

Test	SiC, lbs./ton of steel	Analysis		Yield Point	Ultimate Strength	Elongation	Red. in Area	Quality Factor
		Per cent C	Per cent Si					
				P. s. i.	*P. s. i.*	*Per cent*[1]	*Per cent*	
A		.25	.42	34,800	69,700	30.1	48.3	71.9
B	1.1	.26	.46	35,500	68,250	31.75	50.55	74.3
C	1.8	.26	.64	37,333	72,000	32.5	51.2	75.8
D	2.2	.23	.59	36,800	70,200	31.4	51.8	76.2

[1] In 2 in.

It will be seen from this table that the addition to steel of silicon carbide as a deoxidizer results in a general improvement in its physical properties even in amounts as small as 1.1 pounds per ton.

The quality factor specified for the steel samples described in Example IV is a figure which has come into use in the steel industry for the evaluation of steels for uses involving strength, toughness, and ductility. The figure is derived from the following equation:

$$\text{Quality factor}=\frac{\text{Ultimate strength plus 6000 (\% reduction in area)}}{5000}$$

It will be seen from the table above that the quality factor has been improved in each test by the addition of silicon carbide as a deoxidizer. In test "D," for example, the quality factor was 106% of that in test "A" in which silicon carbide was not used.

The amount of silicon carbide used for deoxidation may vary, as shown above in Example IV. As shown there, even small amounts have a desirable effect. The amount of deoxidation needed varies in general with the carbon content of the steel. It has therefore been found expedient to adjust the proportion of silicon carbide used as a deoxidizer in accordance with the analysis of the steel. It is preferred that for steels containing under .2% carbon, 6 pounds of silicon carbide per ton of steel should be used; that with steels containing from .2 to .4% carbon, 4 pounds of silicon carbide per ton should be used; and that with steels containing more than .4% carbon, 2 pounds of silicon carbide per ton should be used. It will be understood that these amounts are only approximate since the exact optimum amount of silicon carbide in each case will vary slightly depending upon the exact composition of the steel, its treatment, etc. However it has been found that with amounts of the order of those specified steels of improved properties result. It has also been found that if any considerable amounts of alloying metals such as nickel, chromium and molybdenum are present in the steel that an additional quantity of silicon carbide is necessary for complete deoxidation. In general, in the neighborhood of 2 pounds per ton of steel in addition to that called for by the carbon content of the steel has been found to be proper. It will, of course, be understood that any slight excess of silicon carbide over that necessary to complete the oxidation will not be deleterious as would be the case with other deoxidizing agents.

The drawings heretofore mentioned illustrate quite clearly the improvement in cleanliness and reduction in impurities in the steel which results from the use of silicon carbide as a deoxidizer in accordance with the process of the present invention.

Figure 1 is a representation of a photomicrograph which illustrates the type of inclusions found in acid electric steel (i. e., steel made in an electric furnace having an acid lining) when the steel has had no deoxidizer added in the ladle. Both sulfide and oxide inclusions are shown.

Figure 2 is a representation of a photomicrograph illustrating a typical structure found in acid electric steel, of the same composition as the steel whose structure is illustrated in Figure 1, when the steel has been deoxidized by the addition of aluminum to the ladle. Steel containing areas of impurities such as this would be classified as "dirty" steel.

Figure 3 is a representation of a photomicrograph which shows the structure typical of acid electric steel, having the same composition as the steels whose structure is illustrated in Figures 1 and 2, which has been deoxidized with 4 pounds of silicon carbide per ton of steel added to the ladle in accordance with the process of the present invention. This structure is characterized by random globular inclusions which, unlike the inclusions shown in Figures 1 and 2, do not result in weakening of the steel.

Figure 4 is a representation of a photomicrograph illustrating a network of aluminum sulfide inclusions such as is frequently found in steels which have been deoxidized with aluminum. Steels having such networks of inclusions have a very low ductility.

Figure 5 is a representation of a photomicrograph of a polished section of basic open hearth steel which shows the globular inclusions characteristic of steel deoxidized, in accordance with the process of the present invention, by the addition of silicon carbide to the ladle. This figure is very similar to Figure 3 but at a higher magnification. Figures 3 and 5 make it clear that in such steels there is a complete absence of network or segregated impurities.

Figure 6 is a representation of a sulfur print made on a section of acid open hearth steel containing .03% sulfur. The great number and size of sulfide impurities in the steel is evident from the dark areas of the print.

Figure 7 is a representation of a sulfur print made on a section of steel having the same analysis as that used in preparing the print of Figure 6. However, the steel used in preparing the ingot from which this print was made was deoxidized by the addition of silicon carbide to the ladle in accordance with the process of the present invention. The great effect of the silicon carbide deoxidation in breaking up and dispersing segregations of sulfide inclusions is strikingly evident from the lesser darkening of this print in comparison with that shown in Figure 6.

By the deoxidation of steel with silicon carbide in accordance with the process of the present invention, it is also possible to obtain another effect which is frequently desirable—increase of the grain size of the steel. This enlarging effect on the grain structure increases the hardenability and creep strength of the steel to a degree which could otherwise be obtained only by the use of appreciable quantities of alloy additions. The following example shows the effect on the hardenability of a steel by the use of silicon carbide as a deoxidizer.

Example V

A molten steel having an analysis showing 0.51% carbon, 0.34% silicon and 0.85% manganese was divided into three samples. In one sample (A) no deoxidizer was used. In another sample (B) silicon carbide was added in the ladle as a deoxidizer in accordance with the process of the present invention and in the third sample (C) boron, known to be very effective in imparting hardenability to steel, was added in the ladle. Specimens for Jominy hardenability tests were taken from castings of the three samples. The tests of the three specimens gave the following results expressed in Rockwell "C" readings:

Distance from End	Specimen		
	A	B	C
1/16 in.	57.25	58.5	59.5
2 in.	14.5	20.25	24.5

It will be seen from these data that the silicon carbide, while not improving the hardenability to as great an extent as the boron, nevertheless distinctly and clearly gives a very much greater hardenability to the steel than it would have had otherwise.

It will be evident from the foregoing description of the present invention that the employment of silicon carbide as a deoxidizer for steel in accordance with the process therein disclosed is both simple and extremely effective in producing steel having an improved microstructure and such improvement in physical properties as to increase its strength, its ductility, and its hardenability. It will further be recognized that the description above given is not intended to be limiting since it is possible for those skilled in the art to make many changes in the process set forth without departing from the spirit of the present invention. It is not desired therefore that the present invention shall be narrowly construed in view of the foregoing description but it is desired that it shall be construed broadly and restricted only by the terms of the appended claims.

We claim:

1. The process of producing steel having an increased yield point, ultimate strength, elongation, percentage reduction in area and quality factor which includes the steps of adding to the molten steel pouring into a ladle, as it comes from the furnace at a temperature of 2900° F., 50 mesh silicon carbide, in combustible containers, in the proportion of about 4 pounds of silicon carbide per ton of steel, to produce thorough mixing of the silicon carbide in the molten steel, and retaining the molten steel in the ladle for at least 15 minutes before casting whereby the silicon carbide is decomposed and the steel is deoxidized.

2. The process of producing steel having an increased yield point, ultimate strength, elongation, percentage reduction in area and quality factor which includes the steps of adding to the molten steel as it pours into a ladle from the furnace at a temperature of at least about 2900° F. 36 mesh silicon carbide, in combustible containers, in the proportion of about 4 pounds of silicon carbide per ton of steel, to produce thorough mixing of the silicon carbide in the molten steel, and retaining the molten steel in the ladle for approximately 15 minutes before casting whereby the silicon carbide is decomposed and the steel is deoxidized.

3. The process of producing steel having an increased yield point, ultimate strength, elongation, percentage reduction in area and quality factor which includes the steps of adding to the molten steel, as it pours into a ladle from the furnace at a temperature of 2900° F., 50 mesh silicon carbide, in combustile containers, in the proportion of from about 1.1 to 6 pounds of silicon carbide per ton of steel, to produce thorough mixing of the silicon carbide in the molten steel, and retaining the molten steel in the ladle for at least 15 minutes before casting whereby the silicon carbide is decomposed and the steel is deoxidized.

4. The process of producing steel having an increased yield point, ultimate strength, elongation, percentage reduction in area and quality factor which includes the steps of adding to the molten steel, as it pours into a ladle from the furnace at a temperature of at least 2900° F., finely divided silicon carbide, in combustible containers, having a mesh size of 50 and finer in the proportion of from about 1.1 to 6 pounds of silicon carbide per ton of steel, to produce thorough mixing of the silicon carbide in the molten steel, and retaining the molten steel in the ladle before casting for a period of time sufficient for the decomposition of the silicon carbide and the deoxidation of the steel.

5. The process of producing steel having an increased yield point, ultimate strength, elongation, percentage reduction in area and quality factor which includes the steps of adding to the molten steel, as it pours into a ladle from the furnace at a temperature of at least about 2900° F., 36 mesh silicon carbide, in combustible containers, in the proportion of from about 1.1 to 8 pounds of silicon carbide per ton of steel, to produce thorough mixing of the silicon carbide in the molten steel, and retaining the molten steel in the ladle before casting for a period of time sufficient for the decomposition of the silicon carbide and the deoxidation of the steel.

6. The process of producing deoxidized steel castings which includes the steps of introducing 36 mesh silicon carbide, in combustible containers, into molten steel having a temperature of at least 2900° F. as it pours into a ladle, in the proportion of about 4 pounds of silicon carbide per ton of steel, to produce thorough mixing of the silicon carbide in the molten steel, and holding said mixture in the ladle before casting for a period of at least 15 minutes whereby the silicon carbide is decomposed and the steel is deoxidized.

7. The process of producing deoxidized steel castings which includes the steps of introducing 36 mesh silicon carbide, in combustible containers, into molten steel having a temperature of at least 2900° F. as it pours into a ladle, in the proportion of from about 1.1 to 8 pounds of silicon carbide per ton of steel, to produce thorough mixing of the silicon carbide in the molten steel, and holding said mixture in the ladle before casting for a period of at least 15 minutes whereby the silicon carbide is decomposed and the steel is deoxidized.

8. The process of producing deoxidized steel castings which includes the steps of introducing 50 mesh silicon carbide, in combustible containers, into molten steel having a temperature of at least 2900° F. as it pours into a ladle, in the proportion of from about 1.1 to 8 pounds of silicon carbide per ton of steel, to produce thorough mixing of the silicon carbide in the molten steel, and holding said mixture in the ladle before casting for a period of at least 15 minutes whereby the silicon carbide is decomposed and the steel is deoxidized.

9. The process of producing deoxidized steel castings which includes the steps of introducing 50 mesh silicon carbide into molten steel having a temperature of at least 2900 F. as it pours into a ladle, in the proportion of from about 1.1 to 8 pounds of silicon carbide per ton of steel, to produce thorough mixing of the silicon car-

bide in the molten steel and retaining said mixture in the ladle before casting during the time necessary for decomposition of the silicon carbide and the deoxidation of the steel.

10. The process of deoxidizing steel by the use of 36 mesh silicon carbide which includes the steps of introducing said silicon carbide into molten steel at a temperature of at least approximately 2900° F. as it pours into a ladle, thoroughly mixing said silicon carbide and molten steel and retaining said mixture in the ladle before casting during the time necessary for decomposition of the silicon carbide and the deoxidation of the steel.

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FRANCIS SIDNEY KLEEMAN.

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The following references are of record in the file of this patent:

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