1965

A study of sulfide inclusions in medium carbon steels

Shane Shiang Yen

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INTRODUCTION

Sulfur is a very important component in steel. Usually it is present as an impurity in commercial steels. In these materials the sulfur content is 0.05 percent maximum but may be higher or lower than this in some steels.

There are a number of well known effects produced on steels by sulfur. It can make steel red short or hot short, brittle at high temperature, and this effect had to be overcome in commercial practice. On the other hand, high sulfur is known to improve the machinability of steel and sulfur is intentionally added, in amounts exceeding 0.25 percent, for this purpose.

It is generally believed that sulfur has a deleterious effect on the mechanical properties of steels. Originally this investigation was to deal with this aspect of sulfur in steels but the work did not progress to this stage. An effort was made to vary the nature of the sulfides in several experimental heats of steel by controlling their composition. Variation in the nature of the sulfides did result and the major effort was devoted to a metallographic study of the sulfides in fifteen experimental heats.

The presence of appreciable iron sulfide in the ingots of heats containing manganese was unexpected. This steel was not found to be hot short. However, after hot-working or annealing at high temperatures for short periods of time
only manganese sulfide inclusions could be found in these steels.
II REVIEW OF LITERATURE

Sulfur is an element that is present in all steels. Usually, sulfur is considered to be harmful and the steel-maker attempts to keep the sulfur content as low as possible. There are some steels to which sulfur is intentionally added to improve machinability.

Very little sulfur is soluble in iron and, therefore, most of the sulfur is normally present in steel as sulfide inclusions. These sulfides can have at least three very important effects:

1. Sulfides can cause hot shortness
2. Sulfides can cause low ductility, and
3. Sulfides can improve machinability.

The necessity to control these effects has stimulated much of the research into the nature of sulfides in steel.

Hot-shortness was one of the serious problems of early ferrous metallurgists. Sulfur was recognized as the source of this difficulty and the addition of manganese was found to be the solution to the problem (1, 2, 3, 4, 5 and 6).

Sauveur (1) claimed that 0.02 percent sulfur was sufficient to produce hot-shortness in the absence of manganese. However, hot-shortness has been reported in steels of lower sulfur content. It had been known for some time that manganese and sulfur have a very great affinity for each other and it had been assumed that when brought
together they combine chemically to form manganese sulfide. Manganese sulfide has a high melting point and is practically insoluble in iron. It occurs as sulfide inclusions whose color is generally described as pale or dove gray, sometimes as slate color.

In the absence of manganese it was claimed (2) that sulfur formed iron sulfide which occurs as grain boundary inclusions. On the other hand, manganese sulfide inclusions occur as randomly distributed globules.

The older theory of the cause of hot-shortness from sulfur was based on the fact that an iron-iron sulfide eutectic forms which melts at 988°C. The formation of a liquid phase at the grain boundaries was believed to destroy cohesion between the grains and result in failure during hot working. The formation of manganese sulfide which melts above the hot working temperature range was supposed to eliminate the liquid phase. The discrete, globular, solid manganese sulfide inclusions would not interfere with malleability. In more recent years the old theory of hot-shortness has been questioned (7,8), and some of this work is discussed below.

Sims and Lillieqvist (9) recognized the effect of aluminum on the nature of sulfide inclusions in cast steel before the more recent investigations into the cause of hot shortness. Sims and Lillieqvist found that when they added aluminum to acid arc-furnace steel the ductility was much
lower than that of open hearth steels which had not been deoxidized with aluminum. They observed a marked change in the nature of the inclusions when the steel was deoxidized with aluminum. They also observed a correlation between ductility and the nature of the inclusions. In particular, the distribution of the inclusions rather than their amount determined ductility.

In steels that were not deoxidized with aluminum, ductility was no problem and, the inclusions were essentially randomly distributed, globular inclusions of three types:

1. Dark colored silicates,
2. Light gray sulfides, and
3. Duplex, containing substantial amounts of both silicate and sulfide.

The silicates and sulfides were believed to be "practically miscible in the liquid state".

In aluminum deoxidized steels with low ductility the inclusions are "confined exclusively to the grain boundaries of primary crystals or dendritic fillings, and have all the earmarks of being a part of an eutectic that was the last mother liquor to solidify".

Sims and Lillieqvist distinguished between "natural" inclusions and other inclusions such as inadvertent bits of refractory or slag. Natural inclusions were believed to form during cooling and solidification of the steel. Most
heats of a given type steel contain approximately the same amount of inclusions. This would follow if all insoluble material floated out of the melt rapidly at steelmaking temperatures and the "natural" inclusions formed by precipitation during cooling and solidification; they do not exist except as solute in the molten steel prior to this time. The amount and character of the inclusions were assumed to be determined largely by the composition and temperature of the molten metal which would be essentially constant for a given type steel. The inclusions are mostly sulfides and, therefore, steels with high sulfur tend to have a high inclusion count.

The fact that the average size of the inclusions depends on the size of the casting also indicates that the inclusions are formed during solidification and are in solution above the melting point. Small castings or rapidly cooled metal such as chilled surfaces contain small inclusions while larger castings and more slowly cooled metal contain larger inclusions. Other things being equal, there is no observed change in size or quantity of inclusions with holding time in the liquid state. This means the inclusions cannot float out because they do not exist prior to the start of cooling; the inclusions, mostly sulfides, are soluble at steel-making temperatures.

Sims and Lillieqvist concluded that aluminum affected the nature and distribution of sulfides, the most prevalent
type of inclusion, because it affected the oxygen content of the liquid metal which affected the solubility of other materials. Other factors such as higher carbon content and lower metal temperatures which would give lower oxygen concentrations in the bath tended to act the same as aluminum with respect to the inclusions. These factors gave grain boundary sulfides which lowered ductility. Low carbon contents, high metal temperature and the addition of iron ore to the melt gave castings of good ductility. These factors would favor higher oxygen concentrations in the bath and they yielded globular, randomly distributed inclusions.

Sulfide solubility was used to account for variations in sulfide inclusions. Higher oxygen reduces sulfide solubility in the molten metal and causes the inclusions to precipitate as a liquid phase during cooling and before solidification starts. These particles of liquid are trapped and become globular, randomly distributed inclusions which do not markedly reduce ductility. The sulfur is assumed to be much more soluble in metal of low oxygen content. With low oxygen the inclusions are not precipitated prior to solidification. They remain in solution until near the end of the solidification process when the sulfides and other inclusions form by an eutectic reaction in the grain boundaries of the primary crystals. The continuous grain boundary network of inclusions embrittle the steel.
Aluminum and deoxidation practice are now recognized as affecting sulfides in steel (4,5). Crafts, Egan and Forgeng (10) proposed mechanisms for the formation of inclusions in steel castings. They attempted to explain how the deoxidation practice determined the size, shape and distribution of the inclusions. According to their explanation the amount of aluminum added to the steel served as a basis of classification of the inclusion types.

Gaydos (11) reported on the study of the influence of sulfides on the machinability of C 1213 steels. He found two kinds of sulfides: 1) elongated sulfides containing green streaks tended to be present in metal of low oxygen content, and 2) oval sulfides of amber to red color which form in steel of higher oxygen levels. The green sulfides tended to occur near the mold walls, in the lower part of ingots and in higher carbon heats. Oval sulfides were found in upper portions of ingots and in lower carbon heats. The sulfides were small and numerous near the surface of the ingot and increased in size toward the center of the ingot.

Gaydos found some of the sulfides were associated with oxide or silicate phases which formed "tails" on the sulfide inclusions. The nature of the tails seemed to affect the sulfide. Siliceous tails were found on green type sulfide while oxide tails tended to form on red sulfides. Oval or red type sulfides were desired in free-machining steels.
Van Vlack (12) also studied high sulfur steels and determined some of the factors which affect the shape and size of inclusions in rolled resulfurized steel. The inclusion characteristics are governed by:

1. The silicon content of the steel,
2. The sulfur content of the steel,
3. The mechanical working which the steel received, and
4. Possibly by the oxygen content of the sulfide phase.

High silicon increased the length to width ratio of the sulfides and both silicon and carbon increased their frequency. At high rolling temperatures, the sulfide inclusions are plastically deformed and pinched off; at lower hot rolling temperatures they were observed to be fractured. Van Vlack showed that the plasticity of the inclusions varied with silicon content of the steel and concluded that the composition of the sulfide phase varies with silicon content of the steel. Silicon reduces the solubility of oxygen in the sulfide phase. Steel with a low oxygen analysis had plastic inclusions, even with a low silicon content. Aluminum increases the plasticity of sulfide inclusions during rolling.

Josefsson, Koeneman and Lagerberg (7) investigated sulfur and oxygen as causes of red-shortness. It was concluded that oxygen by itself did not cause red-shortness. Their work showed that the solubility of sulfides varied
with temperature in steel. At high temperatures, 1050-1300°C, sulfides could be dissolved and they tended to precipitate at the austenite grain boundaries at lower temperatures, 850-950°C, where the steel was hot-short.

The grain boundary sulfide network and the dissolved sulfur were both believed to cause hot shortness. It was found that the grain boundary network could be spheroidized by holding at 950°C and that this eliminated hot shortness. The dissolved sulfide could also be taken out of solution by holding at lower temperatures. Manganese was believed to counteract the effect of sulfur by decreasing the solubility of the sulfur and by forming manganese sulfide which does not form grain boundary films.

Ramsey and Graper (13) concluded that steel with sulfur added as sodium sulfite can be rolled as well as though no sulfur were added. The sodium sulfite forms sulfur dioxide when it decomposes. It is assumed that, in this case, the oxygen of the sulfur dioxide forms part of the sulfide inclusions in the steel and raises their solidification temperature enough so that the formation in the steel of a low-melting eutectic is prevented. The result is the prevention of hot-shortness and a more uniform distribution of inclusions.

Van Vlack, Riegger, Warrick and Dahl (8) recently studied the metallography of sulfides in steel. They determined the effect of manganese, silicon and oxygen concen-
tration on surface energy of liquid sulfide/metal and other interfaces in steel at elevated temperatures. The effective dihedral angle was measured because this angle determines the shape of sulfides. A large angle produces globular sulfides while a small angle leads to intergranular penetration of the liquid sulfide yielding film-like grain boundary sulfides.

It was found that the liquid sulfide in a simple iron-sulfur alloy contained about 85 percent iron and had a low dihedral angle. This means that liquid sulfide/metal surface energy is low relative to grain boundary energy and the liquid tends to penetrate the grain boundary. The addition of oxygen to the alloy reduced the solubility of the iron in the liquid sulfide. This reduced the similarity of the liquid and solid phases and increased the dihedral angle. The penetration of grain boundaries by the oxygen-enriched liquid was restricted and tended to give a more globular sulfide.

Manganese tends to produce insoluble solid sulfides and to increase the dihedral angle of any liquid sulfide phase. The addition of oxygen to an iron-manganese-sulfur alloy introduces a liquid which fluxes the solid sulfide and leads to duplex sulfide-oxide inclusions. Adding both oxygen and silicon results in a siliceous liquid phase saturated with sulfide.

Van Vlack and co-workers believe that the sulfides in
a manganese-bearing steel are not necessarily solid at hot rolling temperatures. They postulate that the oxygen content is very important because it determines how much sulfide is fluxed or dissolved. If so much liquid is formed that it is not saturated with manganese sulfide the liquid phase will have a tendency to penetrate grain boundaries and cause hot shortness. "On this basis manganese may have a two-fold purpose in alleviating hot-shortness. Steels with higher manganese contents would have more of the oxygen actually removed from the liquid metal so that less sulfide is fluxed and the nonmetallic liquid is saturated with manganese sulfide. Furthermore, and as previously realized, additional manganese will produce a higher melting sulfide."
III EXPERIMENTAL PROCEDURE

A. TESTING METHOD USED IN EXPERIMENTS

Macroscopic Examination

Macroscopic examination was used to determine the distribution of the sulfide inclusions in the steels. Two procedures, deep etching and sulfur printing, were used.

a. Deep Etch Test

Samples were prepared for deep etching by first grinding flat on a belt grinder and then polishing on 240 and 320 grit abrasive papers. A 50 percent hot hydrochloric acid solution at 160°F was used for etching. Samples were heated to 160°F in hot water before being put into the acid. Etching time was 30 minutes.

b. Sulfur Printing

The distribution and concentration of the sulfide inclusions in the ingots was studied by making sulfur prints.

The surface of the specimens was prepared by grinding on 240, 320, 400, 600 grit abrasive papers to produce a smooth clean surface. Photographic bromide paper was soaked in a 2 percent solution of sulfuric acid for 3 minutes. The paper was removed from the acid solution and allowed to drain free of excess solution. The emulsion side of the paper was then placed on the prepared surface of the sample
and allowed to remain in contact under moderate pressure for one minute. The sulfur prints were rinsed in tap water, fixed in a photographic fixing solution for about 15 minutes, washed in running water for approximately 30 minutes and then dried.

**Metallographic Examination**

Preparation of metallographic samples consisted of mounting in bakelite, belt grinding, polishing on 240, 320, 400, 600 grit abrasive papers and then finishing on polishing laps. Two wheels were used. A coarse alumina abrasive was used on Metcloth for the first lapping operation. Final polishing was done on a Microcloth covered wheel with Linde B as the polishing compound.

The identification of inclusions in steel using bright field illumination and ordinary metallographic examination is based on characteristic color, shape, size and distribution of the various types of inclusions. The addition of polarized light to the microscope makes possible the detection of optical properties which help in the identification. The characteristics of various inclusions and the procedures used are described in the literature (5,14,15).

In this work sulfide inclusions were of interest. Sulfides in steel are frequently manganese sulfide. This
sulfide is described as dove gray in color. It tends to form globules during solidification. Manganese sulfide is plastic and is deformed during deformation processes. The sulfides in wrought steel products are frequently elongated and in the form of stringers.

Iron sulfide is not common in commercial steels. It is described as having a khaki or yellowish color. Inclusions were found during this study which were believed to be iron sulfide and some had a pink color. The color of iron sulfide seems to be variable -- rather it might be said that iron sulfide in steels is frequently "contaminated" and is variable in nature. Iron sulfide tends to form grain boundary films during solidification. These films were found to be long thin films on polished sections. When the amount of iron sulfide was not so great it was found to form inclusions which were not film-like but neither were they globular. With a small amount of iron sulfide present it was found as a discontinuous grain boundary network of slightly elongated inclusions of irregular shape.

Examination of sulfides with polarized light between crossed nicols frequently permits differentiation between iron sulfide and manganese sulfide because the former is optically anisotropic whereas the latter is optically isotropic.

An optically anisotropic material will resolve incident plane polarized light into two components, polarized
parallel and perpendicular to a certain crystallographic direction in the material, giving elliptically polarized light. The net effect is that a component of the light is produced with its plane of polarization perpendicular to that of the incident light and this component is transmitted through the second nicol prism when the material is being viewed through crossed nicols. The intensity of this transmitted light depends upon the angle between the crystallographic direction and the plane of polarization of the incident light. If an anisotropic material is rotated about an axis normal to its surface it will show four light maxima per revolution. An optically isotropic material does not affect the incident polarized light and does not give the bright-dark change during rotation. Isotropic substances remain black during rotation between crossed nicols.

In spite of the differences between iron and manganese sulfides, their positive identification with an optical microscope can be difficult at times. Not all gray inclusions are sulfides. Furthermore, the inclusions are not always pure substances and, therefore, a given type inclusion does not always behave in the same manner. In this study, iron sulfide was found to be particularly variable. Inclusions were assumed to be iron sulfide when they were optically anisotropic and were either found in heats to which manganese had not been added or were similar to sulfides found in such heats. It should also be noted here
that the variation of brightness during rotation between
crossed nicols was not the same for the iron sulfide in the
various heats. The maximum brightness varied considerably.
Those heats to which manganese had not been added contained
sulfides that gave a very noticeable bright-dark change. In
some of the other heats to which manganese had been added,
anisotropic sulfides were found and their brightness change
was variable; in some heats it was pronounced and in others
it was very slight.
B. STEEL MAKING PROCEDURES

The steels studied in this investigation were all experimental heats melted in an induction furnace using a 20 KW Ajax High Frequency Converter.

The raw materials for making the steels were:

IRON

Armco ingot iron punchings whose analysis is given below was the base metal for the steels.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.012</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.017</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.025</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>0.005</td>
</tr>
<tr>
<td>Silicon</td>
<td>Trace</td>
</tr>
</tbody>
</table>

SILICON

For Heats No. 1, 2 and 3, a 50 percent grade of ferro-silicon of unknown composition was used. For all subsequent heats a high purity grade whose composition is given below was used.

Ferrosilicon

<table>
<thead>
<tr>
<th>Element</th>
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<tbody>
<tr>
<td>Silicon</td>
<td>48.52</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.025</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.007</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>0.022</td>
</tr>
</tbody>
</table>
MANGANESE

Electrolytic manganese was used for all heats.

CARBON

Graphite electrodes were crushed into coarse pieces which were used for the carbon additions.

COPPER

The copper addition was in the form of electrolytically refined copper.

CALCIUM

In Heat No. 9 calcium carbide sufficient to provide the calcium and carbon was used. Pure calcium metal was added to Heat No. 16.

ALUMINUM

Aluminum wire was inserted into the bath toward the end of each heat as a deoxidizer.

SULFUR

Roll sulfur from E. H. Sargent and Company was used.

The ingot iron was cleaned in a Wheelabrator Tumblast Machine for two to three hours. Ten pounds of the cleaned punchings were placed in a seventeen pound crucible which filled it to within one half inch of the top. The crucible was covered with a piece of transite to cut down on
radiation heat loss and heating was started. The iron melted in approximately 35 minutes. Various additions were then made in the order shown in Table No. 1. After the various additions had been made, the slag which had accumulated on the surface of the melt was skimmed. Heating was continued for three to five minutes after skimming the slag and then the heat was poured. The total time for melting and working the heats was approximately 55-60 minutes.

The metal was cast into three graphite molds in which the ingots were allowed to cool to room temperature.

The molds had been made by drilling 3 inch graphite electrodes to give ingots approximately 1.25 inches in diameter and 6 inches long. A riser 2 inches in diameter and 1.5 inches long was provided on each mold. After drilling, the mold was cut into two halves which were held together for casting by metal bands. Ten pounds of liquid steel was sufficient to fill two of the molds and partially fill the third mold.

The first heat was used as a practice run and was not subsequently used. Heats No. 2 and 3 were prepared to determine the percentage recovery of the alloy additions and to determine how well a heat could be duplicated. These two heats were analyzed giving the compositions shown in Table No. 2. On the basis of these analyses the recovery of various additions was as shown in Table No. 3. The percentage recovery used for calculating charges for
<table>
<thead>
<tr>
<th>Heat Crucible No.</th>
<th>Charge to Cold Crucible</th>
<th>Weight of Addition in Grams and Order in Which Added During Melting</th>
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</thead>
<tbody>
<tr>
<td>2</td>
<td>10lb Fe</td>
<td>90g C 25g Mn 65g Al 25g</td>
</tr>
<tr>
<td>3</td>
<td>10lb Fe</td>
<td>90g C 25g Mn 65g Al 25g</td>
</tr>
<tr>
<td>4</td>
<td>10lb Fe</td>
<td>26g C 20g Mn 65g Al 4.5g</td>
</tr>
<tr>
<td>5</td>
<td>10lb Fe</td>
<td>26g C 20g Mn 65g Al 4.5g</td>
</tr>
<tr>
<td>6</td>
<td>10lb Fe</td>
<td>26g C 20g Mn 65g Al 4.5g</td>
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<td>14</td>
<td>10lb Fe</td>
<td>26g C 20g Mn 65g Al 4.5g</td>
</tr>
<tr>
<td>15</td>
<td>10lb Fe</td>
<td>26g C 20g Mn 65g Al 4.5g</td>
</tr>
<tr>
<td>16</td>
<td>10lb Fe</td>
<td>26g C 20g Mn 65g Al 4.5g</td>
</tr>
</tbody>
</table>

* First digit is crucible number and second digit is number of melt made in the crucible, e.g., 6-3 is third heat made in crucible No. 6.
Table No. 2  Composition * of Steel Investigated

<table>
<thead>
<tr>
<th>Heat No.</th>
<th>2**</th>
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<th>6</th>
<th>7</th>
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<td>0.4</td>
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<td>0.25</td>
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<td>±0.3</td>
<td>±0.3</td>
<td>±0.4</td>
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</tr>
</tbody>
</table>

* Approximate compositions calculated on the basis of recoveries shown in last column of Table No. 3.

** Analyzed composition.
all subsequent heats are also shown in Table No. 3. These percentage recoveries were used to calculate the approximate heat analyses shown in Table No. 2.

Table No. 3
Recoveries of Elements in Steel Making

<table>
<thead>
<tr>
<th>Elements</th>
<th>Percentage Recoveries of Element</th>
<th>Percentage Recoveries Used for Charge Calculation</th>
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<td>Heat No. 3</td>
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<tr>
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<td>94</td>
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<tr>
<td>Sulfur</td>
<td>70</td>
<td>83</td>
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</table>

Samples were cut from the top and bottom of the ingots from each heat and examined. One sample from each heat was deep etched. The deep etch samples revealed no gross segregation or defects other than the holes which could be seen without deep etching. Some of the ingots from heats to which no manganese had been added had such holes.

Sulfur prints were made to determine sulfur distribution and the relative amount of sulfur in the heat. Since a standardized procedure was adopted, the density of the sulfur prints would be directly proportional to the sulfur content of the metal. The various heats could be separated into groups according to the density of the sulfur prints.
and these groups corresponded to the calculated sulfur content for the heat. The sulfur content of the various heats was at least approximately the amount shown in Table No. 2. Sulfur was relatively uniformly distributed in the heats. A thin surface layer on some heats may have had low sulfur content.

The carbon contents of the heats were checked by metallographic examination. The pearlite in the ingots was relatively coarse indicating a relatively slow cooling and a close approach to equilibrium. The relative amount of ferrite and pearlite in the samples indicated the carbon contents shown in Table No. 2.
IV EXPERIMENTAL RESULTS

A. GENERAL METALLOGRAPHIC OBSERVATIONS

The sulfide inclusions in the ingots of the various heats were examined with a metallograph. The individual heats will be described after pointing out some general observations.

Most of the ingots could be divided into two portions on the basis of the nature of the inclusions. There was a surface layer in which the inclusions were very fine and more or less randomly distributed. In the central portion of the ingot the nature and distribution of the inclusions varied somewhat in the different heats.

The fineness of the inclusions in the surface layer made it very difficult to study them. Frequently it was not possible to determine accurately their color in ordinary light. The edge effect prevented definite determination of characteristics in polarized light. In some of the ingots it was not certain that sulfide inclusions were present in this layer.

After examining many samples it became apparent that the sulfides in the central portion of the ingots of many of the heats could be divided into two types. The two types could be identified easily in some heats where they differed in shape. In these heats one type was spheroidal while the other consisted of long thin films forming a grain boundary.
network. Careful examination of other heats revealed that while the first type usually was spheroidal, the other was not always so film-like. The two types of inclusions will be called "globular" and "grain boundary" types. They differed in a number of ways. The identifying characteristics of each type will be described.

The globular sulfides were "dove gray", the color usually associated with sulfides in steel. When examined under polarized light with crossed nicols, these inclusions invariably remained dark in all positions while being rotated with the stage of the microscope. This indicated that these inclusions were manganese sulfides. Figures 2 and 3 show the inclusions in an ingot of Heat No. 2. Figure 2 is an ordinary photomicrograph in which a number of the globular sulfides are marked "MnS". In Figure 3 the same area is shown as it appeared through crossed nicols. It will be seen that the globular inclusions are black under crossed nicols.

The globular sulfides were usually either randomly distributed or arranged in a dendritic pattern. A region in which a rather pronounced dendritic pattern was found is shown in Figure 5. As mentioned above and as shown in Figure 5 the globular sulfides were usually spheroidal in shape.

The grain boundary sulfides had a number of distinguishing characteristics. However, they varied somewhat from
heat to heat and it was necessary to consider all their characteristics in order to identify them because in some heats one or more of their characteristics was not particularly pronounced.

One of the distinguishing characteristics of the grain boundary inclusions which created the impression that these inclusions were indeed different from the globular inclusions was their distribution. They were almost always found in a grain boundary network as the name implies. The grain boundary network was not always continuous or complete but at low magnification it was apparent as shown in Figure 7 and Figure 23.

The shape of the grain boundary sulfides varied considerably in the different heats. In some of the heats they were long thin films as mentioned above and they could be identified easily in these heats. However, in other heats they were not particularly long and some were even spheroidal as shown in Figure 2, where some of these inclusions are marked "D". Even when these grain boundary inclusions were not particularly long, some could still be identified by their shape because their location at the junction of grain boundaries made them triangular or some other irregular shape having one or more corners or points. This is illustrated by the inclusion marked "G" in Figure 2.

The color of the grain boundary inclusions frequently helped to differentiate them from the globular sulfides.
The color of the grain boundary sulfides varied. One observer saw the grain boundary sulfides as a lighter gray than the globular type. Another observer was able to detect a pinkish cast in some grain boundary sulfides while others were a khaki or yellowish color. The ability to see colors in these inclusions could be used advantageously in identifying the grain boundary sulfides. However, the grain boundary sulfides in all the heats could not be identified by color.

Another characteristic of the grain boundary sulfides that made their identification positive in some heats was their appearance in polarized light with crossed nicols. These inclusions were frequently iron sulfide or duplex, partially iron sulfide and partially manganese sulfide. Since iron sulfide is anisotropic it has the ability to rotate the plane of polarization of light and can appear bright in certain positions when viewed through crossed nicols. An anisotropic material like iron sulfide will undergo changes from bright to dark as it is rotated with the stage of the metallograph. In one complete revolution, there were four bright and four dark positions.

The bright-dark change could not always be used to identify the grain boundary inclusions because they did not always display this characteristic. The brightness of the inclusions in their bright positions with crossed nicols varied considerably. With some grain boundary inclusions the maximum brightness was such that the observer could
not be certain a bright-dark change was occurring and with other grain boundary inclusions it appeared to be absent entirely.

Figure 2 and 3, as mentioned above, show inclusions from Heat No. 2 with ordinary light and with polarized light using crossed nicols. A number of grain boundary inclusions are marked "D" in Figure 2. It is apparent in this photomicrograph that these inclusions are duplex and that a difference in color existed between the grain boundary sulfides and the globular sulfides marked "MnS". The iron sulfide part of the grain boundary sulfides is lighter than the manganese sulfide part or the globular sulfides which are also manganese sulfide. In Figure 3, one of the bright positions of the iron sulfide is shown. In this sample the anisotropic nature of the grain boundary iron sulfides is very definite as is their duplex nature. As mentioned above, the manganese sulfide is isotropic and remained dark in all positions.

Several other general observations can be noted before describing the heats individually. There was some tendency for the grain boundary sulfides to be longer toward the center of the ingot, some times they were very much longer than they were near the surface. The grain boundary sulfides indicated a tendency for the grain size in the ingots to increase toward the center of the ingot.

The sulfide inclusions in the heat mentioned was in
B. DESCRIPTION OF INDIVIDUAL HEATS

Heat No. 2

The surface layer of fine inclusions was about 2.5 mm thick. The inclusions in this layer were numerous and essentially randomly distributed, Figure 1. However, in some regions there was a tendency to reveal the dendritic structure of the ingot. The inclusions in the surface layer were too fine to identify positively. Sulfides were believed to be present.

In the central portion of the ingot relatively large globular sulfides were found. They were more or less randomly distributed.

The grain boundary sulfides were more frequent toward the center of the ingot. They displayed a pinkish cast and could be identified relatively easily in this heat by their color. They were also frequently duplex as shown in Figure 2. Their maximum brightness with crossed nicols was relatively intense, Figure 3, and this too helped in their identification. The bright-dark change indicated that much iron sulfide was present in this heat. The grain boundary sulfides were not particularly film-like.

Heat No. 3

The sulfide inclusions in this heat resembled those in
FIGURE 1. SURFACE LAYER ON THE INGOT FROM HEAT NO. 2.
UNETCHED
FIGURE 2. CENTER OF THE INGOT FROM HEAT NO. 2,
ORDINARY LIGHT.

MANGANESE SULFIDE INCLUSIONS ARE MARKED "MnS". DUPLEX
INCLUSIONS MARKED "D" SHOW DARK MANGANESE SULFIDE AREAS
AND LIGHTER IRON SULFIDE AREAS. INCLUSION MARKED "G" SHOWS
ANGULAR SHAPE CHARACTERISTIC OF SULFIDES LOCATED AT
JUNCTION OF GRAIN BOUNDARIES.

UNETCHED, 500 X

FIGURE 3. CENTER OF THE INGOT FROM HEAT NO. 2,
POLARIZED LIGHT.

SAME FIELD AS THAT SHOWN IN FIGURE 2. IRON SULFIDE IS IN
A BRIGHT POSITION.

UNETCHED, 500 X
FIGURE 4. CENTER OF THE INGOT FROM HEAT NO. 3.
UNETCHED, 500 X
Heat No. 2, Figure 4. This was expected because the two heats were made with an effort to produce identical material. However, some differences were observed.

In Heat No. 3 a larger portion of the sulfur was present as globular sulfides than in Heat No. 2. The globular sulfides in Heat No. 3 were somewhat bigger. Near the center of the ingot a few regions were found in which the globular sulfides formed a pronounced dendritic pattern, Figure 5.

The iron sulfide inclusions in this heat were more frequent toward the center of the ingot. They were less elongated than in Heat No. 2. A coarser grain size was found at the center of the ingots of Heat No. 3 than that found at the center of Heat No. 2 ingots.

Heat No. 4

The surface layer was about 1.0 mm thick. The inclusions in the surface layer were distributed in a columnar, grain boundary network, Figure 6.

This heat contained no manganese addition but did have the equivalent of 1.5 percent copper added. A small amount of manganese, that in the ingot iron stock, was present. Almost all the sulfide inclusions in this heat appeared to be grain boundary iron sulfides. Some fine globular sulfides were found but they were not frequent.

The bright-dark change with crossed nicols was not
Figure 5. Center of the ingot from Heat No. 3. Unetched, 150 X

Figure 6. Surface layer on the ingot from Heat No. 4. Unetched, 150 X
pronounced for the sulfides in this heat. The maximum brightness was greater for inclusions near the center of the ingot than for those near the surface.

Near the surface of the ingot the sulfides were relatively short or spheroidal even though they were the grain boundary type. Longer inclusions were found upon moving toward the center of the ingot and very long and very thin grain boundary sulfides were found at the center, Figure 7. Black spots in these thin film-like inclusions were found. The thinness of the inclusions made it difficult to determine if these black spots were oxides or other types of inclusions or if they were places where the sulfide had been removed in polishing.

This heat had been made with the expectation that copper sulfide might be present. Inclusions were found in which portions were a blue gray color. Copper sulfide should be bluish in color with ordinary light and should show a blue color with polarized light. The blue-gray regions were black with crossed nicols and showed spots of other colors at their edges. Thus, identification of copper sulfide was not positive but duplex iron sulfide-copper sulfide inclusions may have been present.

Heat No. 5

Three layers rather than two were found in the ingot
UNETCHED, 150 X

FIGURE 8. MIDDLE LAYER IN THE INGOT FROM HEAT NO. 5.
UNETCHED, 150 X
of this heat. The surface layer, about 1.25 mm thick, contained fine inclusions that were randomly distributed. With polarized light using crossed nicols most of these inclusions were identified as glassy silicate inclusions. It was not certain that any sulfide inclusions were present in this layer.

The middle layer was about 6.75 mm thick and contained fine globular sulfides in a dendritic pattern, Figure 8.

In the central portion of the ingot the sulfides were arranged in a dendritic pattern which, as shown in Figure 9, was a coarser pattern than that of the middle layer. At the junctions of the rows of sulfides, clusters of inclusions were frequently found. Essentially all the sulfides were located in the dendritic pattern with intervening metal free of inclusions.

All the inclusions remained dark in polarized light with crossed nicols. For some unexplained reason they did not appear black like the manganese sulfide inclusions in other heats. The very faint brightness effect may have been due to the presence of very bright spots which were scattered throughout the sample. These bright spots could have been caused by other inclusions or polishing pits. None of the sulfides showed a bright-dark change and all were believed to be manganese sulfide inclusions of the globular type. The inclusions were relatively small.

No evidence of copper sulfide was found.
Heat No. 6

This heat was similar to Heat No. 5 in composition and in sulfides present. Each heat had the equivalent of 1 percent manganese and 1.5 percent copper added. Heat No. 6 contained approximately 0.3 percent sulfur while the equivalent of 0.1 percent sulfur had been added to Heat No. 5.

Heat No. 6 had only one surface layer, 0.75-1.0 mm thick which was similar to the surface layer of Heat No. 5 in one respect; it was difficult to positively identify sulfides in this layer. In some parts of this layer the inclusions were randomly distributed while in others they were present in a dendritic pattern.

The dendritic pattern in the central portion of the ingot was finer than that in Heat No. 5, Figure 10. All the inclusions appeared to be globular manganese sulfides which remained uniformly black in polarized light with crossed nicols. The clusters of inclusions in Heat No. 6 were larger and more frequent than those in Heat No. 5 but the individual sulfides making up the clusters and the dendritic network were about the same size in both heats. In addition to these sulfides, Heat No. 6 contained much larger randomly distributed sulfides which can be seen in Figure 10. These large inclusions did not appear to be associated with the dendritic network.
FIGURE 9. CENTER OF THE INGOT FROM HEAT NO. 5 UNETCHED, 150 X

FIGURE 10. CENTER OF THE INGOT FROM HEAT NO. 6 UNETCHED, 150 X
Heat No. 7

The surface layer, approximately 1.75 mm thick, contained relatively few small, round iron sulfide inclusions. A slight pink cast could be detected in these inclusions and they gave a faint bright-dark change with crossed nicols. They were randomly distributed.

In the central portion of the ingot almost all the sulfides were either iron sulfide or duplex. The sulfides were, to a very large extent, distributed in a grain boundary network. Near the surface of the ingot these grain boundary sulfides were short but they increased in length toward the center and, at the center, Figure 11, some relatively long sulfides were found.

There appeared to be some more or less randomly distributed globular inclusions. These inclusions gave a bright-dark change with crossed nicols. Many of the grain boundary sulfides were round and they looked very much like the apparently randomly distributed sulfides.

In this heat a number of the sulfide inclusions contained silicate inclusions.

Heat No. 8

The surface layer on the ingot was absent or too thin to be noticed. All the sulfides gave a faint bright-dark change under crossed nicols. Most of the sulfide inclusions
UNETCHED, 150 X

FIGURE 12. CENTER OF THE INGOT FROM HEAT NO. 8.
UNETCHED, 150 X
were spheroidal. However, some of the sulfides were somewhat elongated, Figure 13, and they gave a more pronounced bright-dark change than the spheroidal sulfides.

The sulfides were relatively fine, Figure 12. Their distribution was somewhat uncertain because of their small size and the low sulfur content of this heat. At high magnification some of the inclusions, particularly the elongated sulfides, appeared to be located on grain boundaries but at low magnification they looked more like a random array.

The size of the sulfides was uniform throughout the ingot but there appeared to be more sulfides at the center than at the surface of the ingot.

Heat No. 9

In this heat the inclusions were mostly silicates, Figure 14 and 15. Silicates have a characteristic appearance with crossed nicols shown in Figure 15. They light up in two directions forming a "cross". There was no surface layer. Only a few round sulfides were found and these gave a bright-dark change with polarized light. A bright position for one such sulfide is shown in Figure 15. These sulfides were pinkish in color. Their distribution was uncertain. The sulfides were so far apart they appeared to be randomly distributed.
UNETCHED, 500 X
FIGURE 14. IRON SULFIDE INCLUSION IN THE INGOT FROM HEAT NO. 9, ORDINARY LIGHT.

IRON SULFIDE INCLUSION IS MARKED "FeS".

UNETCHED, 500 X

FIGURE 15. IRON SULFIDE INCLUSION IN THE INGOT FROM HEAT NO. 9, POLARIZED LIGHT.

SAME FIELD AS THAT SHOWN IN FIGURE 14. IRON SULFIDE INCLUSION IS IN A BRIGHT POSITION.

UNETCHED, 500 X
Heat No. 10

A surface layer about 1.0 mm thick was found on the ingot of this heat. Iron sulfide inclusions were found randomly distributed in the surface layer.

Almost all the sulfides in the central portion of the ingot were iron sulfides. There appeared to be no random manganese sulfides in this heat even though the equivalent of 0.5 percent manganese had been added. Some manganese sulfide was found but it was all part of duplex sulfides.

Most of the sulfides were grain boundary type, Figure 16 and 17. Some of the elongated sulfides showed a less intense bright-dark change with polarized light than the spheroidal sulfides.

Clusters of black inclusions such as that shown in Figure 16 were found in this heat. The inclusions in these clusters were not identified but they were crystalline in shape and were bright in polarized light with crossed nicols.

Heat No. 11

No surface layer was found on the ingot of Heat No. 11. However, just below the surface a few sulfides with a pink tint were found and they were anisotropic with polarized light indicating iron sulfides. Almost all the sulfides in this heat were dove gray manganese sulfides. A few iron
UNETCHED, 150 X
FIGURE 17. CENTER OF THE INGOT FROM HEAT NO. 10. UNETCHED, 500 X

FIGURE 18. CENTER OF THE INGOT FROM HEAT NO. 11. UNETCHED, 500 X
sulfide inclusions at the surface and a few duplex inclusions in the interior were found. The iron sulfide part of the duplex sulfides was pink.

The sulfides were very small and appeared to be distributed in a grain boundary network, Figure 18. In some portions of the ingot the network had some characteristics of a dendritic pattern causing some doubt about the nature of the distribution of the sulfides. The sulfides in this heat were somewhat similar to those in Heats No. 5 and 6 in which the sulfides were definitely arranged in a dendritic pattern. Heat No. 11 contained clusters of sulfides similar to but much smaller than those in the other two heats.

Furthermore, in each of these three heats most of the sulfides were located in the network with very few sulfides being randomly distributed. Only Heat No. 6 with its very high sulfur content had randomly distributed globular sulfides.

Heat No. 12

This heat was melted with only sulfur added to the iron. The resulting inclusions were unusual. Most were more or less spheroidal and appeared to be two-phase but they did not look like duplex iron sulfide-manganese sulfide inclusions. Part of the inclusions gave a faint bright-dark change with crossed nicols and could have been iron sulfides but they were anisotropic iron sulfides. Most of these sulfides were knaki colored.
sulfides. The other phase in the inclusions was dark in polarized light and showed no bright-dark change. This phase was believed to be iron oxide.

The inclusions were lined up in a pattern of some kind, Figure 19, and were also found to be randomly distributed. They increased in size toward the center of the ingot.

Heat No. 13

There was no surface layer on this ingot. Only carbon and sulfur were added to the melt. Numerous silicate type inclusions were found.

Most of the sulfides were anisotropic in polarized light giving a bright-dark change, Figure 21 and 22. Their color varied considerably. Most of the sulfides were somewhat yellow or khaki colored. However, some had the pink color found in the iron sulfide inclusions in some of the other heats. None of the inclusions was dove gray.

A large portion of the sulfides were grain boundary type. Near the surface many of the sulfides in the grain boundaries were more or less spheroidal but near the center of the ingot long film-like sulfides were frequent, Figure 23.

Some of the spheroidal sulfides, especially near the surface, appeared to be randomly distributed like globular sulfides but they were anisotropic iron sulfide. Most of these sulfides were khaki colored.
FIGURE 19. CENTER OF THE INGOT FROM HEAT NO. 12.
UNETCHED, 150 X

FIGURE 20. CENTER OF THE INGOT FROM HEAT NO. 12.
UNETCHED, 500 X
FIGURE 21. CENTER OF THE INGOT FROM HEAT NO. 13, ORDINARY LIGHT.

UNETCHED, 500 X

FIGURE 22. CENTER OF THE INGOT FROM HEAT NO. 13, POLARIZED LIGHT.

UNETCHED, 500 X

SAME AREA AS THAT SHOWN IN FIGURE 21. IRON SULFIDE IS IN A BRIGHT POSITION. THE BRIGHT RANDOMLY DISTRIBUTED INCLUSIONS SHOW THE "CROSS" CHARACTERISTIC OF GLASSY SILICATES.
UNETCHED, 150 X

FIGURE 24. CENTER OF THE INGOT FROM HEAT NO. 15.
UNETCHED, 150 X
Heat No. 14

This heat was similar to Heat No. 13 in composition and in sulfides. Ferrosilicon had been added to Heat No. 14. There was a surface layer about 1.75 mm thick on the ingot. In the surface layer the sulfides were spheroidal and randomly distributed. The central portion of the ingot was very similar to that in the ingot from Heat No. 13.

Heat No. 15

The surface layer was about 1.75 mm thick. The sulfides were small and distributed in the grain boundaries of columnar grains.

In the central portion of the ingot the sulfides were a dark gray, darker than dove gray. In polarized light with crossed nicols, they remained dark during rotation of the stage of the microscope. However, during rotation in polarized light they displayed spots of color in various shades of red and brown. The sulfides should have been manganese sulfide since the equivalent of 1.0 percent manganese had been added to the melt but the color of the sulfides and their behavior in polarized light was very unusual.

Most of the sulfide inclusions were spheroidal. They were distributed in a pattern of some kind, Figure 24, which could have been a grain boundary network. However, in some portions of the ingot the sulfides appeared to be randomly
distributed while in other portions the pattern appeared to be somewhat dendritic. Furthermore, in some places where there was a network the sulfides were not aligned in a line of single inclusions as was usual for grain boundary sulfides; the sulfides were sometimes aligned in a band several inclusions wide.

Heat No. 16

The surface layer of the ingot was approximately 1.0 mm thick. Relatively large, spheroidal iron sulfides were found in a random pattern.

Below the surface layer the sulfides were practically all grain boundary type, Figure 25 and 26. They were iron sulfide and were similar to those found in Heat No. 14. The film-like sulfides in this heat were somewhat thicker than those in Heat No. 14.

The density of sulfides at the center of the ingot appeared to be less than it was near the surface.
FIGURE 25. CENTER OF THE INGOT FROM HEAT NO. 16.
UNETCHED, 150 X

UNETCHED, Very high sulfur, 0.38 percent, under 500 X
C. DEFORMATION PROCESSES

Ingots from several heats were worked down into bars. In this limited effort it was found, as expected, that only the heats to which manganese had been added could be worked. Bars were produced from Heats No. 2, 3, 5 and 6. Ingots from Heats No. 4, 7 and 8 failed when hot working was attempted.

The following comments on the effect of working and thermal treatments pertain to observations made on Heat No. 2. Similar observations were made on Heats No. 3, 5 and 6. The ingots were worked into bars by first forging at 1200°C to approximately 1.25 inches diameter. The forged stock was then reheated to 1200°C and hot rolled to about 0.5 inches diameter. The scale was removed from the hot rolled bars and they were then swaged cold to the final 3/8 inches diameter.

The effects of heating and working on the sulfide inclusions can be seen by comparing the as-cast inclusions shown in Figure 27 with those at various stages of reduction in Figure 28, 29 and 30. It can be seen that working elongates the sulfides and produces stringers such as those that can be found in wrought commercial steels. This heat contained very high sulfur, 0.38 percent, and had numerous sulfide stringers in the bars. The stringers did not seem particularly long for material with so high a sulfur content.
FIGURE 27. AS-CAST SULFIDE INCLUSIONS IN HEAT NO. 2.
UNETCHED, 150 X

FIGURE 28. LONGITUDINAL SECTION IN FORGED BAR FROM HEAT NO. 2.
UNETCHED, 150 X
FIGURE 29. LONGITUDINAL SECTION IN BAR FROM HEAT NO. 2 AFTER FORGING AND ROLLING.

UNETCHED, 150 X

FIGURE 30. LONGITUDINAL SECTION IN FINISHED BAR FROM HEAT NO. 2.

UNETCHED, 150 X
Numerous fine inclusions were found after working started, Figure 31. These fine inclusions were not present in the ingot, Figure 2, but were found after forging. Examination with polarized light revealed that some of these fine inclusions were silicates. In ordinary light the fine inclusions appeared to be the same at the various stages of working.

After plastic deformation at 1200°C, all the sulfide appeared to be manganese sulfide. The iron sulfide and duplex sulfides which were present in the ingot could not be found in the forged bars. However, for some unknown reason the sulfide inclusions in the worked material were not the same in the longitudinal and transverse directions. When transverse sections were examined with polarized light using crossed nicols the sulfides were black and stayed black during rotation. However, the sulfides in longitudinal sections behaved differently. Some of the elongated sulfides appeared to give the edge effect in which the edges became very bright in certain positions during rotation with crossed nicols. Other elongated sulfides gave a different optical effect which is somewhat difficult to describe. In these inclusions certain areas of the inclusion appeared to light up during rotation with crossed nicols but the effect was very different from that displayed by iron sulfide as shown in Figures 3 and 22.
The iron sulfide inclusions displayed a uniform brightness. The sulfides in the longitudinal sections became bright only in spots and these spots were not merely bright but were usually colored in various shades of red or brown. The reason for this difference in behavior in transverse and longitudinal directions was not known but the inclusions did not appear to be iron sulfide. It was believed that all the iron sulfide originally present in the ingot had disappeared from the worked material. Apparently manganese had displaced the iron in the sulfide phase.
FIGURE 31. HEAT NO. 2 AFTER FORGING AT 1200°C SHOWING THE FINE INCLUSIONS.

TO BE COMPARED WITH FIGURE 2.

UNETCHED, 500 X

"Pocket"

FIGURE 32. SAMPLE FROM HEAT NO. 2 ANNEALED AT 1200°C FOR TWO HOURS.

"POCKETS" SUCH AS THAT IN THE CENTRAL INCLUSION WERE COMMON IN THIS SAMPLE.

UNETCHED, 1000 X
D. ANNEALING AT HIGH TEMPERATURE

Since the iron sulfide had disappeared from hot worked steel it was decided to heat samples and see if thermal treatment alone would transform iron sulfide into manganese sulfide.

Samples of Heat No. 2 had been annealed at 850°C. These samples were held at temperature for 10 minutes and then furnace cooled. After this treatment it was observed that the boundary between the iron sulfide and manganese sulfide areas of the duplex sulfides appeared to be more distinct. The amount of iron sulfide was found to be essentially the same after this annealing as before.

Samples were then heated to 1200°C for various times. The times at temperature for the samples in this series were 5, 10, 20, 60, 120 minutes. The 20 minute sample was furnace cooled while the others were air cooled. The whole polished surface of each sample was examined carefully for the presence of iron sulfide or duplex inclusions.

The sample held at 1200°C for 5 minutes contained some duplex inclusions. Only two small iron sulfide inclusions were found in this sample. The 10 minute sample had approximately the same number of duplex inclusions as the 5 minute sample but it contained no iron sulfide inclusions. No iron sulfide or duplex sulfide inclusions were found in the 20, 60 or 120 minute samples.
The annealing at 1200°C tended to spheroidize the grain boundary sulfides. The irregular shapes of the grain boundary sulfides as they existed in the ingot were changed to a more spheroidal or globular shape. However, after a long time at temperature the sulfides were found to contain cavities or pockets as shown in Figure 32.

All the duplex and iron sulfide inclusions found in 5 and 10 minute samples were irregular in shape. Only globular sulfide inclusions (inclusions without sharp corners or points) were found in the samples annealed for 20 minutes or more. Furthermore, a dispersion of fine inclusions similar in appearance to those found in the hot worked material and shown in Figure 31 was found in the samples annealed at 1200°C.

The annealing at 1200°C affected the behavior of the sulfides in polarized light. The iron sulfide inclusions in the ingot were anisotropic giving a bright-dark change while the manganese sulfide remained dark in all positions. After annealing at 1200°C, the iron sulfide disappeared as mentioned above and some of the manganese sulfides showed the colors found in the longitudinal sections of the worked samples. The number of manganese sulfide inclusions showing the red or brown colors in polarized light with crossed nicols increased with annealing time up to 20 minutes. There was no further apparent increase in the 60 and 120 minute samples.
A set of samples from Heat No. 7 was annealed at 1200°C. The annealing times were the same as those used for the Heat No. 2 samples: 5, 10, 20, 60, 120 minutes. Contrary to what was expected, most of the sulfides were manganese sulfide after annealing. Only a few grain boundary sulfides were found that showed a bright-dark change in polarized light with crossed nicols. All such inclusions had sharp corners indicating that they were located at the junctions of grain boundaries. Globular sulfides were all manganese sulfides.

There was some concern about the unexpected disappearance of the iron sulfide in the Heat No. 7 samples. No manganese had been added to this heat and the above set of samples was annealed to show that the iron sulfide would not disappear in the absence of manganese. Eventually it was realized that Heat No. 7 was the third heat melted in crucible No. 3 and the first two heats both had manganese additions, see Table No. 1. A certain amount of slag always adhered to the wall of the crucible and this was suspected as a source of manganese since approximately half of the manganese was lost to the slag.

As a check on the above theory that Heat No. 7 had been contaminated with manganese by residual slag on the sides of the crucible it was decided to run another set of samples of Heat No. 14. No manganese had been added to Heat No. 14 and no manganese had been added to either of
the two heats melted before Heat No. 14 in the same crucible.

The samples of Heat No. 14 were annealed at 1200°C for 10, 20, 60, 120 minutes. All these samples contained much iron sulfide. In addition to grain boundary iron sulfides, there were also many globular and randomly distributed iron sulfide inclusions in these samples. Furthermore, the iron sulfide inclusions in the annealed Heat No. 14 samples displayed a good bright-dark change with crossed nicols whereas the relatively few iron sulfide inclusions in the annealed Heat No. 7 samples gave a very faint bright-dark change.
V DISCUSSION OF RESULTS

The nature of sulfides in as-cast steel indicates that the solubility of manganese sulfide in liquid steel is less than that of iron sulfide. The presence of globular and randomly distributed sulfides in the higher sulfur heats serves as the basis for this statement.

It seems reasonable, as postulated by Sims and Lillieqvist (9) that the inclusions are all dissolved in the liquid steel at steelmaking temperatures. The inclusions come out of solution and form separate phases either during cooling to the solidification range or during the solidification process. It is also possible for some inclusions to form after solidification by precipitation from solid metal during cooling.

If a sulfide precipitates in the liquid steel during cooling to the solidification temperature, this type sulfide would be expected to be randomly distributed in the metal that subsequently solidifies. On the other hand, if the sulfide is more soluble and remains dissolved in the liquid steel until near the end of the solidification process, it would be distributed in a pattern. This pattern might be the grain boundaries of the primary grains or it might be an outline of the branches of dendrites. Accordingly, it seems reasonable to assume that randomly distributed sulfides were less soluble in the liquid steel than inclusions present in a grain boundary or dendritic pattern.
Randomly distributed sulfides were definitely identified only in the ingots from heats of higher sulfur content, Heats No. 2, 3 and 6. These heats contained 0.3 percent sulfur or more. The other heats with 0.1 percent sulfur apparently did not contain sufficient sulfur to become saturated above the solidification range.

In Heats No. 2 and 3 iron sulfide was present but the randomly distributed sulfides were all manganese sulfide. In Heat No. 6 all the sulfides, including those randomly distributed, were manganese sulfide. Presumably a lower solubility of manganese sulfide causes it to precipitate during cooling prior to solidification. Iron sulfide did not precipitate in this temperature range.

The presence of much manganese sulfide in both the grain boundaries and in dendritic patterns indicated that at least part of the manganese sulfide remained in solution until near the end of solidification.

It is interesting to note that the only difference in Heats No. 5 and 6 was their sulfur contents. Heat No. 5 contained 0.1 percent sulfur and contained no random sulfides. Heat No. 6 contained 0.3 percent sulfur and random sulfides as well as the sulfides in a dendritic pattern. The 0.1 percent sulfur was not sufficient to give random sulfides.

Grain boundary, iron sulfide, film-like inclusions were triangular in shape and had sharp edges.
were found in Heats No. 4, 7, 10, 13, 14 and 16. Heat No. 10 is the only heat in this group with manganese. None of the other heats to which manganese had been added contained film-like inclusions. It would appear that manganese tends to prevent the formation of film-like grain boundary sulfides.

Heats No. 8 and 9 contained no manganese and had no film-like sulfide. These heats contained only 0.05 percent sulfur and this may be too low a sulfur content to yield film-like sulfides. Heat No. 12 also had no manganese or film-like sulfide. Heat No. 12, contained only iron and sulfur. Since no deoxidizer or carbon had been added it is likely that this heat was high in oxygen. Van Vlack (8) showed that oxygen increased the dihedral angle of the sulfide phase and caused the sulfide to be globular. The sulfide inclusion in Heat No. 12 appeared to have separated into sulfide and oxide phases after their formation.

Study of the sulfides in the worked steels and in the steels that had been annealed at high temperature indicated that iron sulfide was molten at the elevated temperature and that it was present in the austenite grain boundaries. Examination of the annealed Heat No. 7 samples in particular indicated this. The manganese in these samples was limited and only a few iron sulfide inclusions could be found after annealing. Most of these iron sulfide inclusions were triangular in shape and had sharp corners. None were
spheroideal or globular. Their shape indicated that they had been liquid at the annealing temperature and that most had been located at the junction of austenite grain boundaries.

It might also be mentioned that the iron sulfide film-like inclusions broke up very rapidly at the hot working and at the higher annealing temperatures. This may also indicate that the iron sulfide was molten. A solid phase might not spheroidize so rapidly.

One unexpected phenomenon that was observed was the formation of iron sulfide during solidification in manganese containing heats and the subsequent replacement of the iron sulfide by manganese sulfide. Heats No. 2, 3, 10 and 11 all contained 0.5 percent manganese or more. Iron sulfide formed in each of these heats during solidification.

Heats No. 5 and 6 contained 1.0 percent manganese and also 1.5 percent copper. It is believed that iron sulfide would have been formed during solidification of these heats if the copper had not been present. Apparently copper can prevent iron sulfide from forming during solidification when manganese is present. However, copper did not combine preferentially with the sulfur in the absence of manganese and prevent formation of iron sulfide. Heat No. 4 contained 1.5 percent copper but no manganese. All the sulfides in Heat No. 4 were iron sulfide.

The replacement of iron sulfide by manganese sulfide in manganese bearing steels could have been the result
of the solution of the iron sulfide and subsequent reprecipitation of the sulfur as manganese sulfide. The frequent pockets or cavities in the sulfides in the annealed Heat No. 2 samples may have been the result of solution of iron sulfide from duplex inclusions. The numerous fine inclusions found in the samples heated to high temperatures may have been the precipitated manganese sulfide.

Study of sulfides in steel leaves little doubt that they are not pure and simple phases. The sulfides are quite variable and it may be assumed that the variation is due to different chemistry in different sulfides.

The iron sulfides in the various heats varied considerably. Their color was yellow in some heats and pink in others. Sometimes the iron sulfide was almost light gray. The iron sulfide is presumed to be anisotropic in all cases and to give the bright-dark change in polarized light with crossed nicols. However, the degree of anisotropy as indicated by the maximum brightness was variable.

Manganese sulfide was also variable. Some color variation was observed. The behavior in polarized light also varied. The appearance of the red and brown colors in the worked and in the annealed samples indicated changes had occurred. In the worked steels the manganese sulfide did not behave the same in polarized light in the transverse and longitudinal directions.
VI CONCLUSIONS

Pure iron sulfide or manganese sulfide probably do not exist in steels. Each of these sulfides apparently dissolves many elements and their characteristics can change appreciably with changes in composition.

Manganese sulfide is less soluble in liquid steel as reported in the literature and tends to form globular inclusions while iron sulfide tends to form film-like inclusions in the grain boundaries of the austenite.

Iron sulfide forms readily in steel during solidification even when manganese is present. However, the iron sulfide dissolves on subsequent heating to high temperatures and the sulfur reprecipitates as manganese sulfide if manganese is present.
BIBLIOGRAPHY


The author was born on October 6, 1936, at Hu-nan Province of Republic of China. He graduated from the elementary school in Kiang-su Province and finished his high school at Taipei and his college education at Tainan in Taiwan (Formosa).

After he graduated from Cheng-kung University, Tainan, he served in the Army a year. He was one of the instructors teaching primary physics in the Chinese Army Infantry School for four months.

Discharged from the Army, he entered the Union Industry Research Institute as a research assistant for six months.

He entered the School of Mines and Metallurgy of University of Missouri at Rolla in September, 1963.