



THE THERMITE WELDING OF CAST IRON

by

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SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
BACHELOR OF SCIENCE

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

May, 1958

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Department of Metallurgy, May, 1958

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Submitted to the Department of Metallurgy on May 26, 1958

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ABSTRACT

By washing an amount of superheated metal through the joint to be made and allowing the last bit of metal to fill the gap, sound grey iron welds can be made in cast iron without preheating. Steel thermite with additions of amorphous carbon, calcium carbide and ferrosilicon is used as the source of the hot metal. The analysis of the metal produced is 4.2 percent carbon and 2.6 percent silicon. In order to achieve adequate carbon solution large excesses of carbon must be employed. Calcium carbide is necessary to maintain a low carbon monoxide potential when the metal reacts with the oxide or silicate mold materials. Without calcium present porous weld zones are realized. With calcium present less stable oxides or silicates than magnesia, which was used for the majority of tests, may be used for molding materials.

Thesis Supervisor: Clyde M. Adams, Jr., Associate Professor of Metallurgy

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ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Professor Clyde M. Adams under whose guidance the project was formulated and developed, and without whose assistance it would have been impossible. Also, to Messrs. Harold Bishop and Michael Bock of Exomet Incorporated of Conneaut, Ohio, for their many helpful suggestions and to Exomet Incorporated for their sponsorship of the project and for the chemical analyses goes the author's gratitude.

The author wishes to thank the members of the Massachusetts Institute of Technology Experimental Foundry and Welding Laboratory for their assistance.

I. INTRODUCTION

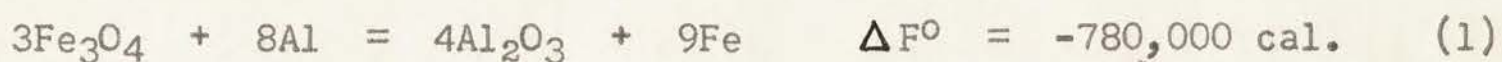
A. General

Grey iron can be successfully welded using any one of a number of methods if, and only if, special precautions are observed. Aside from proper design considerations, true in any welding procedure, the liquid grey iron must be cooled sufficiently slowly to allow the carbon to precipitate as graphite flakes. Cast iron cooled too rapidly will either form hard brittle deposits of cementite or be entirely white iron. Generally, to prevent cementite from forming during solidification and cooling after welding, the part being welded is given a preheat to 600 - 1000°F, sometimes as high as 1450°F. Following the welding operation, to precipitate any dissolved carbon, a postheat is made. It is the preheat and/or, postheat necessary to produce a grey iron structure that is difficult and time consuming.

In repair welding of grey iron castings, by far the largest area of grey iron welding, the needed preheat is costly and inconvenient, not to mention the discomfort of the welder trying to work on a casting at 1000°F. Also, the welding itself, whether it is gas welding, braze welding, or arc welding, demands a high degree of skill on the part of the welder. Therefore, in an effort to find a less expensive, less time consuming way to successfully weld grey iron, an adaptation of the thermite process was proposed. It is the purpose of this thesis to propose a satisfactory method to thermite weld grey iron without any preheat or postheat.

B. Thermite Welding

By reacting iron oxide, usually high purity mill scale, with aluminum powder, super heated molten metal is produced:



The adiabatic temperature of the iron produced is of the order of 5400°F. Suitable alloying elements added to the mixture before reaction will change the product from almost pure iron to either alloy steels or cast irons. The thermite reaction is favorable, that is $-\Delta F^\circ > 0$, for all the common steel alloying elements, cobalt, chromium, molybdenum, nickel, manganese, tungsten, and vanadium. Steel compositions of almost any kind, theoretically, can be made by the thermite reaction.

Industrially this process is used for repair welding of large steel parts. A typical analysis of thermite steel used for welding is: carbon 0.2-0.3 percent, manganese 0.5-0.6 percent, silicon 0.25-0.50 percent, and phosphorous and sulfur 0.03-0.04 percent. The welding is done by enclosing the joint area in a sand mold with a wax pattern to form the weld zone, melting out the pattern, preheating the joint to a bright red heat, and pouring the superheated steel directly from the reaction crucible to the mold cavity. In this process the preheat is used to accomplish complete fusion, not so much to control cooling rates. Again the technique is cumbersome and time consuming. Preheat time may run as long as 24 hours.

For any fusion welding process two requirements must be met: sufficient energy must be supplied to the metal to raise its temperature and

melt it, and filler material must be added to the weld zone. The energy source is usually an acetylene torch or an electric arc. Filler material is added either as wire in the gas welding or non-consumable electrode arc welding or as the electrode itself in consumable electrode arc welding. However, the superheated steel or grey iron developed by the thermite reaction can be used as a source of heat energy and filler metal.

By washing an amount of the hot metal over or through the joint to be made to raise the parent metal temperature and allowing the last bit of metal to fill the joint, complete fusion may be realized without any previous heating. Adams et al have successfully welded three inch diameter steel bar and $3/4$ inch steel plate in this manner.

II. EXPERIMENTAL PROCEDURE

A. Technique

It was decided that to achieve any real saving in time and expense, the process must use no pre- or postheat. Therefore, the method devised by Adams it al¹ on thermite welding of steel pipe, of washing superheated metal over a cold specimen to realize welding, would be applied to cast iron.

The test plates were grey iron rectangular blocks roughly 5-1/2 by 2-1/2 by 1-1/4 inches with a 90 degree vee groove machined parallel to the 2-1/2 inch edge. A typical composition is 3.3 percent carbon, 0.55 percent manganese, 0.03 percent phosphorous, 0.02 percent sulfur and 1.80 percent silicon. A test block is rammed into the drag half of a sand mold so that metal washes through the groove into an overflow well, see Figure 1a. Adjustment of the volume of the well gives some control over the amount of overflow metal. Thermite is reacted in a conical shaped crucible and, after 30-40 seconds from the start of the reaction, the metal is tapped into the mold. Thermite ignition is done with a diluted mixture of barium peroxied and aluminum powder lit with a fuse. Metal is tapped by hitting the tapping pin up into the molten bath.

Using sufficient thermite, about 40 pounds, to produce about 20 pounds of metal, and allowing most of this metal to flow through the groove, complete fusion is realized between the thermite metal and the test plate. The large excess of metal used serves two purposes: 1) a complete, crack free weld is obtained, and, 2) the test plate is so heated

that subsequent solidification and cooling of the weld is slow enough to avoid the formation of hard or brittle deposits. Indeed, one hour after the weld is made the test plate is still red hot.

Forty pounds of thermite was used regardless of the size of the overflow well to keep the heat losses of the metal in the crucible constant. That is, the temperature of the tapped metal, or the amount of superheat, while unknown is kept as constant as possible. The relative sizes of the tap hole in the crucible, the sprue, and runner decrease in the order given. To get complete fusion the flow rate has to be high; the sprue diameter must be about one inch; the tap hole, 1-1/4 inches; and the runner, slightly smaller than the sprue. With a semi-stoppered system such as we have, the metal tends to build up in the pouring basin which keeps the gates full during the pour.

The mold design is given in Figure 1b. (Note the crown or weld bead formed in the mold above the test plate groove. In the first test, made with no crown, the metal froze in the notch preventing any fusion at all.) This design was completely satisfactory and only a few minor changes were made throughout the test series. The overflow was moved from the drag to the cope to aid in keeping the runner full and to prevent non-metallic inclusions. Also, the sprue was made square (3/4" x 3/4") to help keep the metal from forming a whirl pool which leads to slag entrapment.

Molds, thermite, and later amorphous carbon, were, after the first few runs, oven dried over night at 350°F. Without drying the thermite

reactions and mold metal reactions are excessively violent. In shipping and storage the thermite picks up a little moisture which causes the violence. Water in the molds leads to violent mold reactions with the metal plus sufficient hydrogen pick-up by the liquid metal to cause porosity in the solid metal.

Most all of the successful runs, successful in the sense that some weld was achieved, were analysed for carbon and silicon. Usually the sample was cut out of the overflow and the surface mold sinter ground off. In some tests the sample was taken from the runner; in all cases the metal was assumed to be representative of the weld zone. There may be some dilution in the weld zone from the base plate but most of the erosion is done by the overflow, not the filler metal.

B. Cast Iron Thermite

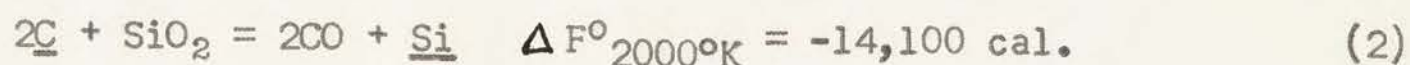
Cast iron thermite, aside from the usual iron oxide and aluminum, contains 1 percent ferromanganese, 1 percent ferrosilicon, 3 percent graphite, 7.5 percent cast iron shot, 2 percent silicon carbide and 4 percent aluminum-magnesium alloy. Used without any addition cast iron thermite will produce a metal analysing approximately 2.25 percent carbon and 2.5 percent silicon. All experiments using this thermite were performed in silica sand molds, either green or dried, and, therefore, the measured silicon contents were about 3.5 percent.

As received, cast iron thermite gives a hard but machinable fusion zone. The graphite flakes are finely dispersed and the hardness is about Rockwell C 35 for the weld metal at the edge of the fusion zone. Additions

of silicon of 2 percent of the metal produced, reduces the hardness to that of a high strength grey iron. Carbon and silicon contents for these tests are 2 percent and 5-6 percent respectively.

The main difficulty with this type of thermite is chemical in nature:

1) severe porosity in the fusion zone and surface of the weld plate, see Figure 2, and 2) abnormally low carbon, high silicon iron in the weld deposit. These two problems are not independent. Firstly, low carbon cast irons tend to form porosity due to shrinkage if not properly risered. Secondly, it appears likely that the carbon dissolved in the metal is reacting with the mold material to form silicon and carbon monoxide:



It is this reaction that leads to the peculiar metal composition and contributes to porosity. The carbon monoxide formed is trapped between the mold sinter product and the metal causing extensive porosity on the surface of the specimen, see Figure 2. It should be remembered that the original groove width is one inch and the weld crown also is about one inch wide.

If no side reaction took place between the metal and either the air or the mold, the metal produced would have 4.8 percent silicon and 6.5 percent carbon. Actually, however, much carbon and some silicon is lost from air oxidation. Most tests in this series have been run with a 1 percent silicon addition, in this case theoretical silicon concentration

is 5.8 percent. The fact that measured silicon contents are as high as 6.6 percent proves that some metal mold reaction is taking place.

It was impossible using cast iron thermite plus silicon additions to get sound grey iron welds in silica or other silicate sand molds. Even thorough de-oxidation with excess aluminum does not influence porosity. One sample had a residual aluminum content of 1.7 percent and still had severe porosity. No improvement in weld zone characteristics was attained using more stable silicates than silica, that is zircon, kyanite, or olivine.

C. Steel Thermite

In order to gain a larger degree of control over the thermite metal composition than could be achieved using cast iron thermite, it was decided to change to the use of steel thermite, and make our own additions of carbon and silicon to produce grey iron.

A series of tests were performed in baked magnesia molds adding from 6-10 percent, of the metal produced, carbon as either or both amorphous carbon and calcium carbide. Silicon was added to about 2 percent as ferrosilicon or calcium silicide. Chemical analyses of these two elements were made to study the absorption of carbon and the pick up of silicon from sources other than those added to the thermite.

Two mechanical techniques were tried to promote the solution of carbon in the crucible reaction and aid in complete de-oxidation of the melt. These included disposition of excess amorphous carbon above a small charge of thermite but below the main charge and increased crucible holding times. Since the small thermite pocket at the bottom of the crucible would ignite

after the main reaction had gone to completion, the amorphous carbon would be thoroughly mixed. This would lead to better carbon pick up and better de-oxidation by carbon.

Three tests were performed with an exothermic pad placed over the test plate. When the molten metal came in contact with the pad it would be ignited. The burning of the pad slowed down the cooling rate of the plate and thus aided in the formation of grey iron. However, some difficulty was experienced in obtaining slag-free weld deposits. The fusion zone itself was sound grey iron without any hard cementite present. Due to the slag entrapment and awkwardness of the molding arrangement this phase was abandoned before any significant data were obtained. This method may be used, if properly investigated first, to reduce the amount of thermite required to produce a weld.

Later experiments were performed using large excesses, 15-20 percent of carbon, both as amorphous carbon and calcium carbide in baked silica and baked magnesia sand molds. A few tests were done in air dried and green silica molds which showed that good welds may be achieved in dried molds. Green sand molds give porous welds due to hydrogen pick up.

Generally the fusion zone in the base plate was two to three times as large in cross section as the original groove, see Figure 3. Sometimes, depending on the size of the test plate, there was some variation in size, a mottled structure of grey iron and cementite or white iron with very fine graphite flakes would be found at the edge of the fusion zone. This hard deposit was usually found, if no where else, near the

surface and the fusion zone edge. A weld would be grey iron throughout with just a small amount of white iron here.

D. Molding Materials and Chemical Analysis

Some work was done using other molding material than silica and magnesia sands. Zircon, olivine, kyanite, carbonaceous molding materials, and silica sand plus 10 percent coal were also used. The molds containing carbon gave such violent mold-metal reactions that meaningful results could not be obtained. Olivine, zircon, and kyanite did not improve on the carbon-silica reaction of Equation (2), even though they are, presumably, more stable silicates. Zircon and olivine, especially the former, have a greater chilling effect, higher heat conductivity, than does magnesia and silica. A grey iron weld in silica may, under the same condition, contain some white iron when made in a zircon or olivine sand mold. Being silicates, both olivine and zircon are prone to the mold-metal problem noted earlier.

Generally all refractories tried except silica and zircon gave some molding problems. However, these were due, not necessarily to the nature of the refractory, but to their particle size and size distribution. The best results for ease of molding were obtained from a size range of minus 80 mesh. Olivine, kyanite, and magnesia had some what larger grain sizes, minus 30 to plus 90 mesh. It was the large particles that caused the trouble. The large particle sizes gave a more friable mold when dried than did the minus 80 mesh grains. Friability, while not an important consideration in the laboratory, may be important in practice; and it is

easily overcome. Carbonaceous molding materials were almost impossible to mold, the particle size was too small and mold plasticity was almost non-existent. Silica plus coal was easy to work but did not solve the problem.

The reason for the shift from silica to the other silicates was the hope of finding a more stable molding material to prevent the carbon-silica reaction. Actually the problem was solved by additions to the thermite and then the molding material was no problem. Magnesia was selected because it does not contain any silicon and the ΔF^0 value for:



is +7900 calories at 2000°K (3000°F). Therefore, the reduction of magnesia by carbon is not favorable and carbon monoxide cannot be formed. Calcium oxide also has a favorable ΔF^0 value but in molding, burnt lime would form calcium hydroxide with the water added. Magnesia does not hydrolyze to any appreciable degree.

III. RESULTS

A homogeneous mixture of steel thermite, amorphous carbon, calcium carbide, and ferrosilicon was developed which will give sound grey iron weld deposits. No sound, gas free weld can be achieved without adding calcium carbide unless the test plate undergoes extremely slow cooling from the liquid. Slow, directional cooling may be realized by using an exothermic pad placed over the weld zone or by allowing the molten slag to settle on the weld crown. This gives the gas generated in the metal sufficient time to diffuse to the surface and out through the mold. These two methods, however, are clumsy and awkward to perform; and not all the slag produced, in fact only a small fraction, ends up in the pouring basin.

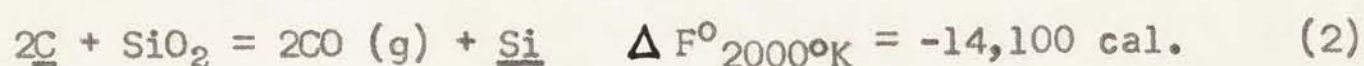
The composition of a mixture which appears to be completely satisfactory for producing grey iron fusion zones in iron castings is:

86.1 percent Steel Thermite
8.6 percent Amorphous Carbon
3.9 percent Calcium Carbide
1.4 percent Ferrosilicon (85-90% Si)

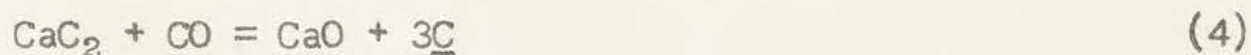
This mixture produces a fusion zone which contains typically 4.2 percent carbon and 2.7 percent silicon. The outstanding features of the mixture are the large excess of carbon involved, only 20 percent finds its way into the metal, and calcium carbide as a de-oxidizer. Calcium is the only element which can be conveniently used that seems to be able to eliminate porosity completely. A few runs made with excess aluminum showed no porosity improvement.

Most work performed involving sound welds were made in baked magnesia molds. However, using the above mixture, without the ferrosilicon, in a dried silica sand mold, also gives good results, see Figure 4. Without the silicon addition the metal composition is about the same for carbon but silicon is reduced to about 1 percent.

Steel thermite will pick up about 1 percent silicon from a silica or silicate mold and about 0.7 percent from a magnesia mold. Supposedly in the latter case there is no silicon present and the metal content of silicon should be close to zero. However, the crucible lining is probably a silicate of some kind, the bentonite clay in the molds, the base plate itself, and the steel thermite are all sources of silicon. Since there are undoubtedly silicates present Equation (2) will occur:



This would be no great problem in the crucible but, as mentioned before, in a silica mold it can lead to porosity. With calcium present, either as the carbide or dissolved elemental calcium, the carbon monoxide formed is immediately reduced to calcium oxide and carbon:

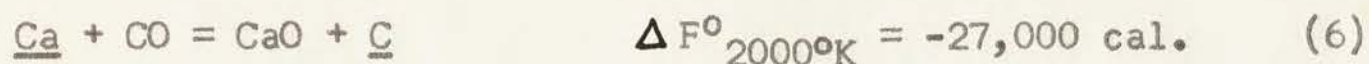


or



High temperatures favor the reaction as written. Calcium carbide may be decomposed, also favored by elevated temperatures, and the dissolved

calcium react as:



or



The calcium oxide formed may then give a relatively protective layer on the weld metal to prevent further reaction.

The K value for Equation (2) is 34.8 at 3000°F. Therefore, to form carbon monoxide at one atmosphere pressure the carbon activity must be about 0.03, if we make the assumption that $A_{\text{Si}} = N_{\text{Si}}$, not strictly true, $A_{\text{SiO}_2} = 1$, and $N_{\text{Si}} = 0.02$ (1% Si). Actually, however, it is closer to 1 since carbon is present in excess and the amount of carbon dissolved is close to saturation. From the equilibrium constant for Equation (6), $K = 10^3$, it may be seen that $A_{\underline{\text{Ca}}}$ doesn't have to be very large to reduce any carbon monoxide to a negligible amount.

It should be noted here the high carbon equivalent, that is, the percent carbon plus one-third the percent silicon, is approximately 5 percent. Figures 9 and 10 show the difference in graphite flakes in the fusion zones of a 1 percent Si and 2.6 percent Si iron. In both cases the carbon content is about 4.3 percent. Figure 9 is from a weld made in SiO_2 and Figure 10 is from one done in an MgO mold. The higher silicon content of the latter tends to give larger flakes of graphite. The fusion zone edge is the same for both cases, some fine pearlite with mostly cementite containing a fine dispersion of graphite

flakes, see Figures 7 and 8. A macrophotograph of the fusion zone edge shows a white iron but the microphotograph shows some fine graphite. In any case the edge of the fusion zone may be easily machined.

The only test bar pulled, mainly to show a cross sectional fracture surface, shows a wide variance in structure across the fusion zone, see Figure 13. Since the variation in structure gives an unequal stress distribution, the fracture strength of 16,500 pounds per square inch is not meaningful.

A few words should be spent on the role of calcium carbide as a carburizer. Approximately 2 percent is about all the carbon that will dissolve in iron from this source, presumably due to its solubility in the slag. No analysis of the slag was made for CaC_2 but pieces soaked in water liberated acetylene, positive proof that it was present. Therefore, in order to supply carbon to the metal some sort of equilibria between slag and metal must be fulfilled with the equilibria favoring the slag. No experiments were made with more than 6 percent carbon as CaC_2 . The thermite metal made with calcium carbide added is sound but white with some porosity from shrinkage. Crucible reactions are extremely quiet, the calmest reaction possible.

From Figure 14 it may be seen that nodular iron can be produced by the thermite reaction. This structure was made by casting the metal into an open zircon sand mold to study, primarily, the mold-metal reaction in zircon. If the sulfur is low, necessary to form nodular iron, graphite may precipitate as spheroids. In passing, let it be said that from this

microstructure it appears that ductile iron can be welded by this process.

IV. CONCLUSIONS

1. Grey cast iron can be welded by the thermite process without any preheat.
2. Sound welds cannot be produced in silica sand molds without adding calcium carbide to the thermite mix.
3. Excess carbon, 15-20 percent of the metal produced, is needed to insure solution of about 4 percent.

V. SUGGESTIONS FOR FUTURE WORK

The use of the thermite process for welding structures without any preheat is new. Work should be done to define amounts of thermite, metal overflow, joint dimension and mold design to insure welding success. Also work on nodular cast iron, and steel should be investigated. For welding large sections quickly and easily this process, especially the idea of washing superheated thermite metal through the joint area to accomplish fusion, can be made useful to industry.

TABLE I

Experiments Using Cast Iron Thermite

<u>Run No.</u>	<u>Mold Material</u>	<u>Addition</u>	<u>Weld</u>	<u>Fusion Zone</u>
C	Green SiO ₂	None	Gasy	White
D	"	2%Si(FeSi)	"	Grey
E	Baked SiO ₂	" + 0.1% Al	"	"
K	Baked Zircon	"	"	Grey-white
L	Baked SiO ₂	" + $\frac{1}{4}$ % Al	"	"

Runs F through J were similar to E except the amount of overflow was reduced each time from 20 pounds to 12 pounds. Runs M, N, O were unsuccessful tests with carbonaceous molding materials.

TABLE II

Experiments Using Steel Thermit

<u>Run No.</u>	<u>Mold Material</u>	<u>Additions</u>	<u>Weld</u>	<u>Fusion Zone</u>
T	Baked MgO	10%C as CaC ₂	Sound	White
U	"	18%(a • c)*	"	Grey
(Slag settled on top of fusion zone)				
W	Baked SiO ₂	5%C(CaC ₂)5%(a•c)	"	White
X	Baked MgO	" + 1%Si(CaSi)	"	"
Y	"	10%C(a•c)	Gasy	Grey-white
Z	"	" + 1%Si(CaSi)	"	"
DD	"	18%C(a•c)	"	Grey
EE	"	" + 1%Si(FeSi)	"	"
FF	"	" + 2%Si(CaSi)	"	"
GG	"	" 2%Si(FeSi)	"	"
HH	"	" + 3%C(CaC ₂)2%Si(FeSi)	Sound	Grey
LL	"	" " "	"	"
PP	Baked SiO ₂	" " "	"	"

Runs AA, BB, CC had an exothermic pad over weld plate, all had slag entrapped in the fusion zone, all had grey iron weld metal. II, JJ, KK, MM, NN, were repeats of HH.

*Amorphous carbon.

TABLE III

Carbon and Silicon Pick-up by Steel Thermit

<u>Run No.</u>	<u>Mold Material</u>	<u>%Si Added</u>	<u>Si Analysis(%)</u>	<u>%C Added</u>	<u>C Analysis</u>
T	MgO	0	0.40	6(CaC ₂)	1.85
U	"	0	0.61	18(a.c.)*	4.29
W	SiO ₂	0	0.97	5(a.c.) 5(CaC ₂)	3.72
X	MgO	1(CaSi)	2.12	5(CaC ₂)	0.81
Y	"	0	0.71	10(a.c.)	1.57
Z	"	1(CaSi)	2.87	"	3.68
DD	"	0	0.87	18(a.c.)	3.96
EE	"	1(FeSi)	2.28	"	4.16
FF	"	2(CaSi)	3.41	"	3.25
GG	"	2(FeSi)	2.68	"	3.86
HH	"	"	2.83	18(a.c.) 3(CaC ₂)	4.66
PP	SiO ₂	0	1.02	"	4.38

*Amorphous carbon.

TABLE IV

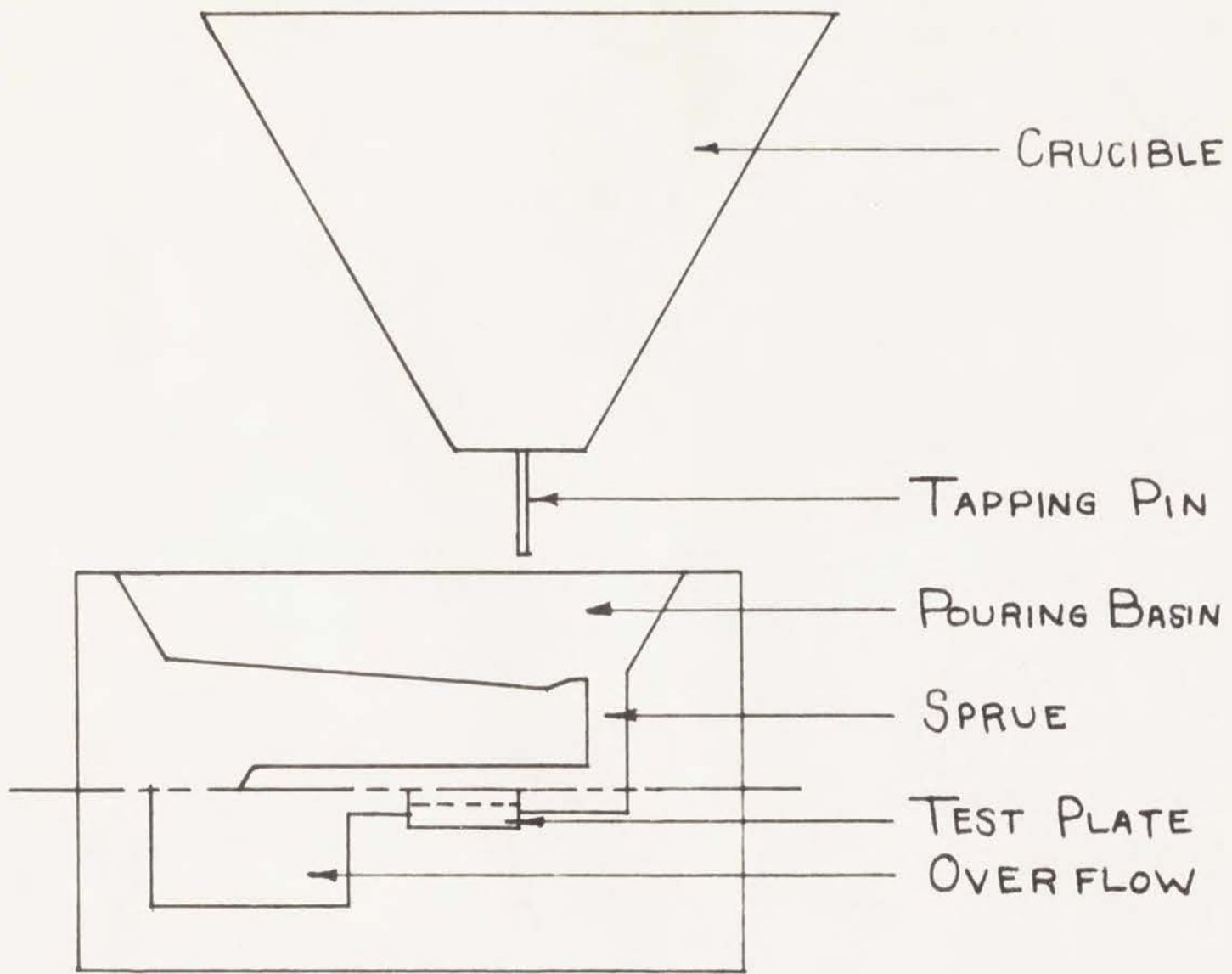
Carbon and Silicon Pick-up by Cast Iron Thermitite

<u>Run No.</u>	<u>Mold Material</u>	<u>%Si Added</u>	<u>Si Analysis(%)</u>	<u>%C Added</u>	<u>C Analysis(%)</u>
C	SiO ₂	0	3.79	0	2.26
E	"	2(FeSi)	5.12	0	1.04
G	"	"	6.10	0	2.04
K	Zircon	3(FeSi)	6.60	0	2.26
J	SiO ₂	"	6.00	0	2.06
L	"	2(FeSi)	6.65	0	1.60

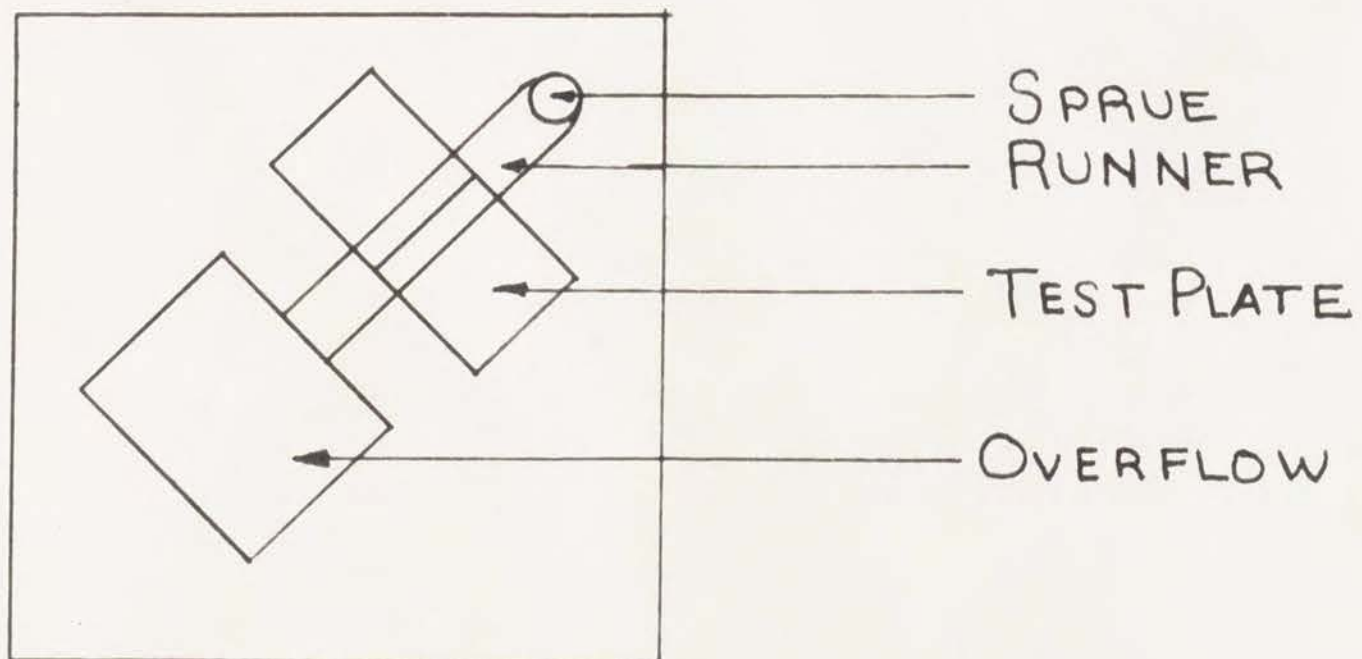
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FIG. 1



b. SCHEMATIC OF MOLD LAYOUT



a. DRAG HALF OF THE MOLD

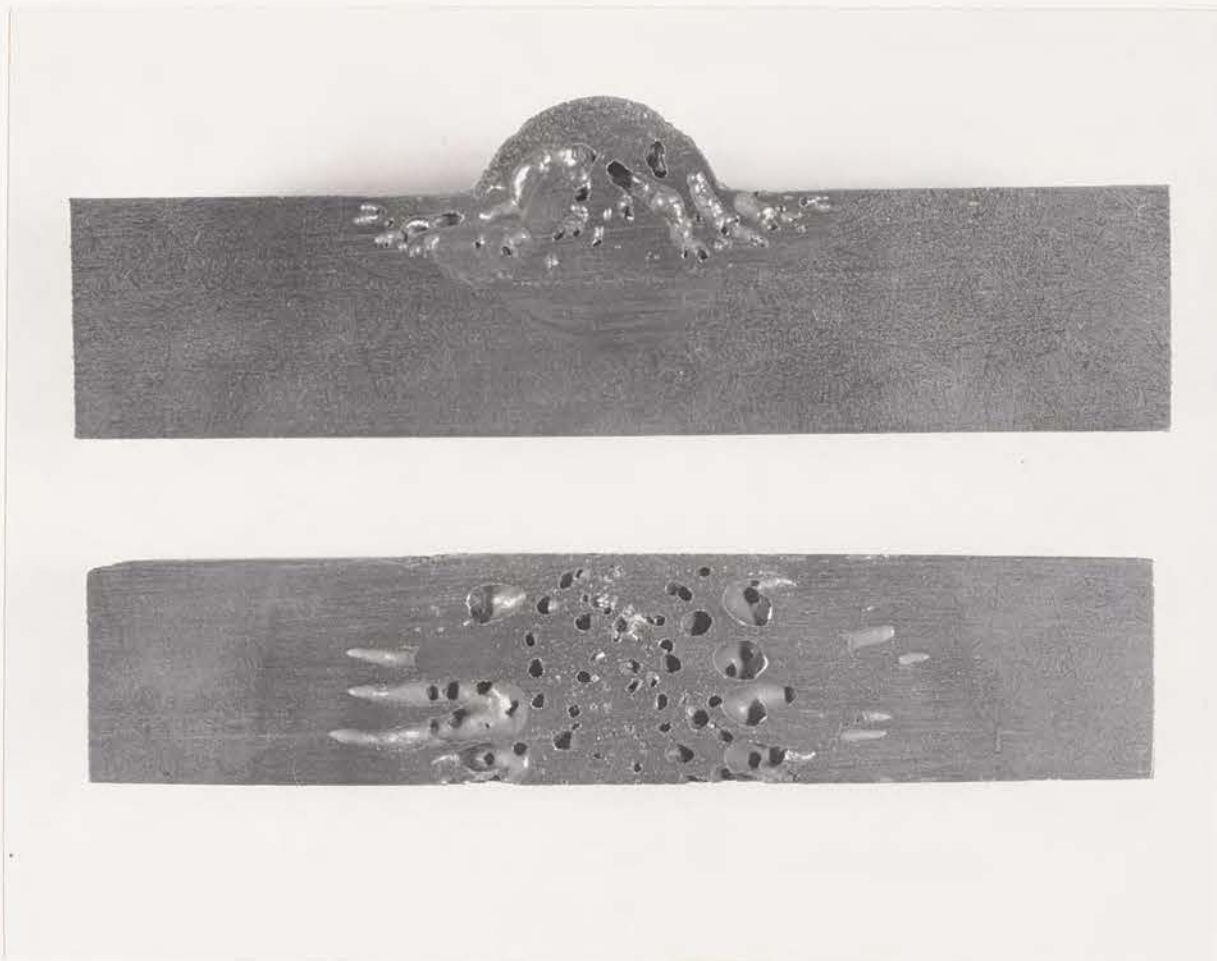


Figure 2: Two tests performed in silica sand molds with cast iron thermite, note extensive porosity in the surface of the specimen.

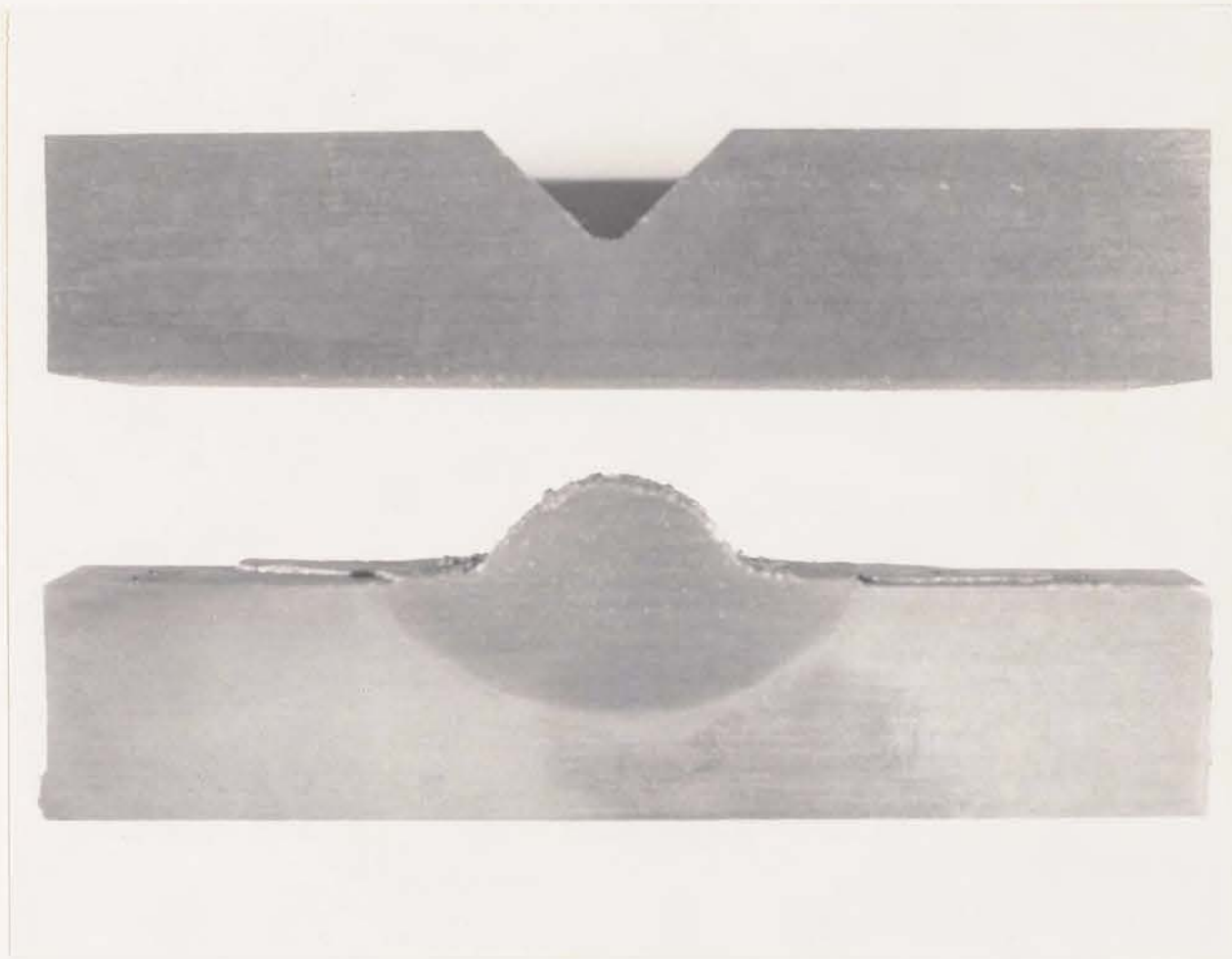


Figure 3: A comparison of a typical fusion zone with the size of the original groove.

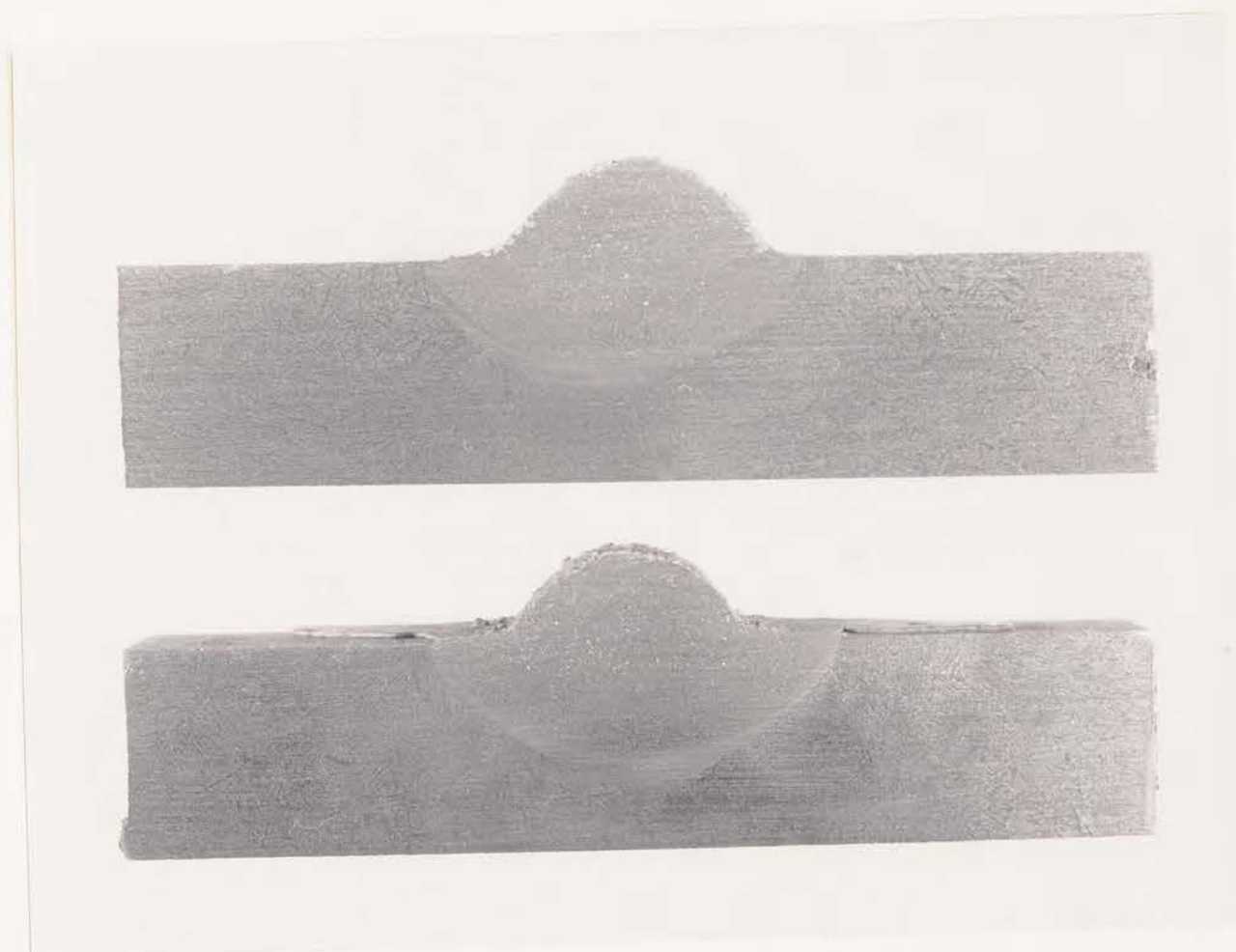


Figure 4: Top specimen was made in a SiO_2 mold, the bottom one in a MgO mold, both molds baked over night.



Figure 5: Heat affected zone of a typical weld plate, unetched, 200X.



Figure 6: Heat affected zone of a typical weld plate, etched with 1 percent Nital, 500X.



Figure 7: Edge of a typical fusion zone, unetched, 200X.

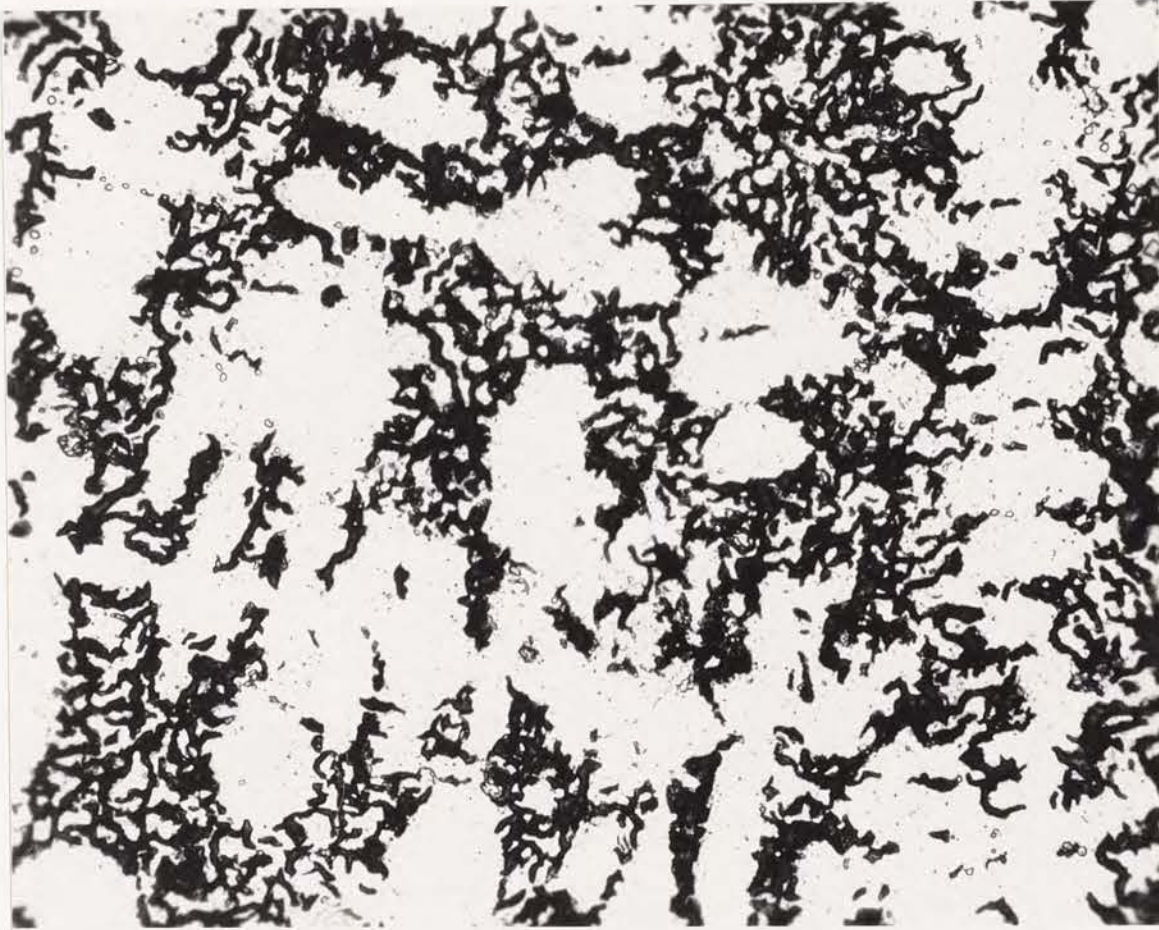


Figure 8: Edge of fusion zone etched with 1 percent Nital, 500X.



Figure 9: Fusion zone of a 1 percent silicon cast iron.
Weld performed in a SiO_2 mold. Unetched 200X.



Figure 10: Fusion zone of a 2.7 percent silicon cast iron. Weld performed in an MgO mold. Unetched 200X.



Figure 11: Fusion zone of 1 percent silicon cast iron.
Etched with 1 percent Nital, 500X.



Figure 12: Fusion zone of a 2.7 percent silicon cast iron.
Etched with 1 percent Nital, 500X.



Figure 13: Fracture surface of a tensile test bar. Note variation in structure. 5X.



Figure 14: Nodular iron produced by the thermite process.
Unetched 200X.