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THE EFFECT OF THE RARE EARTH ELEMENTS ON THE HOT WORKABILITY OF INGOT IRON

BY

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A

THESIS

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I. ABSTRACT

The effect of mischmetal and rare earth oxides on the hot workability of ingot iron in the hot-short region was studied. Thirteen heats were melted in air in a basic-lined induction furnace. All heats were thoroughly deoxidized with aluminum prior to the rare earth additions. Mischmetal was added in amounts of 0.1, 0.3 and 0.5 per cent. Rare earth oxides were added in amounts of 0.1 and 0.2 per cent. Temperatures were maintained at approximately 2900°F and holding intervals between mischmetal additions and pouring at two minutes. Bars were hot rolled and swaged for hot twisting in the hot-short region. Sulfur distribution was studied by sulfur printing and inclusions were studied by metallographic methods.

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III. INTRODUCTION

The improvement of the physical and mechanical properties of metals and alloys has always been of prime importance to the metallurgist. These desired properties have often been instilled in metals by relatively small quantities of alloying elements. The rare earth elements have in recent years come to the forefront as such alloying elements in steelmaking.

The true significance of the rare earths as alloying elements in steelmaking has been realized only since 1950. Among the benefits reported derived from their use in steels are improved hot workability and in a number of instances significant desulfurization. A literature survey revealed no report of the rare earths having been investigated as alloying additions to ingot iron.

Ingot iron is produced in the open hearth much the same as steel. Due to the greater purity reguirements of the iron, however, the temperature must be appreciably higher toward the end of the refining process. The extent of oxidation is therefore much greater than in steel production and the resulting iron is quite high in iron oxide. The oxygen content may run as high as 0.10 per cent. Armco Steel Corporation lists a typical analysis of their ingot iron as:

C	0.015 per cent
Mn	0.028
P	0.005
S	0.025
Si	0.003
Fe	balance

The maximum values of the impurity contents in per cent are: 0.010 P; 0.030 S; 0.15 Cu; and 0.10 total of C, Mn, P, S and Si.

Ingot iron is inherently hot short in the temperature range from 1600 to 1950°F (870-1065°C). Hot shortness is most frequently attributed to impurities of sulfur, oxygen and copper. Aluminum has been reported to contribute to hot shortness. In the absence of sufficient manganese, sulfur contents in excess of 0.010 per cent cause hot shortness. Due to corrosion, electrical and magnetic specifications, ingot iron does not contain sufficient manganese to effectively tie up the sulfur in a harmless form. Susceptibility to corrosion, electrical resistivity, and hysteresis loss all increase with increasing manganese content. High oxygen contents are always present in ingot iron as a result of the method of manufacture. Copper contents in excess of approximately 0.10 per cent lead to a hot-short condition in low carbon steel. Copper contents of iron and steel have been increasing annually due to copper in recycled scrap metal. Copper is not removed in iron and steel refining. Aluminum is used to deoxidize ingot iron in the ladle and small percentages of aluminum are always present in the finished iron.

Under favorable conditions, the rare earth elements are both strong deoxidizers and desulfurizers in steel. Their effect on copper in steel has not been investigated. Rare earth oxides have been reported to oxidize aluminum in aluminum-killed steels.

This investigation was undertaken to study the effects of the rare earths as additives to ingot iron. The rare earths in metallic form and as oxide mixtures were used in the investigation--both separately and in combination. The primary objective of the research has been to study the effects of the rare earths on the hot workability of ingot iron in the hot-short region.

IV. REVIEW OF LITERATURE

Considerable research has been performed, particularly during the last ten years, concerning the use of the rare earth elements as additives in steel with the aim of instilling more desirable properties. The results reported have often been contradictory and inconclusive. In the literature review which follows, quantitative data have been included only when a specific investigation has been concerned with desulfurization and hot workability. The summaries are of necessity brief, and some investigations have been omitted to avoid unnecessary repetition of similar results.

1. Early Research

The early research goes back to the post World War I period. Although the true significance of the rare earths as alloying elements in steel was not realized until 1950, this early work was, nonetheless, of importance in laying the foundation for the later work.

In 1917 Vogel(1) determined the cerium and iron phase diagram. Cerium was reported to be soluble in alpha-iron to a maximum of approximately 12 weight per cent, and in gamma-iron to approximately 15 weight per cent. An eutectic was found to occur at about 4.5 weight per cent iron. The system was studied by metallographic methods.

Allison and Rock(2) in 1920 added "cela" (cerium-lanthanum alloy) in amounts of 0.10 and 0.15 per cent to four heats of a carbon steel. They found no significant change in yield point, tensile strength, elongation and reduction in area. They concluded that the "cela" conferred no evident benefit.

In 1922 Burgess and Woodward (3) at the Bureau of Standards reported the results of an extensive study of ten carbon steel heats to which various amounts of cerium* had been added. They found that with about 0.25 per cent cerium, the tensile properties were increased with an accompanying loss in ductility. With cerium contents of more than 0.30 per cent, a heavy segregation occurred. They mentioned that cerium was thought to be a desulfurizer but presented no data on sulfur contents.

Spring (4) in 1922 reported the results of adding a mixed metal containing 50 per cent cerium, 25 per cent lanthanum, and the balance other rare earths to four heats of converter cast steel. The sulfur contents before and after the cerium alloy additions are tabulated below:

Converter Blow No.	Cerium Alloy Added (Per Cent)	Sulfur before Cerium Alloy Additions (Per Cent)	Sulfur after Cerium Alloy Additions (Per Cent)
1565	0.5	0.086	0.043
1598	1.0	0.088	0.036
1643	1.0	0.081	0.027
1823	1.0	0.084	0.041

In contrast to the findings of Burgess and Woodward, <u>ibid</u>., Spring found that the steel was much cleaner, displayed no ingotism, and was more ductile as a result of the rare earth

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*Mischmetal was often referred to as simply cerium during this period.

additions.

In 1922 Gillett and Mack(5) of the United States Bureau of Mines published the results of an extensive study of the effects of various alloying elements in steel. The investigation was initiated during World War I. Mischmetal additions of a compound containing 10 per cent iron and 90 per cent rare earth elements were made to 12 heats. No deoxidizers were used for these heats. The data for these heats are tabulated below:

Heat Number	Cerium Added (Per Cent)	Cerium Recovered (Per Cent)	Sulfur before Cerium Additions (Per Cent)	Sulfur after Cerium Additions (Per Cent)
1252	1.50	0.45	-----	-----
1253	1.02	0.15	-----	-----
1256	1.00	0.06	0.155	0.067
1257	0.52	0.09	0.085	0.045
1258	1.54	1.00	-----	-----
1259	0.72	0.25	-----	-----
1260	0.02	0.01	-----	-----
1268	0.70	0.20	0.035	0.020
1272	1.01	0.35	-----	-----
1281	0.04	----	-----	-----
1332	0.91	0.38	0.030	0.025
1333	1.05	0.45	0.029	0.015

Considerable segregation occurred in these heats. The segregation was attributed to the rare earth additions.

Due to the somewhat inconsistent sulfur drops, two heats were made with long intervals between the mischmetal additions and pouring. The data for these heats were:

Heat Number	Time from Addition to Pouring (Minutes)	Cerium Added (Per Cent)	Sulfur before Addition (Per Cent)	Sulfur after Addition (Per Cent)
1287	27	1.08	0.135	0.105
1288	26	0.57	0.144	0.129

The rare earth yields for these heats was nil. From these data it was concluded that insufficient reaction time was not the cause of the inconsistent results.

Another group of heats made with mischmetal containing 30 per cent iron and 70 per cent rare earths also produced rather inconsistent results. It was concluded from these data that rare earth additions of less than 0.5 per cent did not result in desulfurization. Reducing conditions were found to aid in desulfurization when other conditions were favorable.

This was the most extensive study made during this period concerning the desulfurization aspects of the rare earth elements in steel. In general, desulfurization was found to take place, but the results were inconsistent.

In 1925 Gillett and Mack (6) published in book form a monograph of molybdenum and cerium steels. As a result of their own investigation and those of others, they concluded that..."cerium appears to have no true alloying effect in steel and to do no good. Since it gives rise to inclusions, it probably does harm. There is a possibility that it might be used as a scavenger to eliminate or control sulfur if means could be found to eliminate the accompanying inclusions".

2. Later Work

During the period from 1925 to 1950 there appears to have been little interest in the use of the rare earths as alloying elements in steel. This was, at least in part, due to the unfavorable report of Gillett and Mack, ibid., page 226.

It was not until 1950 that widespread interest in the rare earths as additives to steel was again revived. Post, Schoffstall, and Beaver (7) in 1951 reported on an extensive study of the effect on hot workability of cerium and lanthanum additions to stainless steel. They found that the rare earth additions improved the hot workability of austenitic stainless steels with nickel contents ranging from four to 70 per cent and 10 to 60 per cent of elements from the group of chromium, molybdenum and tungsten. It was found that the amount of any one element in the latter group must not exceed 30 per cent. The amount of rare earths required to obtain improved hot workability was determined by the nickel content. Cerium and lanthanum additions from 0.02 to 0.04 per cent were effective in promoting better hot workability in high frequency and basic electric arc melted alloys such as types 308, 310, 316 and others. Additions of cerium and lanthanum in the range of 0.08 to 0.18 per cent improved hot workability in nickel-chromium-molybdenum-copper and other high-alloy stainless steels developed for high temperature strength and corrosion resistance.

In 1951 Berry and Dorvell (8) studied the effect of using mischmetal (50-55 per cent Ce, 22-25 per cent La) as a supplementary addition to steel. They reported that the additions eliminated the low ductility and low impact strength of dead-killed steel when only aluminum was used as the deoxidizer. They attributed the improved properties to random distribution of the globular, higher-melting, rare earth sulfide inclusions in contrast to the lower-melting eutectic sulfide inclusions which form intergranular films when aluminum alone is used as the deoxidizer. The mischmetal additions were in the amounts of one to six pounds per ton with aluminum additions up to two and one-half pounds per ton. In one low-alloy steel heat deoxidized with two and one-half pounds of aluminum per ton, sulfur was reduced from 0.031 to 0.018 per cent with a mischmetal addition of four pounds per ton. The mischmetal was found to both desulfurize and randomly distribute the remaining sulfides due to precipitation early in solidification. Comment was made that hot shortness found in some steels may be reduced and in some cases eliminated by rare earth additions.

Knapp and Bolckom[9,10] in 1952 published a summary of the benefits derived from ladle additions of Lan-cer-amp* in stainless steel, tool steel, alloy and electrical steel grades. The additions were made in amounts from three-fourths to six pounds per ton. They claimed superior properties from the use of mischmetal with higher lanthanum contents than ordinary mischmetal. They attributed these superior benefits to be due, at least in part, to the higher boiling point of lanthanum (3275°F, 1802°C) as compared to the boiling point of cerium (2550°F, 1399°C).

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*Trade name of special mischmetals produced by American Metallurgical Products Company.

Among the benefits derived from various additions in cast steels were increased ductility, higher impact values, decreased hot tears, increased fluidity, and higher oxidation resistance. Less grain coarsening in austenitic stainless steels was reported. The additions were successful only in basic electric and open hearth practice.

Under proper conditions, three pounds per ton of Lan-cer-amp were reported to have reduced sulfur contents in basic electric heats from 0.012 per cent to 0.001-0.008 per cent. In basic open hearth heats, two pounds per ton lowered sulfur from 0.027 per cent to 0.012-0.014 per cent.

The authors were of the opinion that desulfurization was not the major function of the Lan-cer-amp additions, but that the desulfurization was indicative that the additions had been made properly and the desired properties instilled. Thought to be of possible greater importance was the effect on nitrogen contents.

In 1952 Lillieqvist and Michelson (11) published the results of an extensive study of the influence of Lan-cer-amp additions on the properties of cast carbon steels. They reported improvement in ductility, impact properties, hot-tear characteristics, weldability, feedability and porosity. Solidification temperature for the treated steel was 2640°F (1449°C) as compared to 2660°F (1460°C) for the untreated steel. Temper brittleness and hardenability were not affected. In production heats in the basic open hearth furnace, sulfur drops on the order of four points were regularly obtained from initial sulfur contents of 0.018 to 0.019 per cent. Production heats with an eight-ton acid electric furnace produced inconsistent sulfur drops. The normal drop was approximately four points although drops as high as seventeen points were obtained. Lan-cer-amp additions in the range of two pounds per ton produced the best results. No sulfur reduction was observed in laboratory experiments in a basic-lined induction furnace, although... "many hundreds of heats"... were made. These Lan-cer-amp treated steels produced in the laboratory, however, were far superior to the untreated steels in physical properties.

Lillieqvist (12) in 1953 reported the results of extensive laboratory research followed by plant scale experiments in production plants at American Steel Foundries. Results revealed that rare earth additions to cast steels improved room temperature ductility properties and impact strength at room temperature and -40°F (-40°C). Both the fluidity and resistance to hot tearing of plain carbon and low alloy steels were markedly increased by small additions. It was found that Lan-cer-amp was about as effective as similar amounts of aluminum in preventing porosity in steel sand castings.

Post and Beaver (13) in 1953 published the results of a study made of the relative effects of mischmetal and rare earth oxide mixtures in stainless steels. They found that the rare earth oxide additions produced effects different from the mischmetal additions. Mischmetal additions to high-alloyed austenitic stainless steels transformed them into ductile alloys. In low-alloyed austenitic stainless steels, the mischmetal produced improved hot workability. On the other hand, the rare earth oxides resulted in improved hot workability of inherently ductile austenitic stainless steels, but produced no improvement in the hot workability of inherently hot-short, high-alloyed, austenitic stainless steels. The rare earth oxide mixtures resulted in little, if any, cerium and lanthanum recovery in contrast to the mischmetal additions which, in general, resulted in cerium and lanthanum recovery.

In 1953 Snellman (14) completed a study of the desulfurization of carbon steels with rare earth elements. A total of 33 induction heats were made. Samples were withdrawn at regular intervals after the mischmetal additions and analyzed for sulfur content. Magnesite lining was used in the furnace and heats were studied under oxidizing, neutral and reducing atmospheres. Mischmetal with an approximate composition of 50 per cent cerium, 30 per cent lanthanum, and the balance other rare earths was used in all but two of the heats. In these two heats, a mischmetal containing approximately 80 per cent lanthanum and 20 per cent cerium was used. In all but one of the heats, the mischmetal was added in the amount of 0.43 per cent. On the remaining heat 0.86 per cent was added. Heats were studied in both the oxidized and deoxidized conditions. Aluminum and silicon were used as deoxidizers. Initial sulfur and carbon contents were varied.

In general, there was a rapid decrease in the sulfur content of the molten metal following the rare earth additions. The minimum sulfur contents occurred within one or two minutes after the rare earth additions. After the minimum sulfur content had been reached, some type of sulfur reversion occurred. Under oxidizing conditions, the sulfur contents of the metal returned to, or just less than, the initial sulfur contents. Under reducing or neutral atmospheres, the sulfur contents after reversion approached values somewhat lower than the initial sulfur contents. High temperature and relatively high minimum sulfur contents resulted in immediate sulfur reversion. Reversion was slowed when the converse was true.

The best result was obtained on a heat made under a nitrogen atmosphere. The mischmetal (50 per cent cerium, 30 per cent lanthanum) addition was in the amount of 0.86 per cent. The temperature was maintained at approximately 1605°C (2920°F). The original sulfur content of 0.40 per cent was reduced to 0.002 per cent--a drop of some 95 per cent.

Sulfur drops ranged up to 90 per cent for the mischmetal additions of 0.43 per cent. Desulfurization took place in both oxidized and deoxidized steels with the desulfurization being more efficient in the deoxidized heats. No significant difference in desulfurization was noted when either aluminum or silicon was used as the deoxidizer. Nor did carbon content appear to have any appreciable influence on sulfur removal. The higher lanthanum mischmetal resulted in no apparent difference in desulfurization.

X-ray diffraction patterns were made of several slag-scum samples. The patterns proved to be very complex and contained many lines. Comparison of samples taken before and after the rare earth additions revealed some 20 additional diffraction lines appearing after the rare earths were added. One of the reaction products was identified as possessing a CeO_2 type structure. An attempt to identify some of the remaining lines as resulting from other rare earth oxides or rare earth sulfides proved inconclusive due to the complexity of the patterns.

In 1954 Russell (15) reported on a study made of the effects of rare earth additions on the surface quality of low carbon steel. He also studied the effects of the rare earths on the mechanical properties of medium-carbon alloy steels. It was found that when surface quality improvement was noted, it appeared to be a result of an increase in low manganese-to-sulfur ratios.

Sulfur drops were noted, in general, for the rare earth metal additions. The additions were various rare earth alloys in amounts up to six pounds per ton. The additions were made in either the ladle or ingot mold. Initial sulfur contents varied from 0.39 to 0.01 per cent. A final sulfur content of 0.006 was reported but the initial sulfur content was not determined. The efficiency of the sulfur removal was found to decrease as the initial sulfur contents were decreased.

Rare earth oxides produced no significant sulfur reductions.

Rare earth metal additions in amounts greater than two pounds per ton were reported to result in a hot-short condition more severe than that due to aluminum alone. Rare earth oxide additions did not have this effect. It was believed that the rare earth oxides reduced the effect of the aluminum by oxidizing it.

Henke and Lula (16) in 1954 reported on a study of the effect of rare earth additives on the hot-rolling characteristics of stainless steel. They reported that the inherent hot shortness of high-alloyed austenitic steels could be counteracted by rare earth additions. Both rare earth metals and oxides were successful. Although not fully understood, the improvements resulting from the rare earth additions appeared to be related to increased ductility at the rolling temperatures. Rare earth additions to martensitic and ferritic steels were considered impractical as these steels roll quite easily without any additions.

In 1954 Tisdale (17) was awarded a patent for fine-grained iron and steel. The patent describes a..."method for the production of iron and steel which comprises preparing an iron containing melt, adding metallics thereto during furnacing, deoxidizing, incorporating a composition containing a rare earth metal, in an amount not more than three pounds per ton, pouring and quick freezing".

Jepson and Duwez (18) in 1955 established conclusively that the solubility limit of cerium in alpha- and gamma-iron in the temperature range 815-1015°C (1499-1859°F) lies close to 0.4 weight per cent. This finding was in contrast to the 12-15 weight per cent reported by Vogel, <u>op</u>. <u>cit</u>., in 1917.

In 1956 Jackson (19) presented a summary of the work which had been performed to date concerning the use of the rare earths in cast steels. He commented on the definite lack of research dealing specifically with the rare earths in cast steels. With the limited data available, he concluded that mischmetal additions in cast steels improve ductility and impact properties but do not prevent temper brittleness in a susceptible steel. He also concluded that mischmetal additions reduce the susceptibility to hot tearing, improve fluidity, do not affect hardenability or weldability, and can be made most satisfactorily to the ladle in quantities ranging from two to four pounds per ton of steel.

He commented on the fact that the precise mechanism by which the rare earths instill the reported improvements in steels was not known; the improvements were most probably due to a number of factors operating simultaneously.

Tisdale (20) in 1956 obtained a Canadian patent on the composition of rare earth oxides for the production of iron and steel. The additive was formed by..."mixing a lanthanon oxide with 0.02-1.0 parts of a reductant such as a boride, borane or silicide of Group IIa metals, manganese, chromium, iron, boron, cobalt or nickel".

In 1958 Wilson (21) reported on the work of two Russian metallurgists, Tageev and Smirnov (22). They had reported that two to four pounds of mischmetal per ton fully eliminated "A"-segregation in steels containing 0.36-0.42 per cent carbon and 1.10 per cent nickel.

In verifying these results and attempting to explain them, Wilson, *ibid.*, reported on an investigation in which 5-50 per cent rare earths were mixed with FeS and the mixture heated to the melting point. It was found that the melting point of FeS was raised from 30° to 270°F (17° to 150°C). FeS melts at approximately 2180°F (1193°C). He concluded that the rare earths minimize or eliminate sulfide segregation by raising the melting point of FeS and enabling earlier solidification of the resultant sulfides.

Perkins and Binder (23) in 1959 studied the non-metallic inclusions produced by deoxidation of steels with silicon, aluminum, titanium and rare earths. They found that the tensile ductility of ingot steel at 2400°F (1316°C) was significantly improved after deoxidation with mischmetal.

In 1959 Singleton (24) reported on a study of the effects of adding pure cerium metal to SAE 1035 steel. The heats were induction melted in magnesia crucibles. Heats were made under both vacuum and air, and studied in both the oxidized and deoxidized conditions. Aluminum was used as the deoxidizer in the deoxidized heats. Aluminum contents of the deoxidized ingots were on the order of 0.10 per cent. The pure cerium metal was added in amounts ranging from 0.05 to 0.25 per cent.

The oxygen contents of the steel decreased with increasing quantities of cerium additions. Cerium oxide inclusions, however, were conspicuously absent in the steel. It was concluded that the cerium oxide which formed--which was not identified as to type--rose to the slag phase with very little remaining in the metal.

Regular sulfur drops were noted. The magnitudes of the sulfur removals increased with increasing cerium additions. A new type of inclusion was found to be definitely associated with the presence of cerium. These inclusions were quite small, complex gray and black in color, and were not found in clusters. Under polarized light with crossed nicols, the inclusions appeared as bright red to orange. The red portions were completely removed after etching with hydrochloric acid, indicating that these inclusions were not oxides. Further tests indicated that the inclusions were not nitrides or silicates. Cerium analyses on electrolytically extracted inclusion residues, both before and after extraction with hydrochloric acid, showed that the cerium species was completely soluble in the acid. As Ce_2S_3 can exist as an orange or red crystal and is soluble in hydrochloric acid, the new-type inclusions were identified as Ce_2S_3.

Cerium appeared to have no effect on nitrogen content. A strong reaction between the cerium and the magnesia crucibles was noted. Rough analyses on several of the crucibles ..."indicated a large loss of cerium into the crucible in amount equal to a good fraction of the cerium added".

This is the gist of the work on the rare earths in steel. Further references are listed in the articles cited.

V. THE RARE EARTH ELEMENTS

1. Electron Configuration

There are two rare earth series as positioned in the periodic table. The Lanthanide Series consists of the elements of lanthanum through lutetium--atomic numbers 57 through 71--and appears in Group 3a of Period 6. The Actinide Series is composed of the elements of thorium through californium--atomic numbers 90 through 98--and falls under Group 3a of Period 7.

These rare earth series are grouped together in the periodic table due to electron configuration. In each of these series, the third outermost electron shell undergoes transition. In the Lanthanide Series the 4f levels of the N shell are filled in the transition. In the Actinide Series the 5f orbitals of the O shell are filled. A transition series usually involves the filling of the second outermost electron shell. As chemical behavior is determined almost exclusively by the action of the two outermost electron shells, it follows that the rare earth elements behave very nearly the same chemically and as a consequence are very difficult to separate. In this investigation, we are concerned with the elements of the Lanthanide Series.

2. Occurrence, Extraction, and Separation

The name rare earth is a "misnomer"(9). These elements are neither rare nor are they earths. They are metals just as iron is a metal. They are not rare if this denotes a lack of abundance. When considered as a group, they are more abundant than zinc, lead, tin or molybdenum. A comparison of the relative abundance as a percentage of the earth's crust is as follows (9):

Rare Earth Elements	0.005 per cent
Zinc	0.004
Lead	0.002
Tin	0.001
Molybdenum	0.001

The principal source of the rare earths is the mineral monozite, found as an alluvial sand in Brazil, India, and domestically in the Carolinas, Florida and Idaho. The mineral is essentially a complex phosphate, containing up to 70 per cent cerium with other rare earths and four to nine per cent thoria. Bastnaesite, a hydrated fluocarbonate, is found in Colorado and California. Other mineral sources are allanite, cerite, gadolinite, samarskite and xenotime.

The first relatively clean separation was performed by Berzelius in Sweden in 1903 when he isolated cerium. The last rare earth element reported to be separated was promethium--then called illinium--which was reported to have been isolated by a group of American researchers in 1926. There is some question, however, as to whether promethium occurs in nature and whether it has ever been separated from a natural mixture. Twelve isotopes of promethium have been identified as products of nuclear reactions.

Separations of high purity were virtually unknown until the 1940's. Then great interest in the properties of the rare earths developed rapidly when it was discovered that the rare earth elements form a large percentage of the ashes of nuclear fission.

Until the late 1940's, the separation of the rare earths from one another had depended on fractional crystallization. This tedious method was then improved upon by the introduction of separations depending upon the oxidation or reduction of some of the elements to other than the tripositive state. Solvent extraction and ion-exchange methods of separation also appeared in the late 1940's. The ion-exchange method is applicable on the tracer scale up to 100-gram lots with impurity contents on the order of less than one part per million.

On the basis of separation, the rare earths are divided into three groups: the cerium group, the terbium group, and the yttrium group. The cerium group includes Ce, La, Pr, Nd and Sm. The terbium group consists of Eu, Gd, Tb and Dy, and the yttrium group of Ho, Er, Tm, Yb, Lu and Y. The groups are so named because of the preponderance of cerium, terbium, and yttrium in the mixtures of the rare earth elements obtained from the minerals in preliminary separation processes. Although not a rare earth, yttrium--atomic number 39--is classed with the rare earths because of its general occurrence with the rare earths and its similarity to them. Mischmetal and the commercial rare earth oxide mixtures consist essentially of the elements of the cerium group.

3. Physical and Chemical Properties

Some of the more important physical properties of the rare earth elements are listed in Table I. The structures,

TABLE I

PHYSICAL PROPERTIES OF THE RARE EARTH ELEMENTS(9)

Element	Symbol	Atomic Number	Atomic Weight	Melting Point (°F)	Boiling Point (°F)	Density (70°F) gm/cc
Lanthanum	La	57	138.92	1580	3275	α-6.194 β-6.180
Cerium	Ce	58	140.13	1420-1470	2550	α-6.78 β-6.810
Praseodymium	Pr	59	140.92	1725-1760	----	α-6.810
Neodymium	Nd	60	144.27	1475-1650	----	α-7.004
Promethium	Pm	61	146 (?)	-----	----	-----
Samarium	Sm	62	150.43	2460	----	6.93
Europium	Eu	63	152.0	2000-2200	----	5.244
Gadolinium	Gd	64	156.9	-----	----	7.948
Terbium	Tb	65	159.2	-----	----	8.332
Dysprosium	Dy	66	162.46	-----	----	8.562
Holmium	Ho	67	164.94	-----	----	8.764
Erbium	Er	68	167.2	2280 (?)	----	9.164
Thulium	Tm	69	169.4	-----	----	9.346
Ytterbium	Yb	70	173.04	3275 (?)	----	7.010
Lutetium	Lu	71	174.99	-----	----	9.740

lattice parameters, and atomic radii are given in Table II. The crystal structures and densities were determined by reducing chlorides of the purified rare earth metals with potassium and making x-ray powder photographs of the resulting mixtures. The known spectra of potassium chloride served as the calibration. The atomic radii, with the exception of europium, ytterbium and samarium show a decrease with increasing atomic number when the elements are in metallic form. This is the "lanthanide contraction" resulting from the increasing nuclear charge. In metallic form, all of the rare earth elements except europium, ytterbium and samarium possess atomic radii characteristic of tri-positive cations. Europium, ytterbium and to some extent samarium approach the radii expected of bivalent metals. In compound forming tendencies, the normal oxidation state is the tri-positive state. In addition to europium, ytterbium and samarium, however, oxidation states of +2 have been reported for lanthanum, cerium, praseodymium, neodymium, gadolinium and thulium. Oxidation states of +4 have been reported for cerium, praseodymium, neodymium and terbium. Praseodymium alone exhibits an oxidation state of +5.

All of the rare earth metals possess an unusually strong chemical affinity for the non-metallic elements normally associated with steel: sulfur, oxygen, hydrogen, nitrogen and carbon. They also alloy readily with most common metals, in many cases forming significantly refractory intermetallic compounds with the parent metal. With the many

TABLE II

CRYSTAL STRUCTURES AND ATOMIC RADII OF THE RARE EARTHS (25)

Element	Crystal Structure*	Lattice Parameters a	Lattice Parameters c	Atomic Radius
α-La	h.c.p.	3.754A°	6.063A°	1.870A°
β-La	f.c.c.	5.294		1.872
α-Ce	h.c.p.	3.65	5.96	1.81
β-Ce	f.c.c.	5.140		1.817
α-Pr	h.c.p.	3.662	5.908	1.824
α-Pr	f.c.c.	5.151		1.821
-Nd	h.c.p.	3.650	5.890	1.818
Sm				
Eu	b.c.c.	4.573		2.042
Gd	h.c.p.	3.622	5.748	1.794
Tb	h.c.p.	3.585	5.664	1.773
Dy	h.c.p.	3.578	5.648	1.769
Ho	h.c.p.	3.557	5.620	1.759
Er	h.c.p.	3.532	5.589	1.748
Tm	h.c.p.	3.523	5.564	1.742
Yb	f.c.c.	5.468		1.933
Lu	h.c.p.	3.509	5.559	1.737

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* h.c.p. is hexagonal closest packing; f.c.c. is face-centered-cubic; b.c.c. is body-centered-cubic

possibilities for reaction with the various constituents in steel, it is not surprising that a detailed explanation of the behavior of the rare earth elements in steel has not been forthcoming.

Table III lists the properties of the rare earth oxides and Table IV the properties of the rare earth sulfides. The properties are compared with the properties of some common oxides and sulfides encountered in steelmaking. The values of the standard heats of formation given are for 25°C and one atmosphere. Lack of data prohibits the calculation of free energy of formation values at the temperature of molten iron. The values given do give an indication of what might be expected to be the relative deoxidizing and desulfurizing powers of the rare earth elements as compared to the other elements listed.

From these data, it would be expected that the rare earths have a very strong tendency to form oxides and sulfides in molten iron. The oxides would be expected to form more readily than the sulfides necessitating deoxidation of the bath prior to the rare earth additions if desulfurization is to be anticipated. Both the rare earth oxides and sulfides have densities less than iron. The normal reaction products of the rare earth elements with sulfur are the sesquisulfides (RE_2S_3), and there is evidence that these are the principal sulfides formed by the rare earths in molten steel. All of the rare earth elements form oxides of the type RE_2O_3. However, the only rare earth oxide tentatively identified as resulting from mischmetal additions to steel

TABLE III

PROPERTIES OF THE RARE EARTH OXIDES (26)

Compound	Density gm/cc	Heat of Formation, ΔH_f^o Gram Calories per Mole (25°C, 1 atm.)	Melting Point °C	Boiling Point °C
La_2O_3	6.51	-458,000	2315	4200
Ce_2O_3	6.9-7.0	-456,000	1692	----
CeO_2	7.3	-233,000	2600	----
Nd_2O_3	7.24	-442,000	----	----
Pr_2O_3	6.88	-444,500	d.*	
Sm_2O_3	7.43	------	----	----
Eu_2O_3	6.55-7.42	------	----	----
Gd_2O_3	7.41	------	----	----
Tb_2O_3	----	------	----	----
Dy_2O_3	7.81	------	----	----
Er_2O_3	8.64	------	----	----
Tm_2O_3	----	------	----	----
Fe_3O_4	5.18	-267,000	1538d.	
FeO	5.7	-63,700	1420	----
MnO	5.43-5.46	-92,000	1650	----
Al_2O_3	3.5-3.9	-389,000	2050	3500
MgO	3.58	-143,840	2800	----
Fe	7.86		1535	3000

---

* d. indicates decomposition upon melting

TABLE IV

PROPERTIES OF THE RARE EARTH SULFIDES (26)

Compound	Density gm/cc	Heat of Formation, ΔH_f^o Gram Calories per Mole (25°C, 1 atm.)	Melting Point °C	Boiling Point °C
La_2S_3	4.91-5.00	-306,800	2100-2150	-----
Ce_2S_3	5.02	-298,700	1925d.	
CeS_2	----	-153,900	-----	-----
Pr_2S_3	5.04	------	d.*	
Nd_2S_3	5.18	-281,800	2200d.	
Sm_2S_3	5.73	------	1900	-----
Gd_2S_3	3.8	------	-----	-----
Fe_3S_4	4.55	------	-----	-----
Fe_2S_3	4.3	------	d.	
FeS	4.84	-22,720	1193	d.
MnS	3.99	-47,600	d.	
Al_2S_3	2.02	-121,600	1100	1550 subl.#
MgS	2.79-2.85	83,000	d.	

---

* d. indicates decomposition upon melting or boiling

\# subl. is sublimation

is CeO_2. Snellman, op. cit., observed a CeO_2 type structure in the x-ray diffraction patterns made from slag-scum samples. The sesquioxides are also thought to be a major reaction product resulting from mischmetal additions to steel. Lanthanum does not exhibit the $+4$ oxidation state.

In the absence of excessive oxygen in molten steel, the rare earth elements are believed to form sulfides with melting points above the melting point of iron, and being of lesser densities than iron, these sulfides float to the slag phase where they are removed. Being refractory, the remaining sulfides occur as spheroidal, well dispersed particles which do not elongate during hot rolling as do the sulfide inclusions in untreated steels. Snellman, op. cit., found that under oxidizing conditions, the rare earths are oxidized after a period of time with the sulfur reverting to the metal phase.

The detrimental effect of extremely small percentages of hydrogen in steel is a well established fact. The rare earths have a strong affinity for hydrogen. The reaction between the rare earths and hydrogen is exothermic while the reaction between iron and hydrogen is endothermic. Regardless of the temperature, the rare earths are capable of dissolving tremendously greater quantities of hydrogen than can iron. The solubility of hydrogen in mischmetal has been reported (9) to be 2000 times greater than that of iron at 2000°F (1093°C) and over 60,000 times as great at 750°F (390°C). The melting points of the rare earth-hydrogen alloys are well above those of the corresponding pure metals (9).

The rare earths are strong carbide formers. The carbides are hexagonal crystals of the general form REC_2. The rare earth carbides can be prepared quite readily by reduction of rare earth oxides with carbon but thermodynamic data are lacking. In plain carbon steels to which rare earth metals had been added, however, varying carbon contents apparently had no significant effect on desulfurization (14).

The rare earths have a strong affinity for nitrogen at high temperatures. The reaction between ammonia and the rare earths produce rare earth nitrides of the type REN by direct union with the metal at temperatures in the vicinity of 980°C. There is little data available on the properties of the rare earth nitrides. It is believed (9) that nitrogen control may be a major factor in the improved properties attributed to the use of the rare earths in steel.

The atomic volumes of some of the rare earths are compared with some other metals in Table V. The large volumes of the rare earth atoms as compared to the volumes of the iron atom is considered (10) to be the reason for the improved oxidation resistance which results when rare earths are added to steel. The atomic volumes of the rare earth elements are greater than the volume of the iron oxide molecule with the result that the rate of diffusion is restricted.

TABLE V

ATOMIC VOLUMES[10]

Element	Volume cc/gm atom
Be	4.96
Fe	7.10
Cu	7.11
Mn	7.4
Mo	9.4
W	9.53
Al	9.99
Au	10.22
Ti	10.6
Si	11.7
Zr	14.32
Sm	19.4
Ce	20.3
Pr	20.5
Nd	20.5
La	22.6
Ca	25.86

4. Applications

Since the late 1940's, the rare earths have been utilized in the production of nodular cast iron. The rare earth elements serve to deoxidize, desulfurize, and act as graphitizers. The rare earths have found wide use in the magnesium and aluminum industries as alloying elements. Other applications vary from the use of rare earth fluorides in cores of arc carbons to the use of mischmetal alloys in cigarette lighter flints.

The most common form in which the rare earths are furnished for metallurgical use is the alloy called mischmetal. The approximate composition of ordinary mischmetal as extracted from the ore is:

Ce	50-55 per cent
La	20-30
Nd	15-17
Other Rare Earths	8-10

The rare earths in mischmetal are primarily from the cerium group. There are several varieties of mischmetal commercially available. The Lan-cer-amp No. 2 used in this study is composed of 30 per cent lanthanum minimum, 45 to 50 per cent cerium, five per cent iron, and the balance other rare earths. The manufacturer claims greater benefits are derived from the use of this alloy as an additive to steel than from the use of ordinary mischmetal. The higher lanthanum content is said to be one factor. Lanthanum melts and boils at higher temperatures than cerium. Lanthanum sesquioxide and sesquisulfide are stable at higher temperatures than the corresponding sesquioxide and sesquisulfide of cerium. It should be noted, however, that CeO_2 melts at a temperature (2600°C) considerably higher than the sesquioxides of either cerium (1692°C) or lanthanum (2315°C). The five per cent iron is added to lower the melting point from 1490°F (810°C) to about 1200°F (650°C).

There are other alloys containing mischmetal available--each developed for a specific application. Lan-cer-amp No. 23 contains 25 per cent mischmetal and 10 per cent zirconium with the balance being low carbon iron. In this study, only ordinary mischmetal and Lan-cer-amp No. 2 were used for the rare earth metal additions.

The rare earths also are available in a number of salts. Of these, the rare earth oxides and fluorides have found application in steelmaking. These salts contain approximately the same proportions of the rare earth elements as ordinary mischmetal. The rare earth oxides do not act as desulfurizers but have been reported by several investigators (7)(13)(16) to increase markedly the hot workability of some stainless steels. Russell, _op_. _cit_., reported that rare earth oxide additions to aluminum-killed plain carbon steel reduced hot shortness attributed to residual aluminum contents. He postulated that the rare earths oxidized the aluminum. A detailed investigation into the mechanism of the rare earth oxide reactions in molten steel has not, as yet, been forthcoming. Rare earth fluoride mixtures have been reported (13) to improve ingot surface quality and malleability of austenitic titanium steels.

VI. HOT SHORTNESS

Hot shortness, sometimes called red shortness, is the tendency of certain metals to exhibit brittleness when worked above a red heat. Sulfur and oxygen are known to be major contributors to hot shortness. The role of copper in hot shortness has, through the years, been the subject of much discussion. Aluminum has been reported to be a cause of hot shortness in aluminum-killed steel.

1. Effect of Sulfur

Sulfur has been known for many years to cause hot shortness in iron and steel. One theory of the mechanism of hot shortness as caused by sulfur was first postulated by Wohrman (27). He attributed hot shortness to the passing of the iron or steel through the A_3 transformation. He was of the opinion that sulfur was soluble in gamma-iron at the A_3 transformation to an extent sufficient to cause embrittling of the gamma-iron. He based his theory in part on the discovery of Sauveur and Lee (28) of the phenomenon of "critical plasticity" at the A_3 transformation. Sauveur and Lee had found that when a bar of iron or low carbon steel is heated at the center of its length to a temperature exceeding the A_3 transformation temperature and then twisted, the twisting occurs not at the center where the bar is hottest, but rather at two points equidistant from the center where the bar is undergoing the A_3 transformation. Wohrman believed that hot shortness disappeared at higher temperatures because of the greater plasticity of the gamma-iron at higher temperatures. This theory, however, has not gained wide acceptance.

Today, the accepted theory is, that in the absence of sufficient manganese, iron sulfide precipitates upon solidification as thin films in the primary grain boundaries. The predominant sulfide is thought to be FeS. FeS forms an eutectic with iron. The Fe-S equilibrium diagram is given in Figure 1. The melting point at the eutectic composition of 44 atomic per cent sulfur is given as 988°C. Pure FeS melts at approximately 1190°C. Upon solidification, this low-melting eutectic is precipitated at the primary grain boundaries. These films become liquid at hot-working temperatures and the metal cracks at the grain boundaries when worked in the hot-short region. Hot shortness occurs only in a temperature range and disappears at higher temperatures. This upper limit of hot shortness is thought to be the result of the molten sulfide being dissolved by the gamma-iron which then regains its continuity and plasticity.

Manganese is an essential ingredient in steel because of its very strong affinity for sulfur. Manganese and sulfur combine to form MnS which has a much higher melting point than the Fe-FeS eutectic. MnS forms as separate, dispersed globules which remain solid at rolling temperatures. Low carbon steels contain a minimum of 0.25 per cent manganese for maximum sulfur contents of 0.050 per cent. Cain (30) reported that in the absence of manganese, hot shortness will be present if the sulfur content exceeds 0.010 per cent.

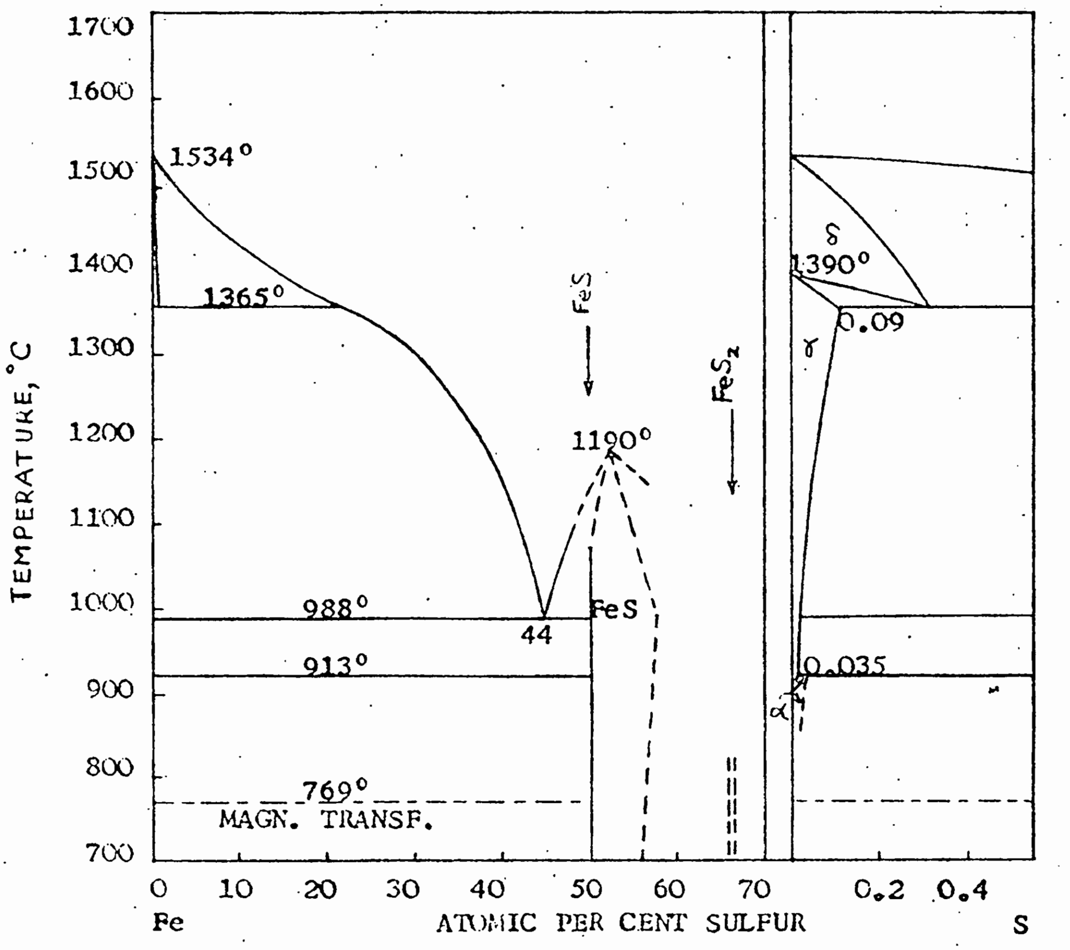

Figure 1. The Fe-S system (29).

2. Effect of Oxygen

A more detailed treatment of hot shortness takes into consideration the role of oxygen. Hilty and Crafts (31) stated that..."all oxide and sulfide inclusions in steel, excluding mechanically entrapped matter, result from modifications of the basic Fe-S-O system". The FeS-FeO system is given in Figure 2. There is an eutectic between FeS and FeO at approximately 55 molecular per cent FeS with the eutectic temperature being at 940°C. In the presence of appreciable quantities of sulfur and oxygen, and in the absence of sufficient manganese to tie up the sulfur, it would be expected that the FeS-FeO eutectic would have a strong tendency to precipitate at the primary grain boundaries and lead to a hot-short condition. In reality, the compound FeO does not exist as such. What was once thought to be the compound FeO is now known to be the phase wüstite. The equilibrium diagram of the Fe-O system is given in Figure 3. The wüstite phase decomposes eutectoidally into alpha-iron and Fe_3O_4. The melting range of wüstite is 1371-1424°C. What are commonly referred to as FeO inclusions in iron and steel are really wüstite and appear as gray-to-black particles in the matrix. Cain, op. cit., found that oxygen contents up to 0.20 per cent do not cause hot shortness in high-purity iron if the sulfur content is below 0.010 per cent.

3. Effect of Copper

Through the years, copper was reported by some investigators to cause hot shortness and by others to reduce it.

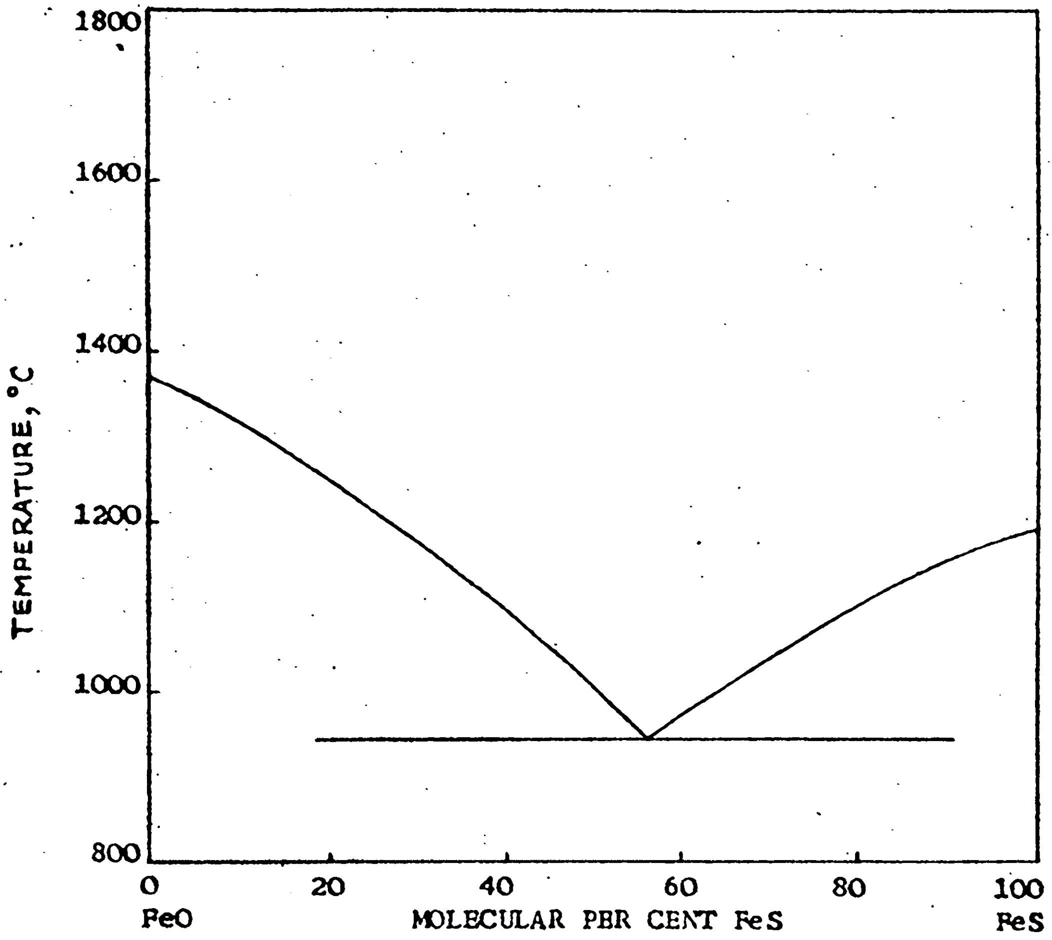

Figure 2. The FeO-FeS system(32).

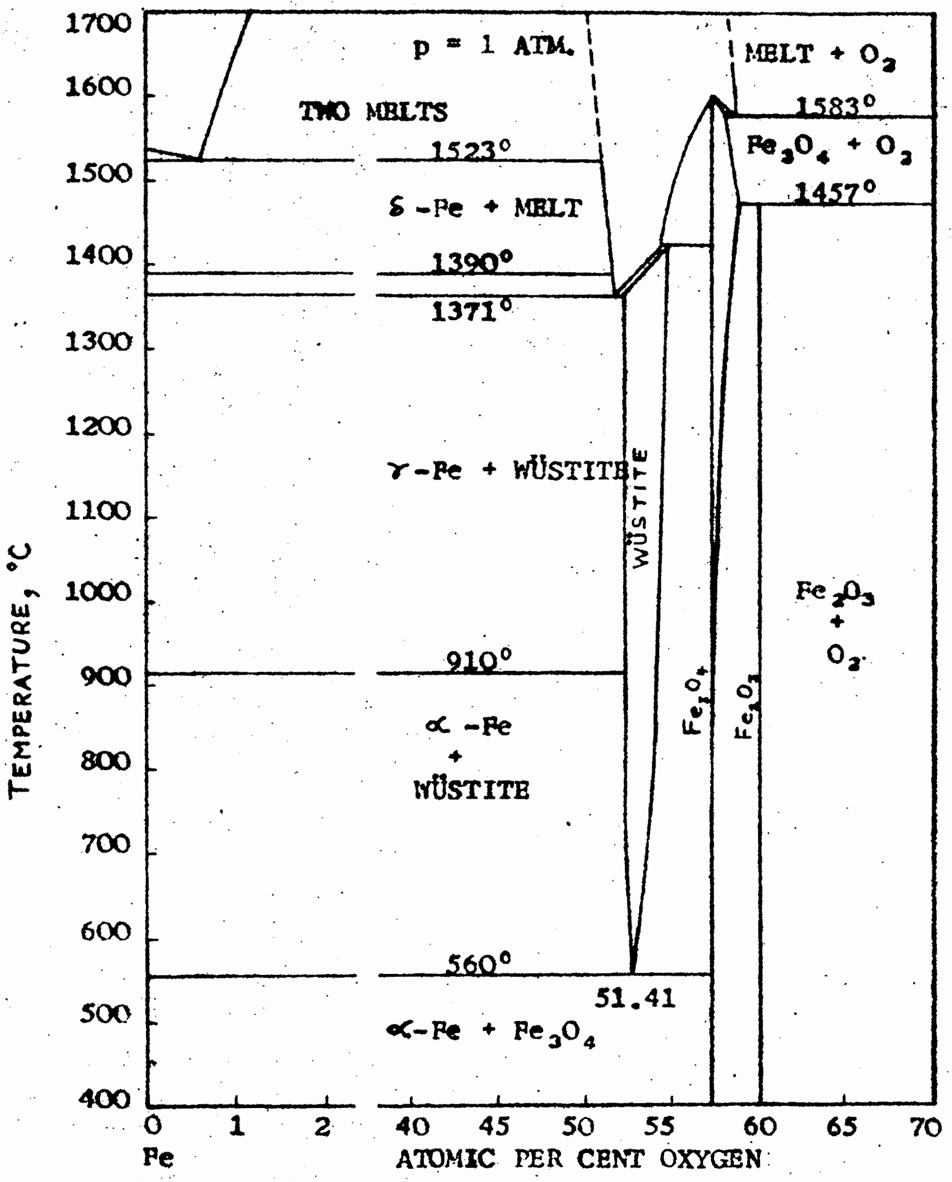

Figure 3. The Fe-O system(29).

Cain, ibid., found that copper contents ranging from 0.05 to 0.5 per cent were of minor importance in affecting hot-shortness in high-purity iron; in a few instances, high copper contents tended to reduce hot shortness. Cornelius (33) in 1940 published, in a book on the effect of copper in iron and steel, the results of an investigation by F. Nehl. In the investigation, Nehl subjected a series of low carbon steels with varying copper contents to a hot-bend test at 1050°C. He showed that copper leads to a hot-short condition when present in amounts in excess of approximately 0.08 per cent. It is to be noted that there was sufficient manganese in each steel to eliminate the effects of sulfur on hot shortness. The Fe-Cu phase diagram is shown in Figure 4.

4. Effect of Aluminum

Aluminum has been reported to be a cause of hot shortness. Russell, op. cit., reported that hot shortness in low and medium carbon steels increased with increasing residual aluminum contents in aluminum-killed heats. Aluminum is extensively soluble in iron (Figure 5). The alpha solid solution extends to approximately 22 atomic per cent aluminum at room temperature. No eutectic occurs on the iron side of the diagram. It is one of the objectives of this research to study the effect of residual aluminum contents on hot shortness in ingot iron.

TABLE VI

THE INFLUENCE OF COPPER CONTENT ON THE CRACKING OF STEELS SUBJECTED TO THE BEND-TEST AT 1050°C(33)

Steel	Per Cent Carbon	Per Cent Manganese	Per Cent Sulfur	Per Cent Copper	Bend-Test*
1	0.12	0.64	0.022	0.02	-
2	0.13	0.66	0.016	0.03	-
3	0.11	0.33	0.037	0.04	-
4	0.11	0.32	0.026	0.04	-
5	0.12	0.35	0.030	0.04	-
6	0.05	0.32	0.035	0.04	-
7	0.10	0.33	0.031	0.04	-
8	0.16	0.41	0.102	0.04	-
9	0.04	0.30	0.037	0.04	-
10	0.13	0.35	0.026	0.05	-
11	0.07	0.34	0.020	0.05	-
12	0.16	0.38	0.024	0.05	-
13	0.05	0.32	0.035	0.05	-
14	0.08	0.35	0.060	0.05	-
15	0.06	0.32	0.038	0.06	-
16	0.09	0.33	0.021	0.06	-
17	0.10	0.39	0.031	0.07	-
18	0.18	0.70	0.032	0.08	-
19	0.07	0.62	0.026	0.08	-
20	0.06	0.32	0.025	0.08	-
21	0.09	0.34	0.030	0.08	•
22	0.04	0.31	0.025	0.08	•
23	0.05	0.26	0.026	0.08	-
24	0.04	0.26	0.023	0.08	-
25	0.07	0.32	0.040	0.09	-
26	0.07	0.27	0.019	0.09	•
27	0.11	0.61	0.020	0.10	•
28	0.06	0.35	0.021	0.11	•
29	0.06	0.23	0.032	0.13	•
30	0.18	0.51	0.021	0.15	≠

(continued on next page)

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* - no cracks; • cracks visible with magnifying glass; ≠ cracks visible with naked eye; ≠ ≠ strong crack formation; ≠ ≠ ≠ very strong crack formation

TABLE VI (con't.)

Steel	Per Cent Carbon	Per Cent Manganese	Per Cent Sulfur	Per Cent Copper	Bend-Test
31	0.05	0.30	0.022	0.15	+ +
32	0.24	0.78	0.020	0.15	+
33	0.32	0.82	0.016	0.16	+ + +
34	0.11	0.52	0.043	0.16	+ +
35	0.12	0.46	0.025	0.17	+ +
36	0.09	0.55	0.032	0.19	+ +
37	0.18	0.78	0.029	0.19	+ +
38	0.18	0.66	0.037	0.21	+ +
39	0.21	1.09	0.035	0.23	+ +
40	0.07	0.41	0.032	0.24	+
41	0.05	0.38	0.025	0.25	∘
42	0.09	0.46	0.039	0.25	∘
43	0.09	0.52	-----	0.30	+ +
44	0.24	0.89	-----	0.50	+

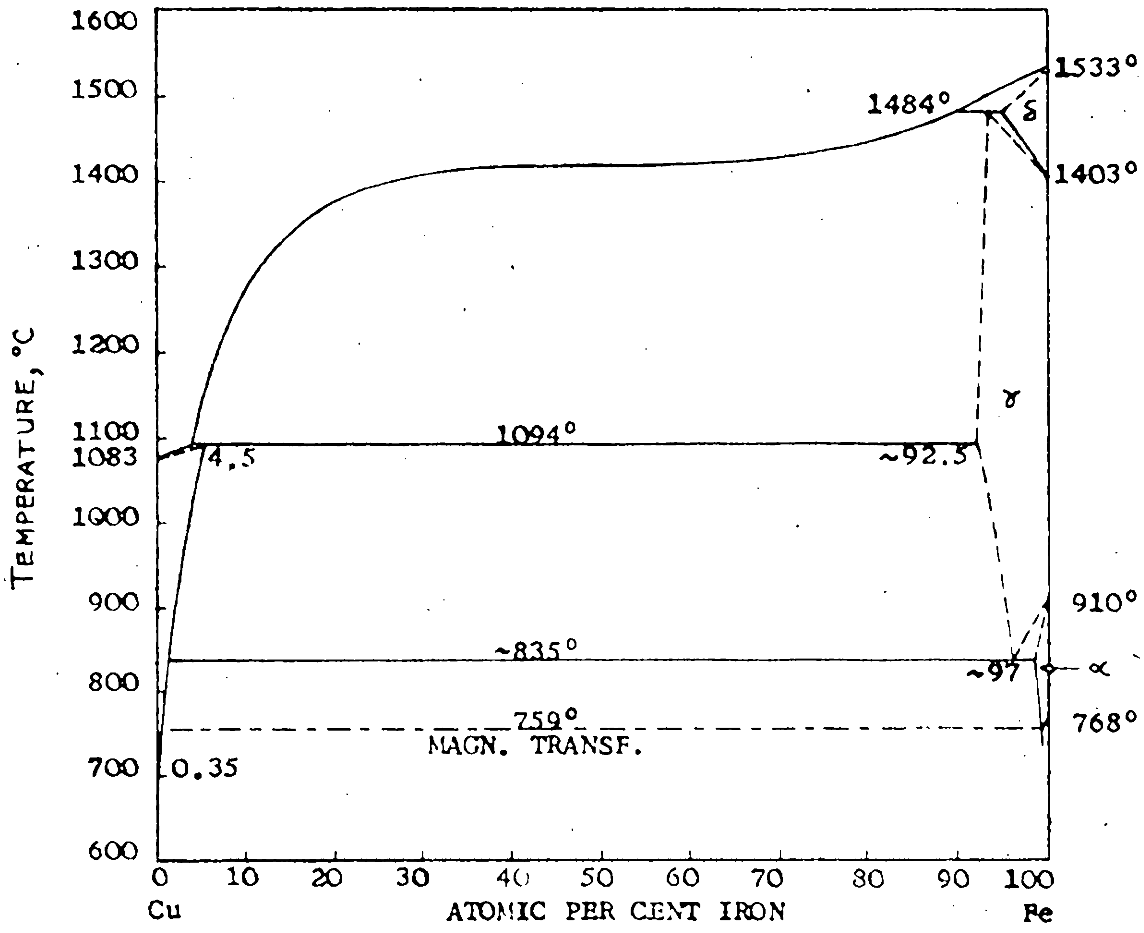

Figure 4. The Fe-Cu system(29).

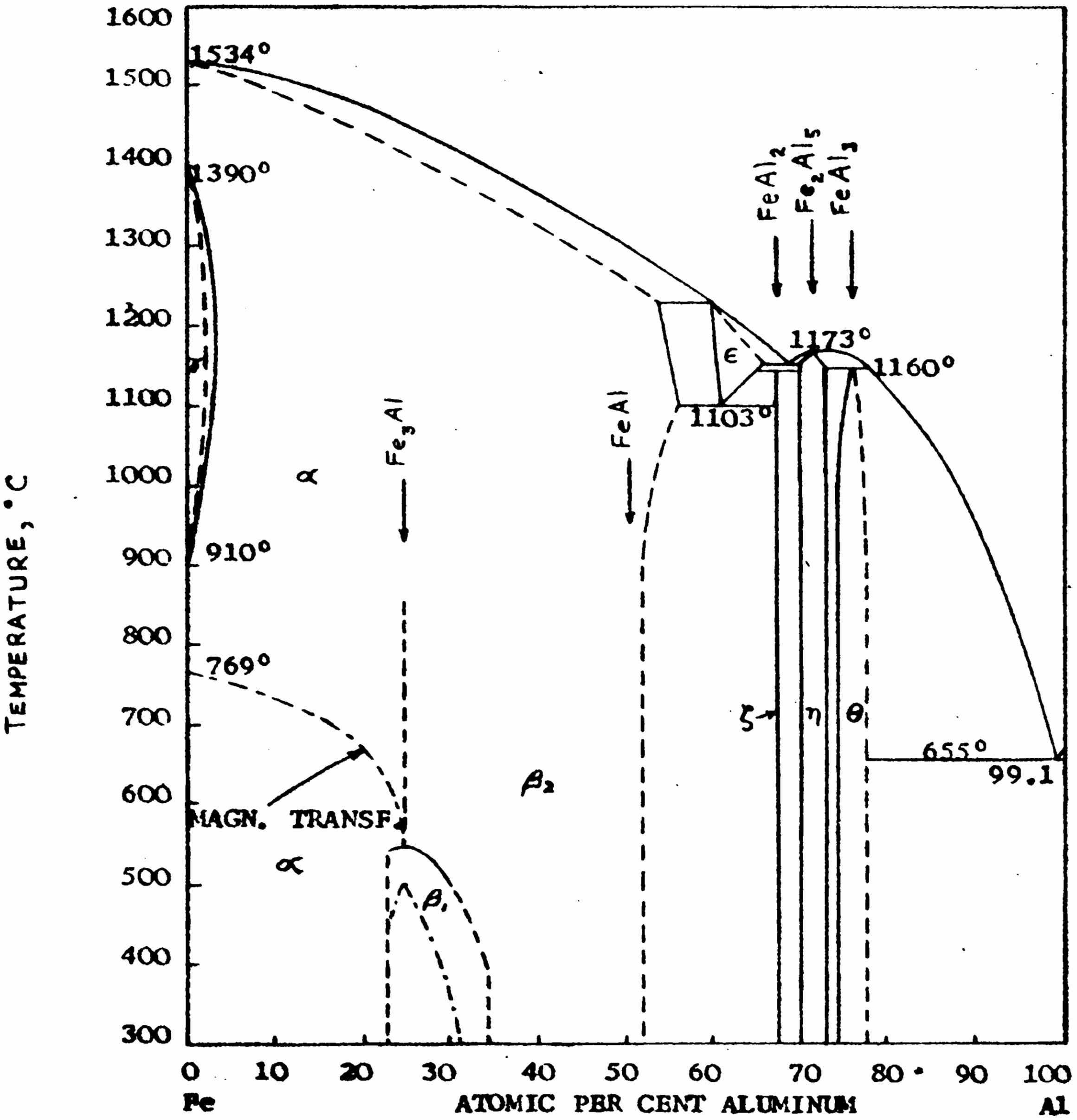

Figure 5. The Fe-Al system (29).

VII. METHODS OF EVALUATING HOT WORKABILITY

The hot working of iron and steel dates back to antiquity. It was not until the 1920's, however, that serious efforts were made to devise methods of evaluating the hot workability of iron and steel in a quantitative manner. Prior to this, the procedure had been that of trial and error.

1. Hot-Bend Test

One method of evaluating hot workability is the hot-bend test. In this test, a bar of iron or steel is heated to a given temperature, quickly removed from the furnace, secured in some manner, and struck with a mallet. Cain, *op. cit.*, used such a method in 1924 to evaluate the hot shortness of iron specimens. After the hot bars were secured in an anvil, he bent them back and forth through 180° as rapidly as possible. If a bar fractured during cooling through the hot-short region it was taken to be hot short; if it did not break, it was assumed to be free of hot shortness. The hot-bend test is still used as a rapid qualitative test of hot workability. Nehl, *op. cit.*, subjected his copper-bearing steels to a single bend and obtained some very useful results. The test, however, can not be expected to subject the test specimen to stresses which closely resemble those encountered in forging or hot rolling.

2. Single-Blow, Drop-Hammer Test

Ellis(34) in 1933 tested the forgeability of different steels at various elevated temperatures by means of a single-blow, drop-hammer test. He prepared test cylinders which were one inch in diameter and one inch in length. The specimens were heated to the testing temperature, quickly removed from the furnace, and placed on the anvil of the drop hammer. The cylinders were then subjected to a single blow of 520 foot-pounds of energy. By testing a series of specimens of a given steel at various temperatures, a quantitative measure of the steel's hot workability could be obtained. Although this test enabled the measurement of quantitative data for the first time, the hot workability was measured for only the instantaneous force of a single blow. Correlation was in many instances lacking in practice, particularly when a metal was subjected to repeated blows by the forge hammer or when the metal work hardened. The instantaneous stresses applied could not be expected to closely parallel the continuous shear stresses encountered in hot rolling. The test was, however, the first of its nature to receive wide recognition, and a considerable amount of useful data was obtained from its use.

3. Hot-Twist Method

The test which appears to provide the best evaluation of hot workability involves the twisting of test bars at elevated temperatures. Sauveur (35) is credited with originating the test in the 1920's. He found that steels in torsion exhibit changes of torsional strength while in the blue-brittle range and when passing through their critical points. His experiments were all conducted at temperatures below 2000°F (1095°C) and at very slow twisting speeds.

The hot-twist method was improved upon at Globe Steel Tubes Company in 1938. By 1944 over 7000 tests had been made at their laboratories to determine the best conditions for the piercing of a wide variety of carbon, alloy and stainless steels.

In 1944 Ihrig(36) described the method used at Globe Steel Tubes Company and some of the results obtained.

Bars of steel 22-24 inches in length are prepared by forging 5/8-inch bars from large billets and cold drawing to 9/16 inch. Figure 6 is a schematic diagram of the apparatus. The bar A is inserted in the furnace B. One end of the bar is clamped in the chuck C and the other end is held in the heavy dog D. The bar is thus free to expand through the bearing E, but it is prevented from rotating on that end while the other end is rotated by the chuck. When the torque is applied, the dog makes contact with the stop F and energizes the electrical counter G, which in turn records the number of revolutions made by the chuck by means of the contact at H. When the bar breaks inside the furnace, the dog drops away from and breaks contact with the counter circuit, and an accurate count of the number of twists to failure of the bar being tested is recorded.

The bar is soaked 20-30 minutes at the test temperature. The furnace temperature is controlled by a regulator and measured by a pyrometer. The furnace is mounted on a movable carriage which facilitates easy removal of the

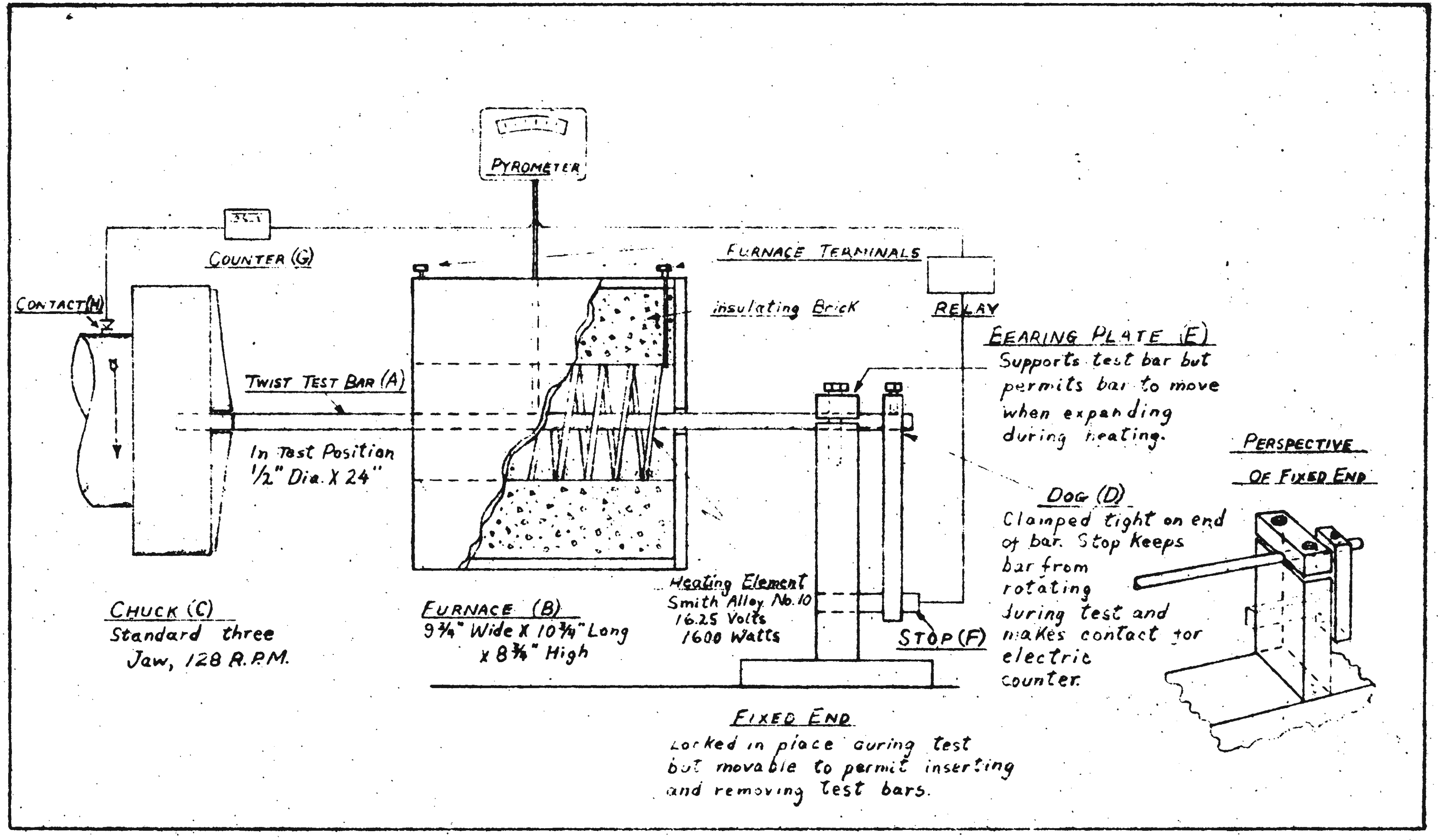

Figure 6. The hot-twist apparatus (37).

broken specimens. The chuck operates at 128 revolutions per minute. Thus the bar, after accurate heating, is rapidly and uniformly worked by twisting until fracture occurs. The bar is held at temperature in the furnace while being twisted and actually rises slightly in temperature from the working during the test. By making a series of tests on the same heat of a given steel at different temperatures, curves can be drawn which reveal the temperature of optimum hot workability of the steel.

Clark and Russ (38) used a similar hot-twist test at Timken Roller Bearing Company. Their apparatus was essentially the same as that described by Ihrig, ibid., with the exception that their apparatus also had a torque-measuring device. There was an extensive discussion of the hot-twist method at the October, 1946 meeting of the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers (39).

Perhaps the most significant feature of the test is that the metal is subjected to continuous shear stresses as are encountered in hot rolling. The temperature of the maximum number of twists before failure is believed (38) to very nearly represent the equi-cohesive temperature of the metal under test. The previous heat treatment of the metal is immaterial as the bar is soaked at temperature in the furnace before twisting. The rate of deformation can be regulated. Above a certain critical twisting speed, the rate of twisting has little effect on results. The equipment involved is simple and inexpensive, the test requires little time, and quantitative results may be obtained.

VIII. EXPERIMENTAL PROCEDURE

1. Melting Technique

An Ajax-Northrup 17-pound, tilting-type induction furnace was used for all of the heats. The high-frequency power source was a 20-kilowatt, Ajax-Northrup hydrogen-type, mercury spark-gap converter. Magnesia crucibles were used for all heats. Powdered magnesia (Normag) was packed between the crucibles and the mica insulating sheets.

The furnace was covered with two insulating bricks to reduce heat loss. Adjoining semi-circular sections were cut in the bricks to facilitate the making of additions and the taking of temperature readings. The furnace assembly and converter unit are shown in Figure 7.

The ingot mold was made entirely of graphite. Two machined graphite cylinders 12 inches in length, with an inside diameter of 1 3/8 inches and an outside diameter of 1 5/8 inches, were joined together by a four-inch machined graphite cylinder. The 12-inch cylinders were machined on one end to an outside diameter of 1 1/2 inches for a distance of 2 1/8 inches from the end. The four-inch joining section, with an outside diameter of 1 3/4 inches, was machined to an outside diameter of 1 9/16 inches to provide a secure fitting. A flat graphite disk was used for the mold bottom and the pouring spout, with a 1 3/8 inch opening, was machined from a 3 1/4 inch diameter graphite cylinder. The disassembled ingot mold is shown in Figure 8.

Temperature readings were taken with a direct-reading

Figure 7. Furnace assembly and converter unit.

Figure 8. Ingot mold assembly.

Leeds and Northrup optical pyrometer of the disappearing-filament type. As a check of the accuracy of the pyrometer, readings were taken on a number of preliminary heats when the metal had just become molten. The readings were always in the range from 2775° to 2790°F. The melting point of iron is 2795°F (1535°C). Readings at the melting points of subsequent heats were also in this range. Ten degrees Fahrenheit were therefore added to all readings and are recorded as such. On this basis, an accuracy of no greater than ± 15°F is claimed on the temperatures recorded. Before taking a reading, the thin slag cover was always parted to insure sighting directly upon the molten metal.

Prior to starting a run, the electrode chamber of the converter unit was purged with hydrogen for 15 minutes. A preliminary check of the power lines with an ammeter revealed that the maximum power that could be drawn without blowing a fuse was 17 kilowatts. The power was maintained between 14 and 16 kilowatts for all of the heats.

The basic charge was 11 pounds (4994 grams) of Armco iron punchings. The percentages of additions were calculated on this basis. Five pounds of the punchings were charged initially--the remainder being added periodically as the melting progressed to prevent bridging.

The time for meltdown averaged one hour and twenty minutes. According to the manufacturer, a charge in the 17-pound furnace can be melted in less than 45 minutes with a power of 20 kilowatts. The long melting times resulted in the dissolving of relatively large quantities of oxygen. The solubility of oxygen in molten iron as a function of temperature is shown in Figure 9. The activity of oxygen in molten iron as a function of percentages of several deoxidizing elements is given in Figure 10.

Due to the high affinity of the rare earths for oxygen, the melt must be well deoxidized if desulfurization is to be anticipated. Aluminum was used as the deoxidant for all of the heats. Silicon was not used as the silicon content of ingot iron is held to a few thousandths of a per cent. The carbon content of ingot iron is on the order of 0.015 per cent and has little effect on reducing the activity of oxygen in the molten iron. Aluminum is used in the commercial production of ingot iron for ladle deoxidation.

In addition to the deoxidation requirements, it was desired to study the effect of residual aluminum on hot shortness in ingot iron. Five preliminary heats were made to determine the quantity of aluminum required. No attempt was made to control the final residual aluminum contents to close limits because of the two-minute holding time and the time variation in making the aluminum additions. The time required for pouring also had an effect on the aluminum retained. By adding the same amount of aluminum to each heat, the amount being in excess of that required for deoxidation, a spread of residual aluminum contents was obtained.

To the first preliminary heat, 25 grams of aluminum (0.5 per cent) were added. It is common foundry practice

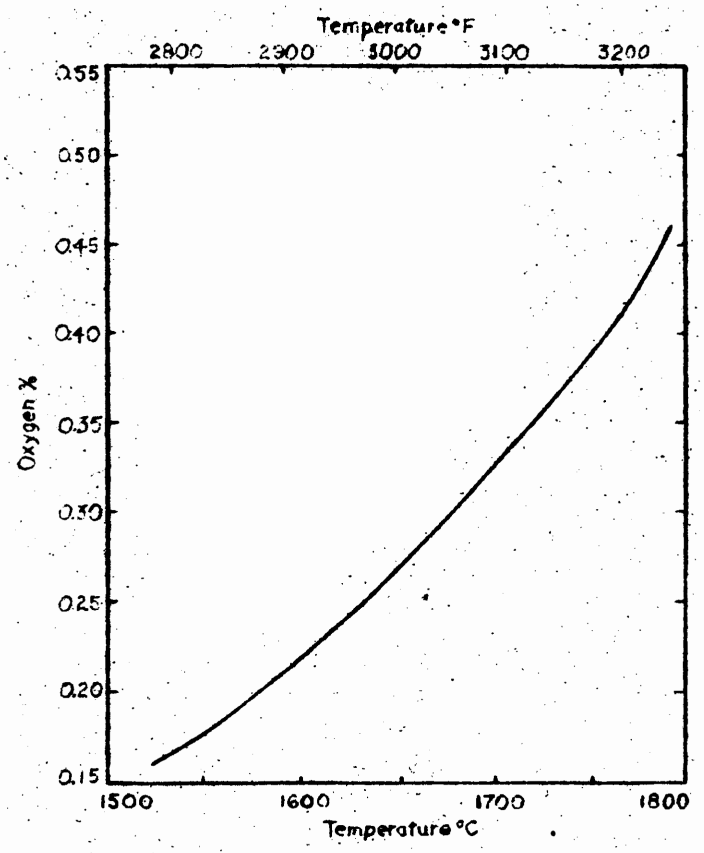

Figure 9. Solubility of oxygen in liquid iron (40).

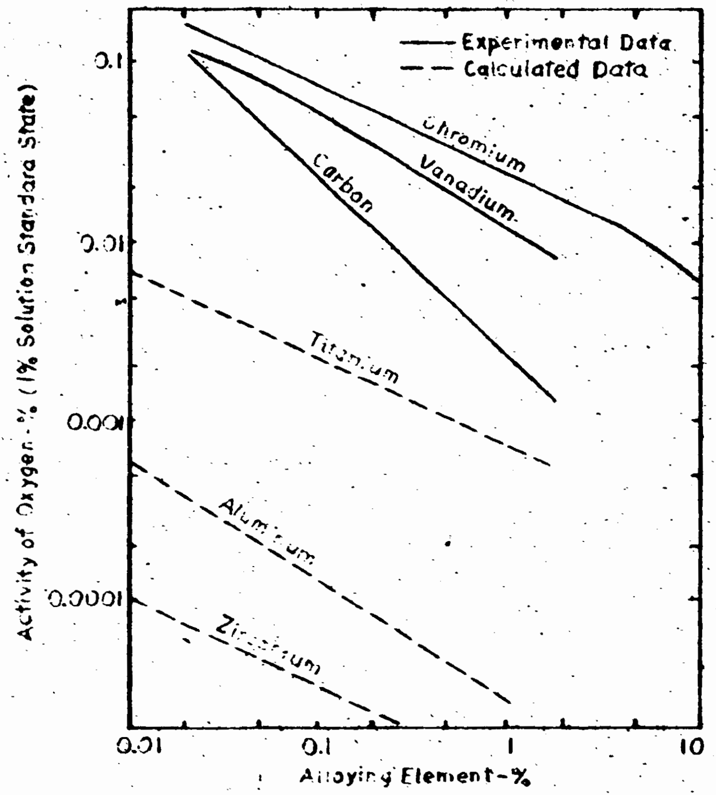

Figure 10. Activity of oxygen in binary liquid iron alloys (1% solution standard state)(40).

to add 0.3-0.4 per cent aluminum for deoxidation of low carbon steel. The heat was poured immediately after the aluminum additions. As in all instances in which deoxidation was incomplete, there was a reaction between the oxygen in the molten iron and the graphite ingot mold. The ingot had numerous blow holes throughout its length.

To the second heat, 40 grams of aluminum (0.8 per cent) were added. This heat was again poured immediately after the aluminum additions and the ingot was sound. There were blow holes only in the top section near the pipe.

Fifty grams of aluminum (1 per cent) were added to the third heat. This heat was held for two minutes before pouring. The molten metal reacted violently with the ingot mold upon pouring and the cavity created by the escaping gases extended to the very bottom of the ingot.

To the fourth heat, 65 grams of aluminum (1.3 per cent) were added. This heat was also held for two minutes before pouring. The metal appeared to be well deoxidized (no bubbling) before pouring. There was no reaction between the metal and ingot mold until the latter part of pouring. Examination of the ingot revealed the bottom half to be sound while the upper half had a number of blow holes.

The last trial heat was made with an addition of 75 grams of aluminum (1.5 per cent). After holding for two minutes, the heat was poured. There was no metal-mold reaction and the ingot was sound throughout its length. To all subsequent heats, 100 grams of aluminum (2 per cent) were added to insure residual aluminum contents.

The aluminum and rare earth metal additions were made by wiring the metal onto the ends of six-inch segments of low-carbon welding rods and plunging the rods below the surface of the melt. This procedure was followed to insure that the aluminum and rare earth metal did not float on the bath surface during melting and become oxidized. The additions were wired double (with steel wire) to enable their melting before or at approximately the same time as the wires melted. All additions were made through the hole in the insulating brick cover.

The aluminum additions resulted in some popping and splashing of metal as the aluminum reacted with the dissolved oxygen. The rare earth metal in no instance resulted in popping due to the thorough deoxidation of the melt prior to the rare earth additions.

The rare earth oxides were added by wrapping the powder in paper, dropping the paper onto the surface of the molten metal, and stirring the powder into the melt with a welding rod. As with all of the additions, the power was left on while the additions were being made to aid in mixing by the electromagnetic stirring action.

The aluminum additions were made when the melt had reached approximately 2900°F. In spite of the exothermic nature of the aluminum-oxygen reaction, the melt temperature remained at approximately 2900°F throughout the addition period. This was in part due to the cold welding rods being added. The melts were slagged with welding rods once during the additions and once immediately thereafter.

The rare earth metal additions were made immediately after the second slagging. The elapsed time between the rare earth metal additions and pouring was approximately two minutes. The two-minute holding period was to enable the rare earths to react with the sulfur but minimize their being oxidized with the sulfur reverting to the melt.

For the heats to which rare earths oxides were added, the elapsed time between the addition and pouring did not exceed one minute. Just prior to pouring, the melt was again slagged with the power off. During pouring, the remaining slag was held back with a welding rod.

The ingot mold and all additions were dried by heating for 1 1/2 hours at 550°C.

Supplemental information on the melting technique is given in Appendix I.

2. Sampling for Chemical Analysis

The ingots were cut off just below the pipes and cut in half. Each section was machined to one inch in diameter. Microscopic examination of the ingots cast from the preliminary heats revealed that the solidification rate was sufficiently rapid for the carbon pickup to be confined to a thin outer shell. Before taking turnings for chemical analysis, the contaminated outer shell was completely removed. The samples for chemical analysis were taken from the remaining turnings--along the entire length to obtain representative samples. No machining oil was used as oil causes sulfur contamination. Oils can not be remoyed adequately with solvents.

3. Hot Rolling and Swaging

The two-high rolling mill which was used was built by U. S. A. Machine Shop and donated to the Missouri School of Mines and Metallurgy by the Aluminum Company of America in 1954. The rolling mill is shown in Figure 11.

The swaging machine and furnace which were used are shown in Figure 12. The swaging machine was built by the Standard Machinery Company and has die sizes ranging from 0.160 to 0.700 inch. An 18-kilowatt, resistance-type, Hevi-Duty furnace with a Wheelco proportional temperature recorder was used for heating the bars prior to rolling.

The machined, one-inch diameter bars were heated for 30 minutes prior to rolling. The temperature was maintained at 870°C to remain just below the hot-short region. The bars were rolled in eight passes. The openings in the rolls extended from the 1 1/8-inch oval to the 5/8-inch round. The 5/8-inch pass was made cold to eliminate mill scale. On the average, two passes could be made before reheating of the bars was necessary.

The cold swaging was accomplished in six passes. The die sizes used were: 0.650, 0.600, 0.550 and 0.500 inch. Each bar was passed once through the 0.650-, 0.600- and 0.550-inch dies. Three passes were made through the 0.500-inch die. Further description of the rolling and swaging is

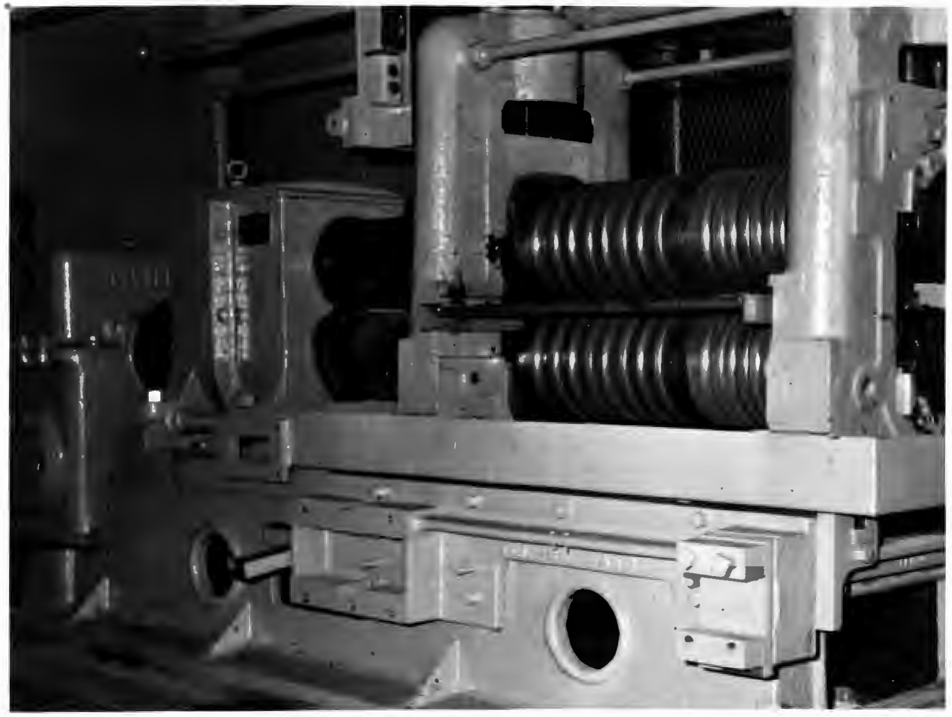

Figure 11. Two-high rolling mill.

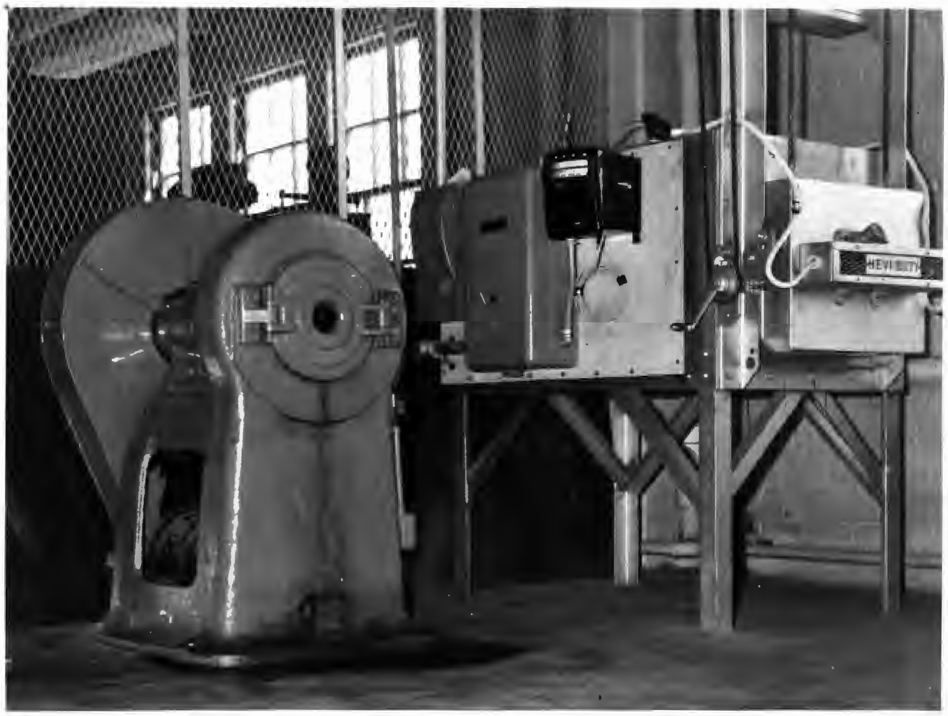

Figure 12. Swaging machine and heating furnace.

given in Appendix III.

Microscopic examination of bars rolled and swaged from preliminary heats revealed the relative grain sizes resulting from different hot- and cold-working treatments. The bars were from heats to which no rare earth additions had been made, i.e., heats with the same nominal composition as heat number one.

In Figure 13a is shown the microstructure of a bar which had been rolled from the one-inch diameter to the 5/8-inch diameter in eight passes--each pass being made with the bar heated. The microstructure shows only the large, spontaneously recrystallized grains.

Figure 13b shows the microstructure of a bar which had been hot rolled as the previous bar, then hot swaged through the 0.650-, 0.600- and 0.550-inch dies, and cold swaged through the 0.500-inch die. The microstructure shows that the large, spontaneously recrystallized grains have been only partially broken up by the cold swaging.

In Figure 13c is shown the microstructure of a bar which had been hot rolled as the previous two bars, but cold swaged through all four of the swaging dies. The microstructure shows only the small grains resulting from the cold swaging. All of the bars which were hot twisted were given this treatment.

The relative sizes of the as-cast ingot sections, the machined sections, and the finished bars are shown in Figure 14.

Figure 13a. Hot rolled. Transverse.

150 X; 2% Nital

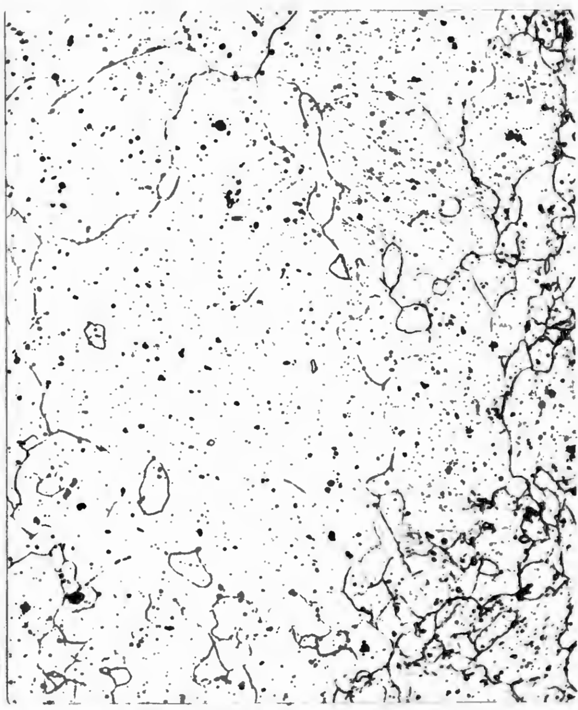

Figure 13b. Hot rolled, hot swaged and cold swaged. Transverse.
150 X; 2% Nital

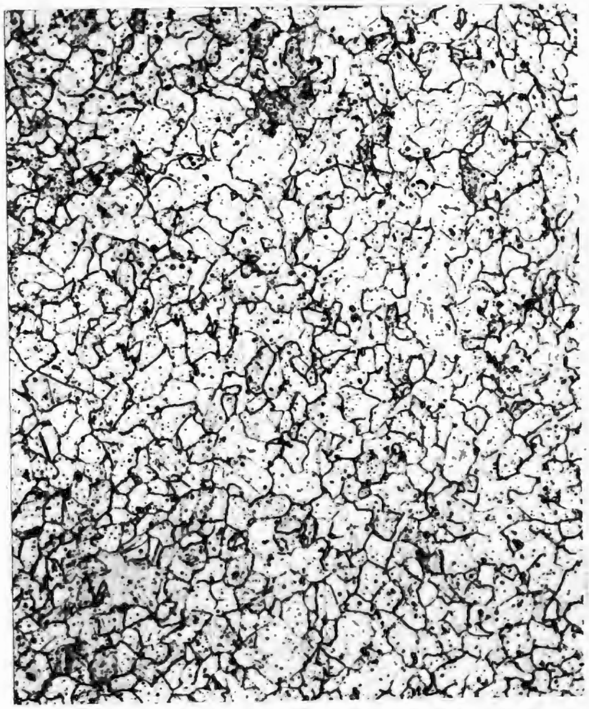

Figure 13c. Hot rolled and cold swaged. Transverse.

150 X; 2% Nital

Figure 14. As-cast ingot sections, machined sections, and rolled and swaged bars.

4. Hot Twisting

The bars were hot twisted on the apparatus developed at Globe Steel Tubes Company*and described previously. The bars were all 22-24 inches in length to fit the chucks of the apparatus. The bars as they appeared prior to the hot twisting are shown in Figure 15a.

The bars were twisted at 1750°F (954°C). This temperature is in the middle of the hot-short region. Near this temperature, hot shortness is most prevalent in ingot iron. According to the theory, the extent of the solubility of the molten iron sulfide in gamma-iron at this temperature is insufficient to alleviate the hot-short condition.

The bars were soaked for 20 minutes at the twisting temperature to insure complete recrystallization. Ingot iron is unlike carbon steel in its recrystallization behavior. Cold-worked ingot iron will not recrystallize below the A_3 temperature unless the extent of cold working has been 70 per cent or more. Kenyon (41) lists a number of references dealing with the recrystallization behavior of ingot iron and its stability to heat treatment below the A_3 temperature. The general consensus of opinion is that, while the impurities in ingot iron offer more nuclei for recrystallization, they also inhibit grain growth even more, with the net effect being the same as if the impurities reduce the number of recrystallization nuclei.

The bars are shown in Figure 15b as they appeared after hot twisting.

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*Now the Babcock and Wilcox Company, Milwaukee, Wisconsin

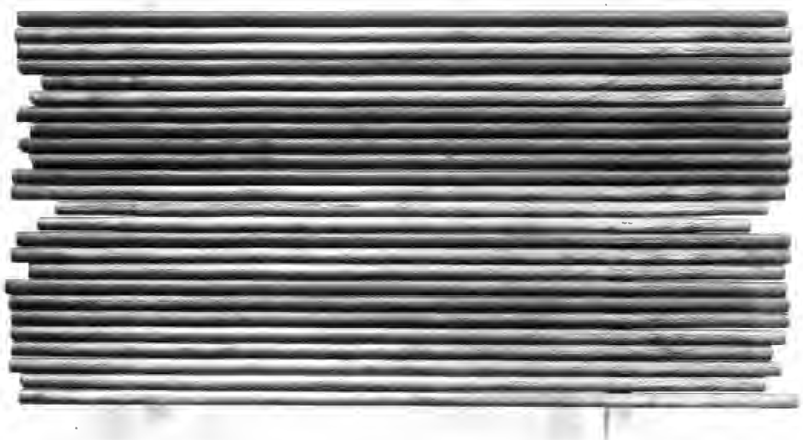

Figure 15a. Bars prior to hot twisting.

Figure 15b. Bars after hot twisting.

IX. EXPERIMENTAL RESULTS

1. Nominal Additions to Heats

The heats and the nominal additions are tabulated in Table VII. The percentages are calculated on the basis of the 11-pound (4994 grams) charge of Armco iron punchings.

To heats 3, 4 and 5, the rare earth metal addition was ordinary mischmetal of the approximate composition:

Cerium	50-55 per cent
Lanthanum	22-25 per cent
Neodymium	17 per cent
Other rare earths	balance

The rare earth metal additions to heats 7, 8, 9, 12, 13 and 14 were Lan-cer-amp No. 2 having the approximate composition:

Cerium	45-50 per cent
Lanthanum	30 per cent minimum
Iron	5 per cent
Other rare earths	balance

The rare earth oxides which were added had the approximate composition:

Cerium oxide, CeO_2	48 per cent
Lanthanum oxide, La_2O_3	24 per cent
Neodymium oxide, Nd_2O_3	17 per cent
Praseodymium oxide, Pr_6O_{11}	5 per cent
Other rare earth oxides	balance

The logs of the heats made are given in Appendix II.

2. Results of Hot-Twist Test

The results of the hot-twist test at 1750°F (954°C) are given in Table VIII. The numbers given preceding the dashes represent the heat numbers. The numbers following the dashes represent the section of the ingot from which the bar was taken. The 1's refer to the bars which were taken from the upper halves of the ingots, and the 2's those taken from

TABLE VII

NOMINAL ADDITIONS TO HEATS MADE

Heat Number	Aluminum Added Grams	Aluminum Added Per Cent	Rare Earth Metal Added Grams	Rare Earth Metal Added Per Cent	Rare Earth Oxide Added Grams	Rare Earth Oxide Added Per Cent
1A	75	1.5				
1	100	2.0				
3	100	2.0	5.2	0.1		
4	100	2.0	15.0	0.3		
5	100	2.0	25.1	0.5		
7	100	2.0	5.3	0.1		
8	100	2.0	15.3	0.3		
9	100	2.0	25.0	0.5		
10	100	2.0			5.0	0.1
11	100	2.0			10.0	0.2
12	100	2.0	5.1	0.1	10.0	0.2
13	100	2.0	15.1	0.3	10.0	0.2
14	100	2.0	25.1	0.5	10.0	0.2

TABLE VIII

NUMBER OF TWISTS TO FAILURE OF BARS TWISTED AT 1750°F

Bar Number	Number of Twists to Failure
1 A	8
1-1	8
1-2	19
3-1	22
3-2	41
4-1	13
4-2	10
5-1	21
5-2	32
7-1	35
7-2	27
8-1	48
8-2	15
9-1	5
9-2	9
10-1	27
10-2	76
11-1	25
11-2	42
12-1	39
12-2	20
13-1	22
13-2	43
14-1	15
14-2	23

the lower halves. Each heat is represented by two bars except heat 1A from which only one bar was made.

3. Results of Chemical Analyses

In Table IX are given the results of the chemical analyses. Time did not permit analyses of all of the samples for aluminum, oxygen, copper, lanthanum and cerium. It is felt that the analyses which were performed for these elements is adequate for evaluation of the results. The analyses were performed by two industrial laboratories.

4. Evaluation of Results

In Figure 15 is plotted the percentages of rare earth metal added versus the number of twists to failure of the bars at 1750°F (954°C). The lines connect points which represent bars which had the higher number of twists for a particular heat. There is some correlation for the 0.1 and 0.5 per cent rare earth additions. The spread is greater for the 0.3 per cent additions.

The only data which could be found concerning the hot twisting of ingot iron is given in Figure 16(36). These bars were not twisted below 2000°F, i.e., the twisting was above the hot-short region of ingot iron. At 2000°F, the rimmed ingot iron twisted only about 10 times before failure. The killed ingot iron, however, twisted some 135 times before failure. These data illustrate the effect of oxygen on the hot workability of ingot iron above the hot-short region and give some indication of the number of twists that may be expected at 1750°F.

TABLE IX

CHEMICAL ANALYSES

Heat No.	Bar No.	C	S	Al	O	Cu	La	Ce
1A		0.0074	0.013*		0.018	0.054		
1	1	0.042	0.014*		0.032			
	2	0.020	0.016*		0.037	0.081		
3	1	0.019	0.010*					
	2	0.012	0.010*		0.022			
4	1	0.041	0.017	0.16			0.001	0.001
	2	0.012	0.016	0.21	0.021		0.001	0.001
5	1	0.015	0.011	0.76	0.027		0.012	0.018
	2	0.015	0.010	0.76			0.011	0.020
7	1	0.020	0.013*		0.015			
	2	0.0087	0.012*		0.014	0.064		
8	1	0.017	0.006*					
	2	0.0077	0.006*			0.063		
9	1	0.11	0.025	0.14	0.050		0.008	0.012
	2	0.016	0.020	0.25	0.052		0.009	0.014
10	1	0.014	0.020	0.78			0.001	0.001
	2	0.012	0.020	0.78	0.022		0.001	0.002
11	1	0.013	0.022	1.07			0.001	0.001
	2	0.020	0.022	0.96			0.001	0.001
12	1	0.014	0.012*					
	2	0.034	0.014*		0.004			
13	1	0.015	0.004*					
	2	0.015	0.004*		0.016			
14	1	0.019	0.010	1.02			0.023	0.035
	2	0.020	0.010	1.05	0.005		0.025	0.035

*S analysis by source 2; other S analysis by source 1

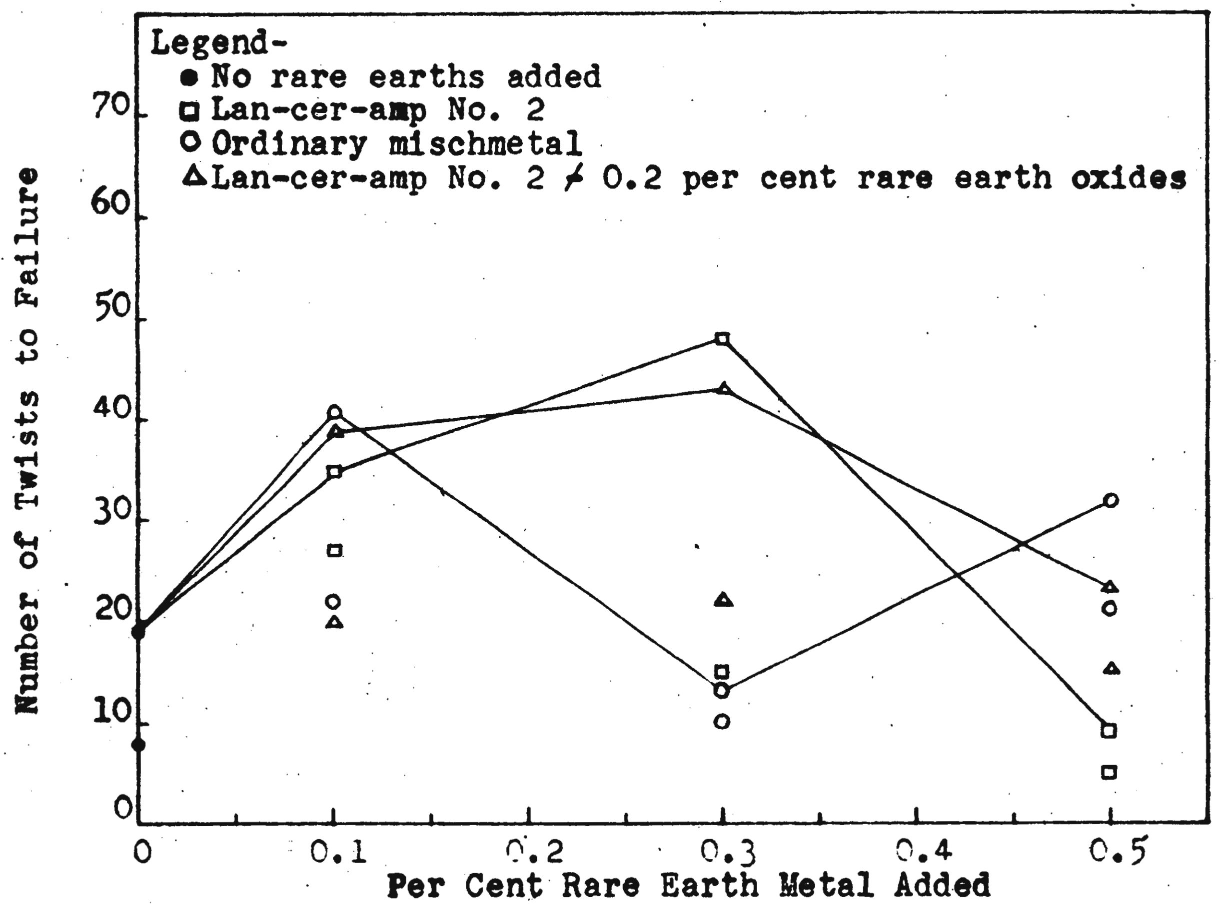

Figure 15. Number of twists to failure versus per cent rare earth metal added.

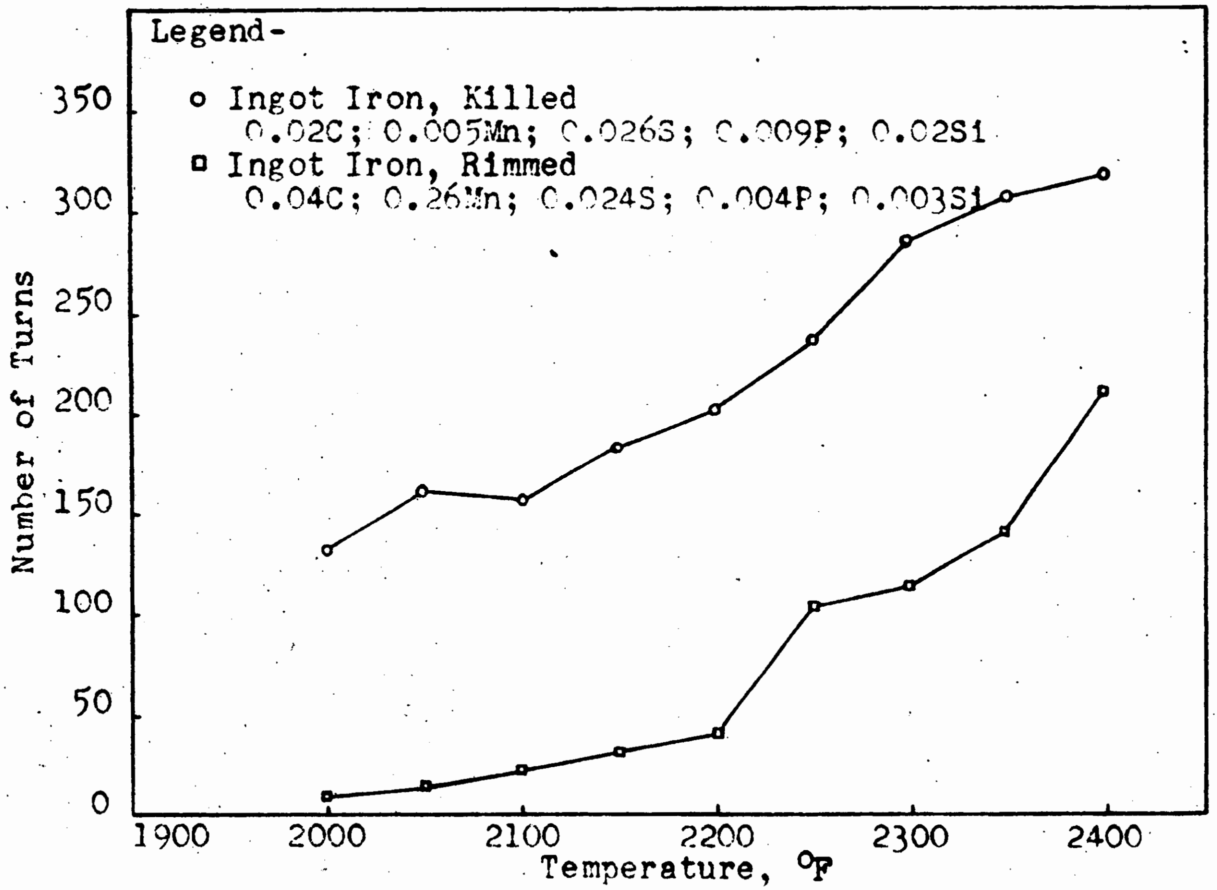

Figure 16. Number of turns to failure of killed and rimmed ingot irons versus temperature of twisting (36).

All of the heats made in this study were thoroughly killed. The bars to which no rare earths were added had twists of 8, 8 and 19. This is approximately the number of twists that the ingot iron withstood at 2000°F. Of the 18 bars to which rare earth metal had been added, 13 twisted more than 20 times while 5 twisted less than 20 times. Some improvement in workability is noted but the lack of correlation indicates that other variables are factors. The bars to which 0.5 per cent rare earth metal was added average less twists (17.5) than those to which 0.1 per cent rare earth metal was added (30.6 twists).

No conclusions can be drawn as to the relative effects of ordinary mischmetal and Lan-cer-amp No. 2. For the 0.1 per cent additions, the points are in fair agreement. For the 0.3 and 0.5 per cent additions, no trend appears.

Closer agreement occurs between the heats to which only Lan-cer-amp No. 2 was added, and those heats to which both Lan-cer-amp No. 2 and rare earth oxides were added. The rare earths apparently have no significant effect in these heats. The rare earth oxide heats will be discussed below.

In Figure 17 is plotted the final percentages of sulfur versus the number of twists. The points are widely scattered with no apparent correlation.

The final percentages of sulfur are plotted versus the percentages of rare earth metal additions in Figure 18. There appears to be a difference in the two sets of analyses performed. By plotting the sulfur analyses from the two sources

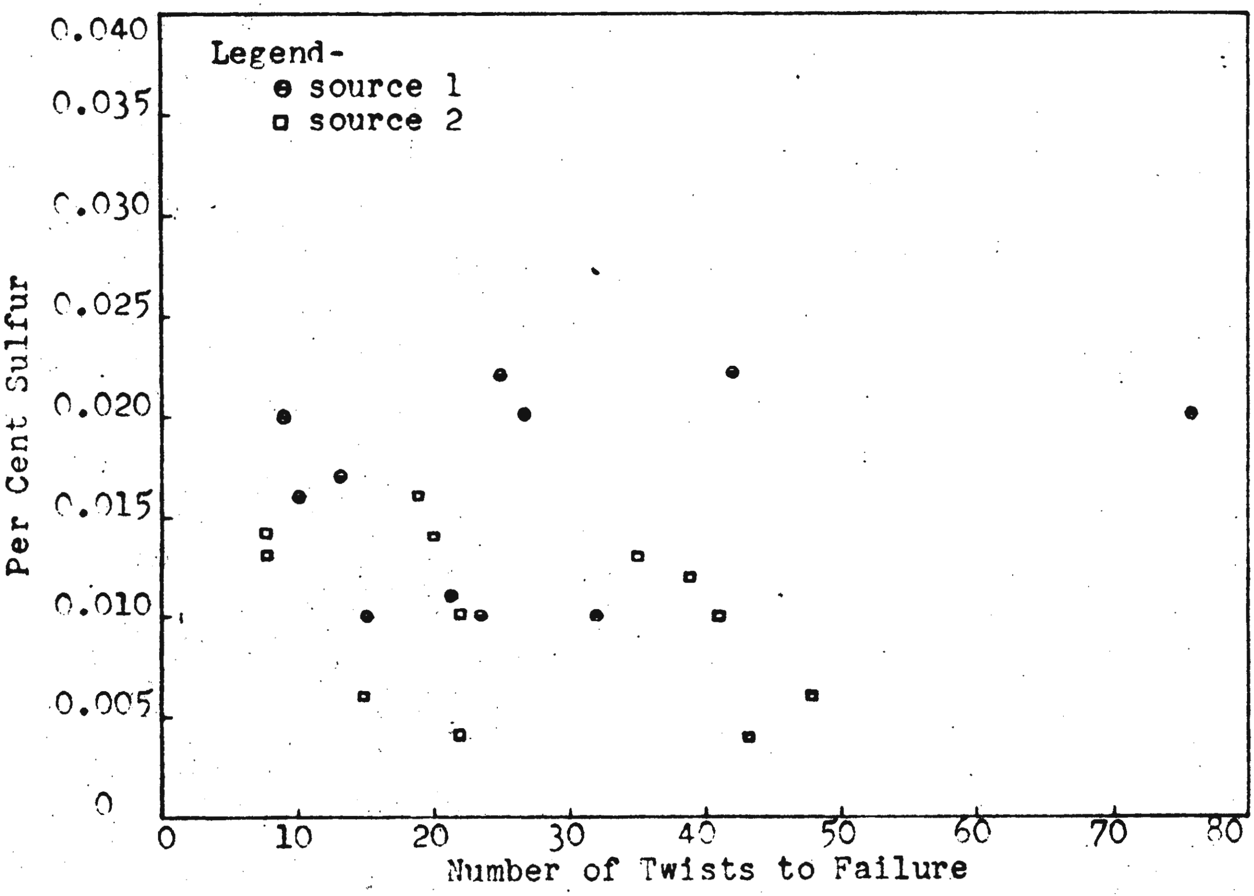

Figure 17. Per cent sulfur versus number of twists to failure.

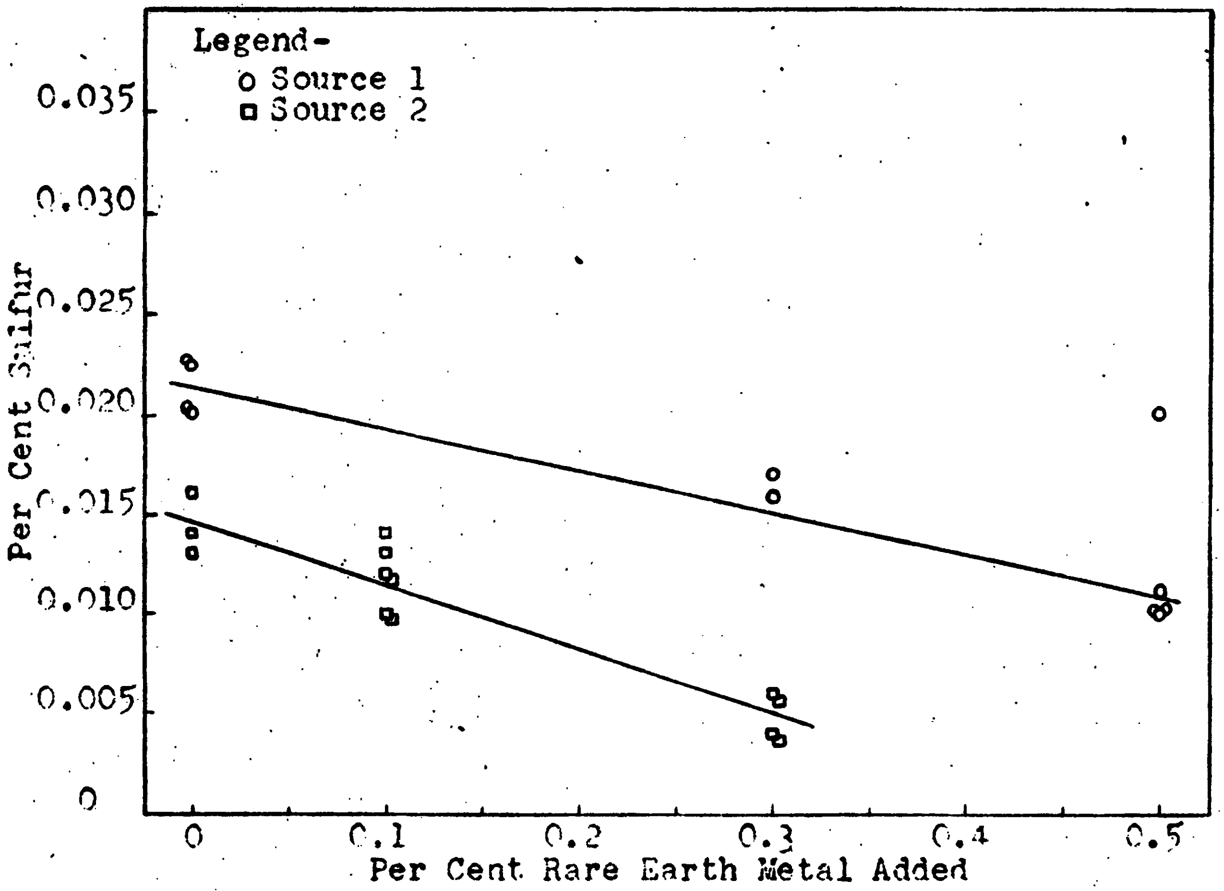

Figure 18. Per cent sulfur versus per cent rare earth metal added.

separately, the two curves shown are obtained. There is a definite decrease in sulfur contents with increasing rare earth metal additions. Source 1 reports the lowest sulfur contents for bars 5-2, 14-1 and 14-2, all 0.010 per cent sulfur corresponding to rare earth metal additions of 0.5 per cent. Source 2 reports the lowest sulfur contents for bars 8-1 and 8-2, both 0.006 per cent sulfur, and bars 13-1 and 13-2, both 0.004 per cent sulfur--all four of these bars having had 0.3 per cent rare earth metal added. Source 2 did not analyze any samples to which 0.5 per cent rare earth metal had been added.

Samples from four bars to which no rare earth metal had been added were analyzed for sulfur by source 1 (bars 10-1, 10-2, 11-1 and 11-2). Samples from three bars to which no rare earth metal had been added were analyzed by source 2 (bars 1A, 1-1 and 1-2). The average sulfur content of the four bars analyzed by source 1 was 0.021 per cent, and the average on the three bars analyzed by source 2 was 0.0143 per cent. Using these values as average initial sulfur contents, the best sulfur drop from the analysis of source 1 is 52 per cent (heats 5 and 14) and from source 2 the best drop is 72 per cent (heat 13).

Bar 9-1 was inadvertently machined with oil. The turnings were soaked for several hours in CCl_4 before submitting for analysis. The sulfur content is 0.005 per cent higher in bar 9-1 than in bar 9-2; as the higher value is believed due to the oil, the sulfur analysis on bar 9-1 is not used.

The substantial sulfur drops noted are not accompanied by a significant increase in hot workability, i.e., a notable decrease in hot shortness.

One of the factors contributing to this lack of correlation is seen in Figure 19 in which percentage of oxygen is plotted versus the number of twists to failure. Although the points are somewhat scattered, a definite trend appears. Below 0.025 per cent oxygen, the percentage of oxygen appears to have little effect on the number of twists. For the five bars in which the oxygen contents exceeded 0.025 per cent, the average number of twists was 12.

In Figure 20 is plotted the percentage of residual aluminum versus the number of twists to failure. The plot has an inverse relationship to the plot of per cent oxygen versus the number of twists, i.e., the higher the residual aluminum content, the lower the oxygen content as would be expected. This is substantiated in Figure 21 in which per cent oxygen is plotted versus per cent residual aluminum. It is interesting to note that, although most of the aluminum is in solid solution, the high residual aluminum contents do not, in themselves, appear to have a detrimental effect on the hot workability; they do in fact, appear to reduce the hot shortness. The near inverse relationship between the plots of number of twists versus oxygen and aluminum, respectively, indicates that the apparent increase in workability accompanying the higher residual aluminum contents is most probably due to the accompanying lower oxygen contents--

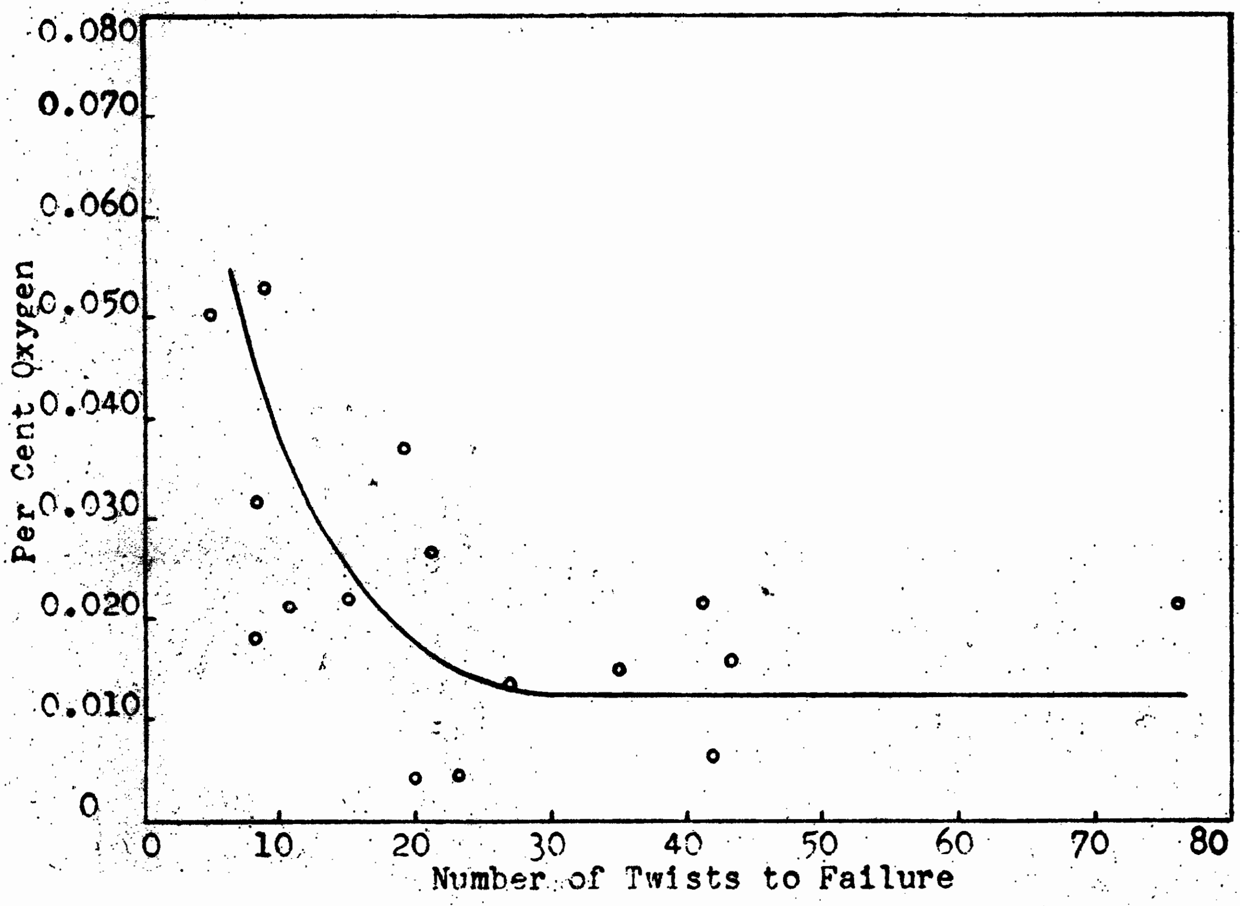

Figure 19. Per cent oxygen versus number of twists to failure.

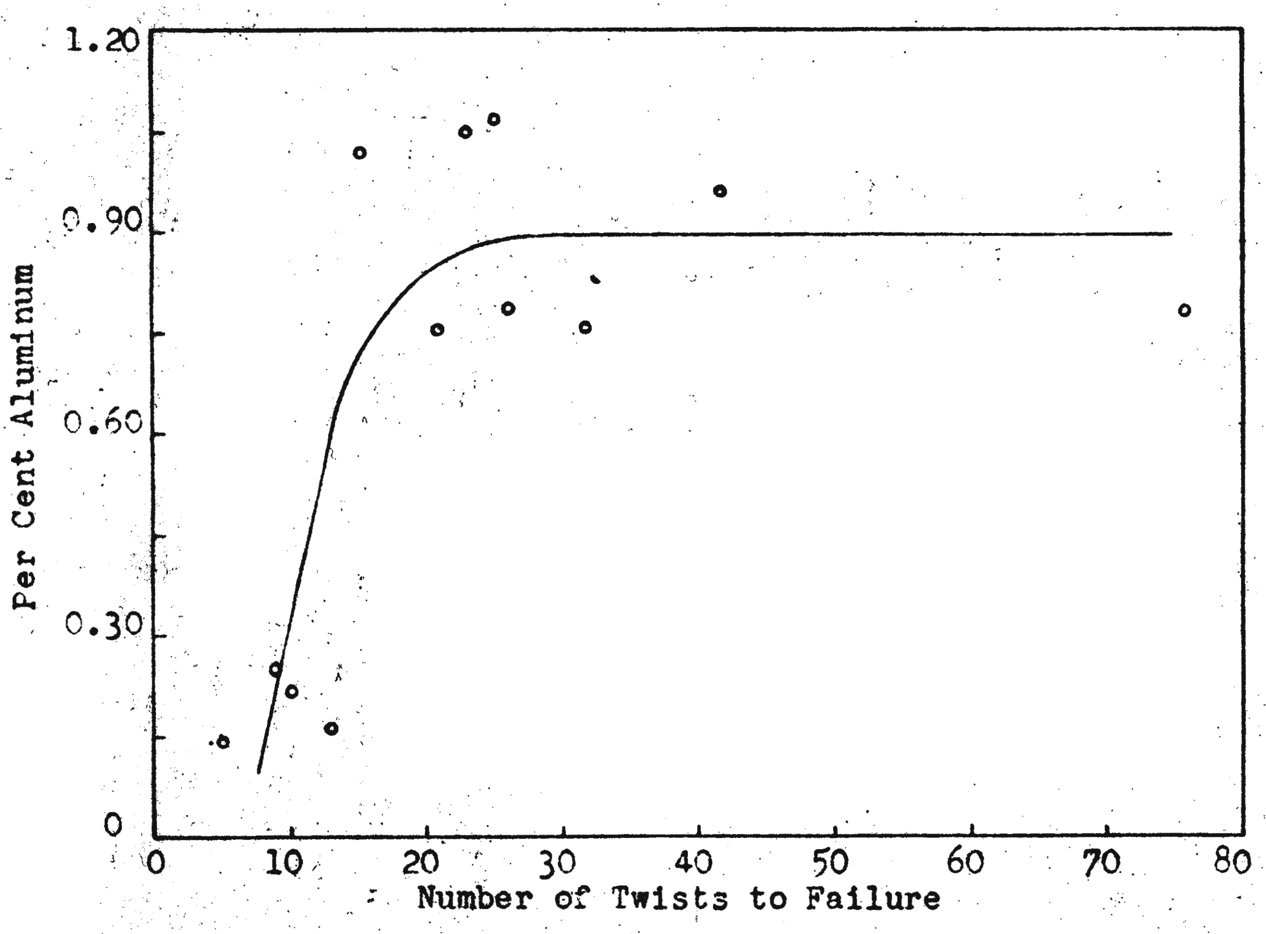

Figure 20. Per cent residual aluminum versus number of twists to failure.

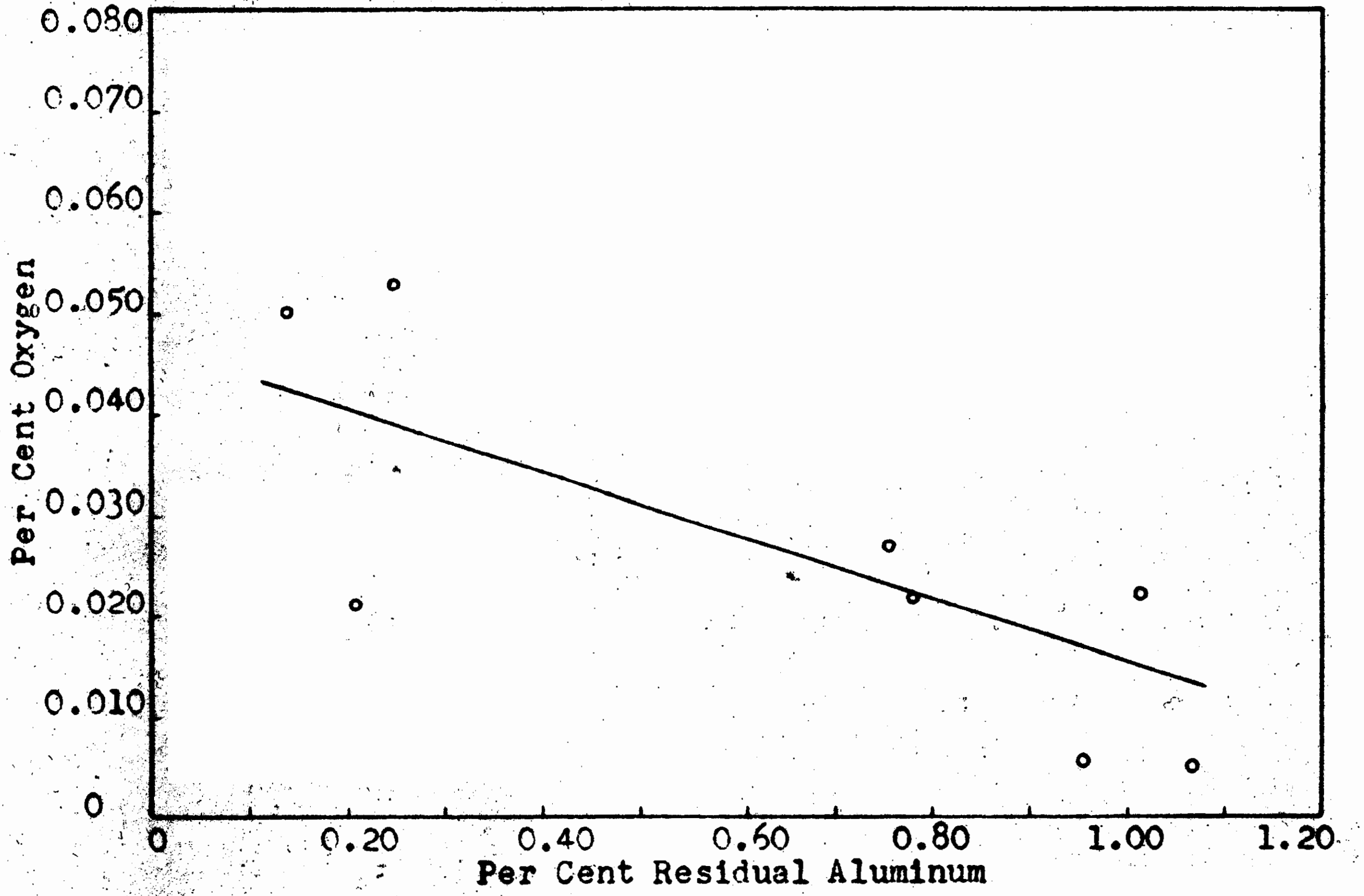

Figure 21. Per cent oxygen versus per cent residual aluminum.

oxygen being a well-known cause of hot shortness.

Samples from only four bars were analyzed for copper as the punchings used for all of the heats were from the same batch. The copper contents are just below--one is the same as--the approximately 0.08 per cent which Nehl(33) had found was the maximum copper which could be present without affecting the hot workability of plain carbon steel at 1050°C. The percentages are considerably lower than the maximum of 0.15 per cent copper specified by Armco for their ingot iron.

The iron-cerium diagram is shown in Figure 22. The solubility limit of cerium in alpha- and gamma-iron in the temperature range 815-1015°C (1499-1859°F) lies close to 0.4 weight per cent(18). The solubility is believed to be lower at lower temperatures. As long as sulfur and oxygen are available in molten iron containing cerium (and lanthanum), the cerium would be expected to continue to react until it was depleted.

The cerium and lanthanum analyses indicate that appreciable residual amounts may be present for only the 0.5 per cent rare earth metal additions. It would have been desirable to have had cerium and lanthanum analyses performed for all of the bars but this was not possible. Also, the analyses given do not differentiate between rare earth compounds and residual rare earth metal in solid solution.

The analyses for heats 5, 9 and 14--all of which had 0.5 per cent rare earth metal added--show appreciable cerium

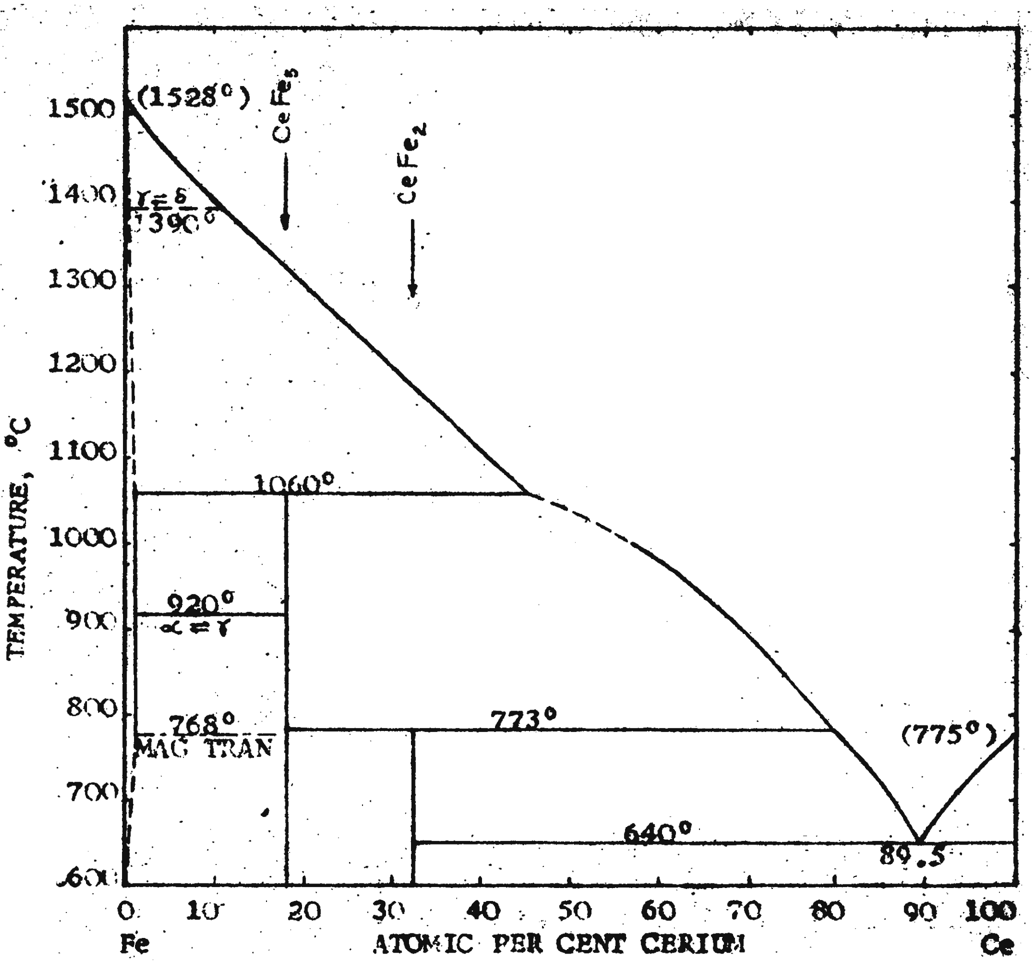

Figure 22. The Fe-Ce system$^{(29)}$.

and lanthanum contents. Heat 4, to which 0.3 per cent rare earth metal was added, has a very low cerium and lanthanum content. Analyses of heats 8 and 13, to which 0.3 per cent rare earth metal was also added, would have been desirable. The sulfur contents are low for these heats. If the cerium and lanthanum contents were also low, the two minute holding interval between the rare earth metal additions and pouring was sufficient for almost all of the rare earths to react; the converse would, of course, be true if the appreciable cerium and lanthanum contents remained. For the 0.5 per cent rare earth metal additions, an additional minute or so of holding interval would have been desirable for more complete reaction.

Worthy of mention is the possibility that these cerium and lanthanum contents may have an effect on hot workability, perhaps by reducing the ductility of the gamma-iron as a result of the solid solubility. This could conceivably be the reason that the heats to which 0.5 per cent rare earth metal was added averaged less twists than those to which only 0.1 per cent rare earth metal was added.

To heats 10 and 11 were added 0.1 and 0.2 per cent rare earth oxides, respectively. The residual cerium and lanthanum contents are small. The method of addition is a factor. The oxides were wrapped in paper and stirred into the melt with a welding rod. The oxides either did not get into the melt, or they immediately floated back to the slag phase. One very unusual result did appear in the hot-twist data on these two heats. Bar 10-2 (0.1 per cent oxide addition) twisted 76 times which is almost twice the highest number of twists of any of the bars. This result can not be explained by the chemical analysis. Bar 10-1, from the same heat, twisted only 27 times. The average of the other three bars from these two heats was 31 twists. This is considerably higher than the average of the heats to which no rare earths were added (12 twists). Perhaps even small quantities of the oxides serve as nucleating agents resulting in a finer grained gamma-iron at the twisting temperature.

The rare earth oxides in heats 12, 13 and 14, however, appear to have no significant effect when compared to heats 7, 8 and 9 which are of the same nominal composition except for the rare earth oxide additions. Further study would be necessary before conclusions could be drawn on the effects of the rare earth oxides. Compacting the oxides into briquettes for the additions may result in more consistent results.

The carbon contents are in the range of 0.015 per cent given by Armco as a typical analysis of their ingot iron. Some of the bars showed some carbon pick-up from the ingot mold but no correlation appeared between hot workability or sulfur drops and carbon contents. Bar 9-1 appears to have been contaminated with carbon by the machining oil and/or the CCl_4 solvent.

5. Sulfur Printing

Sulfur printing affords a convenient means of detecting and permanently recording the distribution of sulfur in iron and steel.

The method consists essentially of placing in intimate contact on a prepared metal surface, photographic bromide paper which has been previously soaked in a dilute solution of sulfuric acid in water.

The reaction of the sulfuric acid with the sulfide regions of the iron or steel produces hydrogen sulfide gas, which reacts with the silver bromide in the paper emulsion, forming a characteristic brown to gray-black deposit of silver sulfide. The sulfur printing technique is described in detail in Appendix IV.

The bottom transverse sections which were sulfur printed were cut approximately one-half inch from the ingot bottoms. The top transverse sections of ingots 1, 11, 12 and 13 were cut just below the pipes, while the other top sections were taken one-half to one inch below the pipes. The sulfur prints of these top and bottom transverse sections of the ingots are shown in Figures 23 through 30.

The sulfur prints of the bottom transverse sections of the ingots show very little sulfide segregation. When sulfide regions do appear, they are toward the ingot edges. This is particularly evident in the bottoms of ingots 12, 13 and 14 (Figures 28b, 29b and 30b, respectively). The appearance of sulfides in the first parts of the ingots to solidify

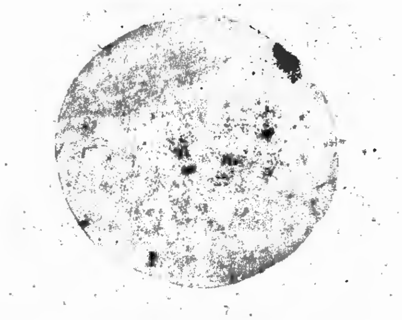

Figure 23a. Ingot No. 1, top. As cast. Transverse.

2% H_2SO_4, 3 minutes

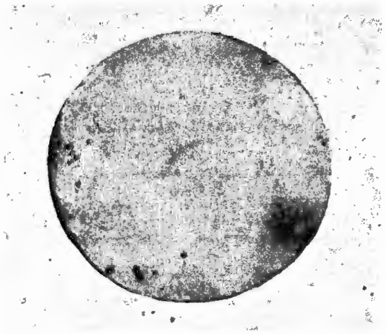

Figure 23b. Ingot No. 1, bottom. As cast. Transverse.

2% H_2SO_4, 3 minutes

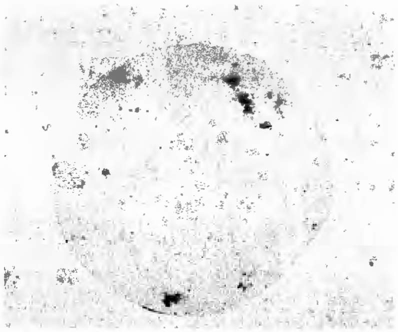

Figure 24a. Ingot No. 5, top. As cast. Transverse.

2% H_2SO_4, 3 minutes

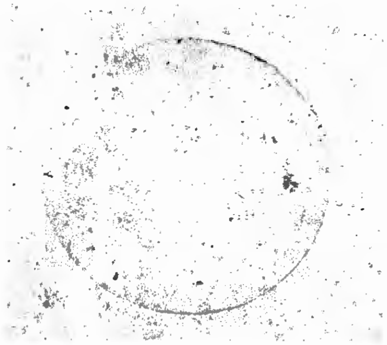

Figure 24b. Ingot No. 5, bottom. As cast. Transverse.

2% H_2SO_4, 3 minutes

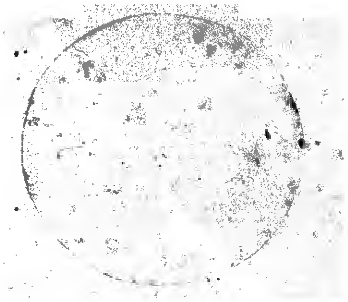

Figure 25a. Ingot No. 7, top. As cast. Transverse.

2% H_2SO_4, 3 minutes

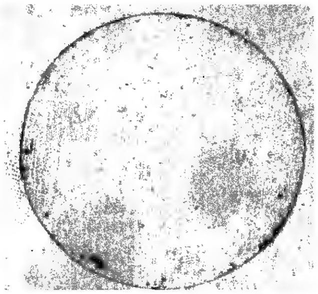

Figure 25b. Ingot No. 7, bottom. As cast. Transverse.

2% H_2SO_4, 3 minutes

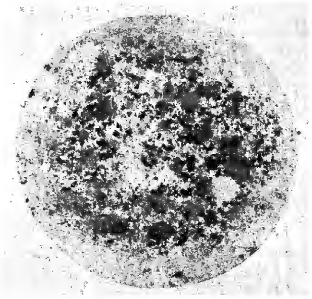

Figure 26a. Ingot No. 9, top. As cast. Transverse.

2% H_2SO_4, 3 minutes

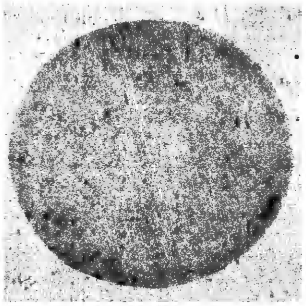

Figure 26b. Ingot No. 9, bottom. As cast. Transverse.

2% H_2SO_4, 3 minutes

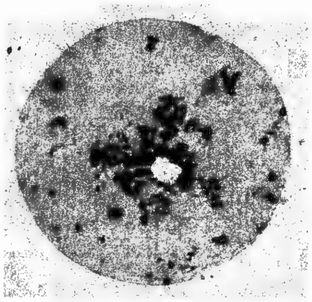

Figure 27a. Ingot No. 11, top. As cast. Transverse.

2% H_2SO_4, 3 minutes

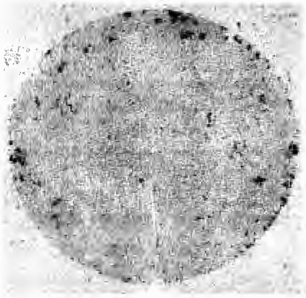

Figure 27b. Ingot No. 11, bottom. As cast. Transverse.

2% H_2SO_4, 3 minutes

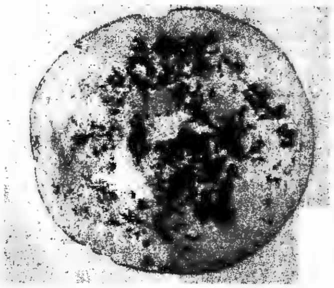

Figure 28a. Ingot No. 12, top. As cast. Transverse.

2% H_2SO_4, 3 minutes

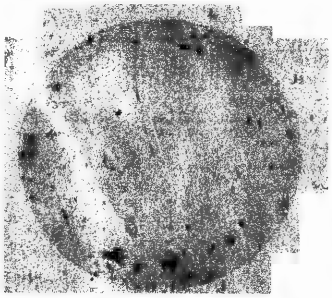

Figure 28b. Ingot No. 12, bottom. As cast. Transverse.

2% H_2SO_4, 3 minutes

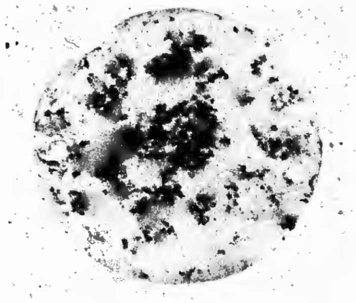

Figure 29a. Ingot No. 13, top. As cast. Transverse.

2% H_2SO_4, 3 minutes

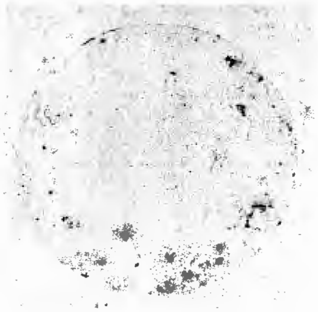

Figure 29b. Ingot No. 13, bottom. As cast. Transverse.

2% H_2SO_4, 3 minutes

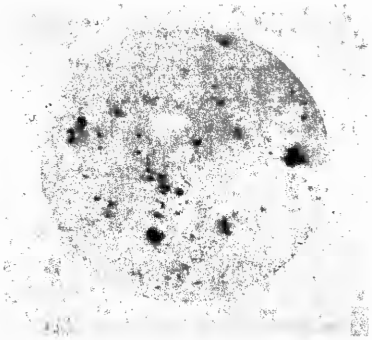

Figure 30a. Ingot No. 14, top. As cast. Transverse.

2% H_2SO_4, 3 minutes

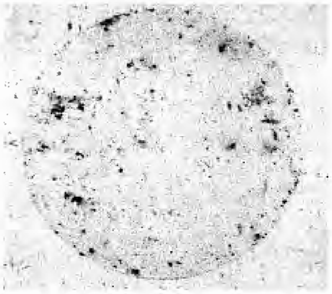

Figure 30b. Ingot No. 14, bottom. As cast. Transverse.

2% H_2SO_4, 3 minutes

indicate that these sulfide inclusions are refractory and were entrapped toward the outsides of the ingots where solidification was most rapid. The relative lack of sulfides toward the centers of the ingots indicates that solidification was sufficiently slow for the sulfides to coalesce and float upward during solidification. The sulfides are more numerous, darker in color, and more sharply outlined in the prints of the ingots to which rare earth metal was added. The prints of ingots 5, 7 and 9, Figures 24b, 25b and 26b, show less of the sharply outlined sulfides while ingots 1 and 11 (Figures 23b and 27b), to which no rare earth metal was added, show none of the sharply outlined, dark sulfides. The sulfide regions of ingots 1 and 11 have diffuse outlines.

The sulfur prints of the transverse sections of the ingot tops appear to the right of the corresponding bottom sections. The prints of the tops of ingots 5 and 7 (Figures 24a and 25a) show sulfides only near the edges. The tops of ingots 9, 12, 13 and 14 show sulfides throughout the cross sections. The tops of ingots 1 and 11, to which no rare earth metal was added, show sulfide segregation predominantly in the pipe region. The sulfides in the tops of ingots 1 and 11, as in the corresponding bottom sections, appear in patches which do not have the regular outlines or dark color of the sulfides in the ingots to which rare earth metal was added.

The difference in appearance of the sulfides in the ingots to which rare earth metal was added indicates that these sulfides are most probably rare earth sulfides. The much more numerous occurrence of these sulfides in the ingot tops shows that they floated upward during solidification of the ingots. The irregular sulfide regions in the tops of ingots 1 and 11 (no rare earth metal) are most probably due to sulfur enrichment of the last metal to solidify. This would mean that these regions are composed chiefly of iron sulfides or iron oxi-sulfides. The tops of ingots 9, 12 and 13, to which rare earth metal was added, show both types of sulfides.

To determine the relative cooling rates in the ingot tops and bottoms, the sections which had been sulfur printed were macroetched for grain structure. The macrostructures of the top and bottom sections of ingots 1, 11 and 13, which are typical, are shown in Figures 31, 32 and 33, respectively. In the ingot bottoms, the cooling rate was slow enough for large, columnar grains to form. In the ingot tops, the cooling rate was considerably more rapid as evidenced by the lack of columnar grains.

Microstructures showing the relative grain sizes in the top and bottom sections (same sections sulfur printed) are shown in Figures 34a, 34b and 34c. The grains are large in the ingot bottoms. The large, columnar grains are met toward the ingot centers by large, equi-axed grains. In the ingot tops, the grains are much smaller indicating a faster cooling rate. The very large grains in the ingot bottoms indicate that the cooling rate was sufficiently slow for

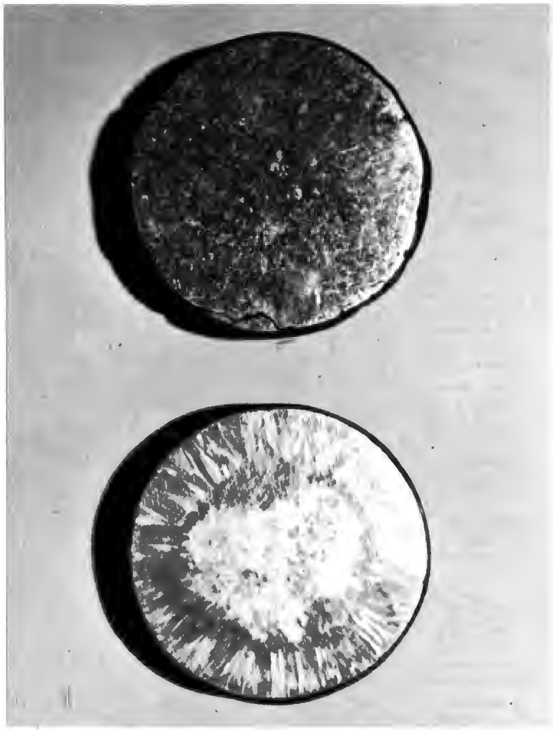

Figure 31. Ingot 1, macro-etched sections. Ingot top, above; bottom, below. 10% Nital, 2 minutes

Figure 32. Ingot 11, macro-etched sections. Ingot top, above; bottom, below. 10% Nital, 2 minutes

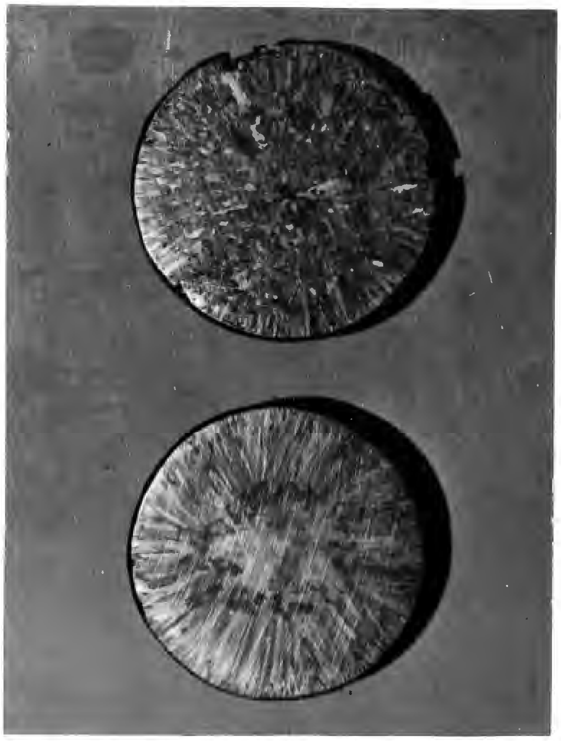

Figure 33. Ingot 13, macro-etched sections. Ingot top, above; bottom, below. 10% Nital, 2 minutes

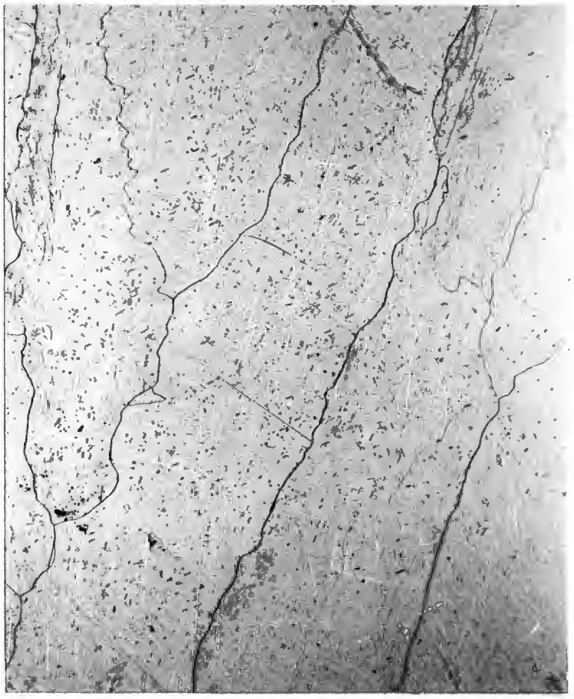

Figure 34a. Ingot No. 11, bottom, near edge. As cast, transverse. 50 X; 2% Nital

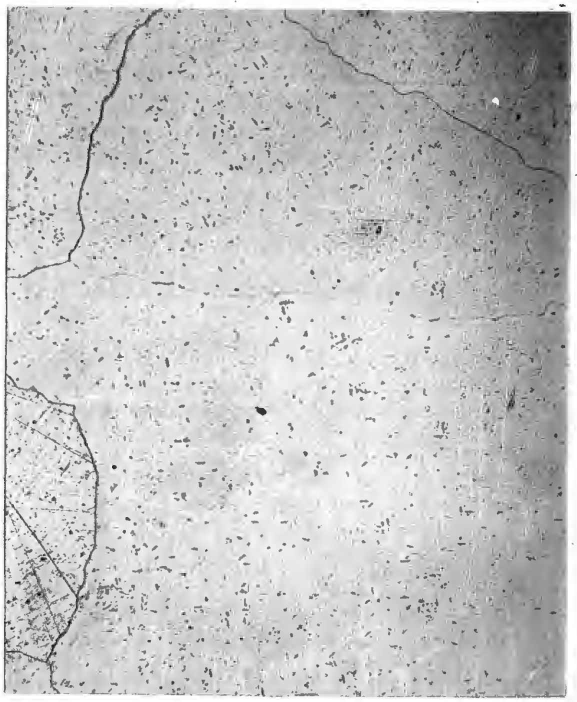

Figure 34b. Ingot No. 11, bottom, center. As cast, transverse. 50 X; 2% Nital

Figure 34c. Ingot No. 11, top, center. As cast, transverse. 50 X; 2% Nital

refractory compounds such as rare earth sulfides to float upward during solidification of the ingots. This would explain the much more numerous sulfide occurrence near the tops of the ingots to which rare earth metal was added.

If the sulfides in the rare-earth metal ingots are rare earth sulfides, then the slag-scum beads should show the same type of sulfides in the slag removed after the rare earth metal additions were made. The slag-scum beads from ingots 1, 5 and 14 were cut in half, polished, and sulfur printed. These prints are shown in Figures 35, 36 and 37. The beads were formed in layers by the slagging during and after the aluminum additions, and after the rare earth additions. The sulfur print of the slag bead from ingot 1, to which no rare earths were added, shows none of the dark, sharply outlined sulfides. The prints of ingots 5 and 14, however, to which 0.5 per cent rare earth metal was added, show a definite accumulation of sulfides in the outer layer--the layer which was slagged off after the rare earth metal additions. These sulfides are the dark, sharply outlined type.

From these evidences and the sulfur drops that occurred, it is concluded that the rare earth metal additions resulted in the formation of rare earth sulfides; these sulfides being refractory, many floated to the slag phase in the two-minute holding intervals. Most of these sulfides were removed in the subsequent slagging; those which were not were either entrapped toward the outsides of the

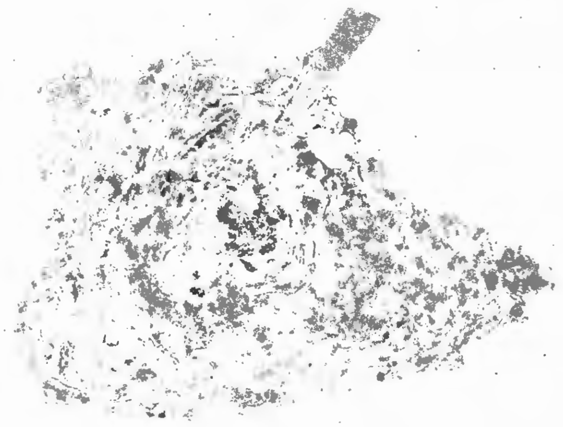

Figure 35. Heat No. 1, slag-scum bead.
Longitudinal section.

2% H_2SO_4, 3 minutes

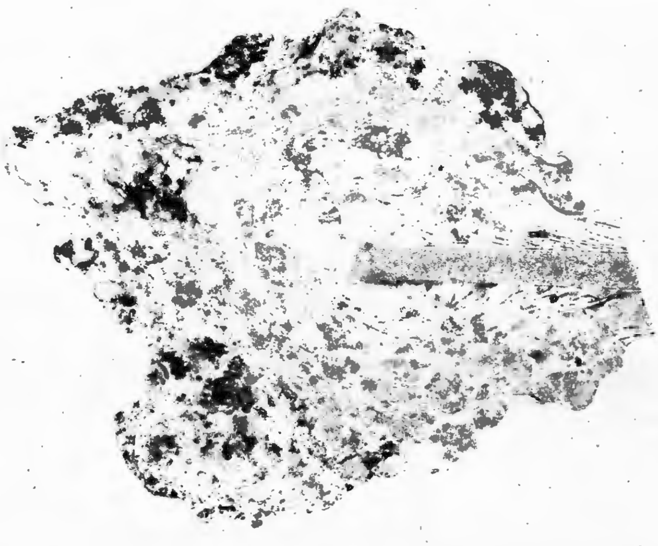

Figure 36. Heat No. 14, slag-scum bead.
Longitudinal section.

2% H_2SO_4, 3 minutes

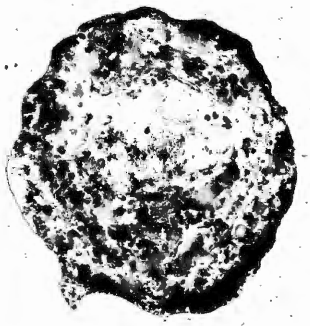

Figure 37. Heat No. 5, slag-scum bead. Transverse section.

2% H_2SO_4, 3 minutes

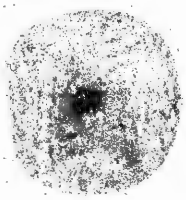

Figure 38. Armco iron punching. Transverse section.

2% H_2SO_4, 3 minutes

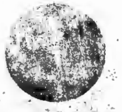

Figure 39. Bar 1-2. Hot rolled and cold swaged. Transverse section.

2% H_2SO_4, 3 minutes

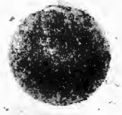

Figure 40. Bar 14-2. Hot rolled and cold swaged. Transverse section.

2% H_2SO_4, 3 minutes

ingots during solidification, or floated up toward the ingot tops. The relative lack of sulfides in ingots 5 and 7 indicate that most of the rare earth sulfides were removed in the slagging.

Figure 38 shows a sulfur print of an Armco iron punching, and Figures 39 and 40 prints of bars 1-2 and 14-2. The sulfide distribution is quite different in the rolled bars than in the cast ingots. Sulfide regions are broken up and redistributed in the hot working of iron and steel, illustrating the necessity of using cast structures in the study of desulfurization mechanisms.

6. Study of Inclusions

In the study of inclusions, use was made of projection of the microstructures onto the ground glass plate of the metallograph, special etching, and polarized light illumination. Table X lists the colors of some compounds which may be expected to appear as inclusions in the various ingots. The true colors of non-metallic inclusions will frequently show very clearly in polarized light while true colors rarely appear in white light. The polishing and etching technique is described in Appendix V.

Figure 41a shows the unetched microstructure of an Armco iron punching at 150 X. The microstructure shows a number of relatively large inclusions. These inclusions are mostly rounded and appear medium gray in color. They are relatively unattacked by a two per cent nital etch (Figure 41b) and exhibit definite outlines upon etching. When projected

TABLE X

COLORS OF CERTAIN OXIDES AND SULFIDES (26)

Compound	Color
FeO	black
FeS	black-brown
Al_2O_3	colorless
MnO	green
MnS	green
CeO_2	colorless
Ce_2O_3	gray green (powder)
Ce_2S_3	red
La_2O_3	white
La_2S_3	red-yellow
Nd_2O_3	light blue (powder)
Nd_2S_3	olive green (powder)

Figure 41a. Armco iron punching. Transverse.

150 X; Unetched

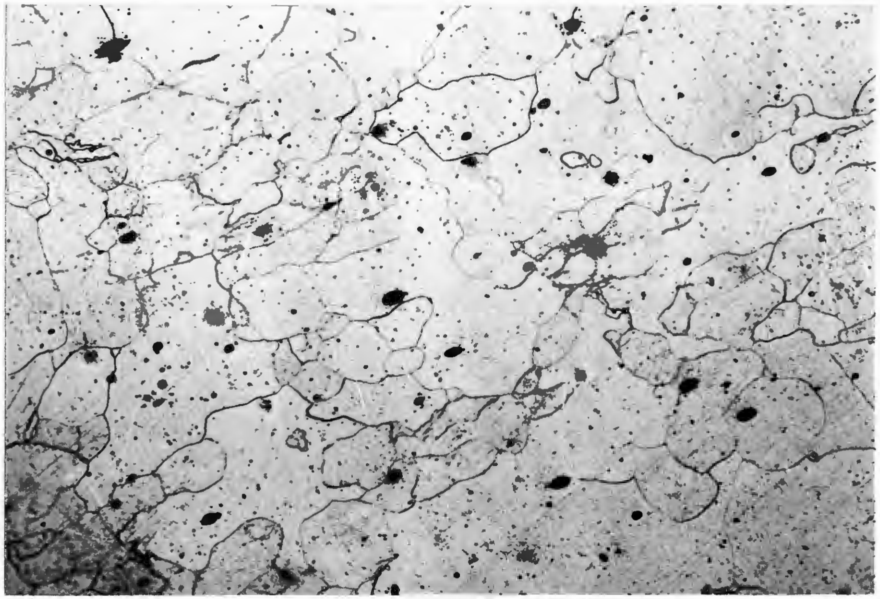

Figure 41b. Armco iron punching. Transverse.

150 X; 2% Nital

onto the ground glass plate of the metallograph with the unfiltered carbon-arc light source, these large inclusions appeared gray. In polarized light, they were black. Iron oxide (wüstite) inclusions are relatively unattacked by nital etching, appear gray when projected onto the ground glass plate, and black in polarized light. These evidences, together with the fact that commercial ingot iron contains up to 0.10 per cent oxygen, identifies these inclusions as being wüstite or wüstite rich. Many of the smaller inclusions appear bright white in polarized light. Their small size and appearance in polarized light indicate that many of these small inclusions are Al_2O_3 resulting from the ladle deoxidation with aluminum. Some of these smaller inclusions are black in polarized light indicating that some of them are also wüstite. Some are green in polarized light indicating that these are MnO and MnS. Iron sulfide inclusions, although some were undoubtedly present, were not identified.

In Figures 42 through 53 are shown the unetched microstructures of ingots 1, 5, 9, 11, 13 and 14 at 150 X. The photomicrographs show the inclusion contents at both the ingot tops and bottoms. The ingot sections shown are in the as-cast condition. Most of the inclusions are small in comparison to many which appear in the Armco iron punching. The photomicrographs were in each instance of the same surfaces as the sulfur prints discussed in the preceeding section.

The microstructures of the tops of ingots 1, 11 and 13 were taken from sections which were cut just below the

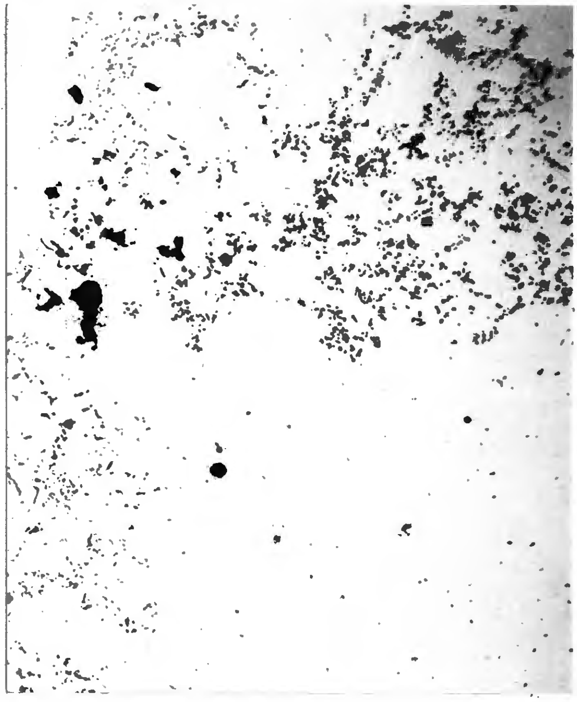

Figure 42. Ingot No. 1, top. As cast. Transverse. 150 X; Unetched

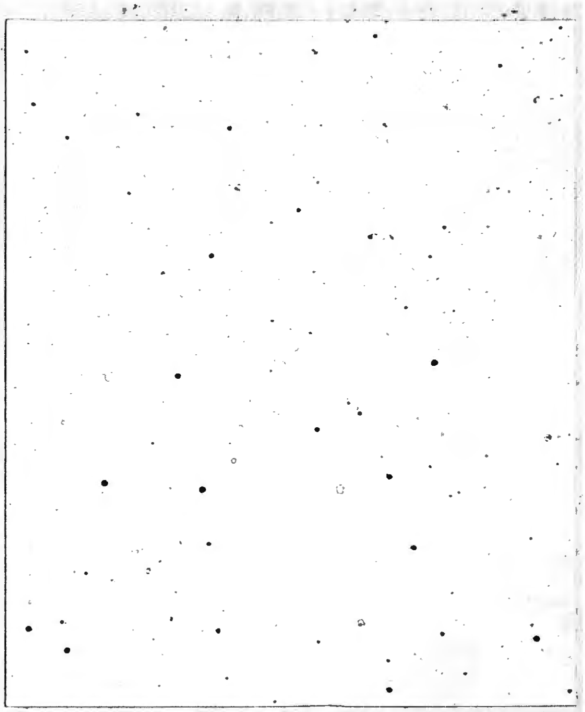

Figure 43. Ingot No. 1, bottom. As cast. Transverse. 150 X; Unetched

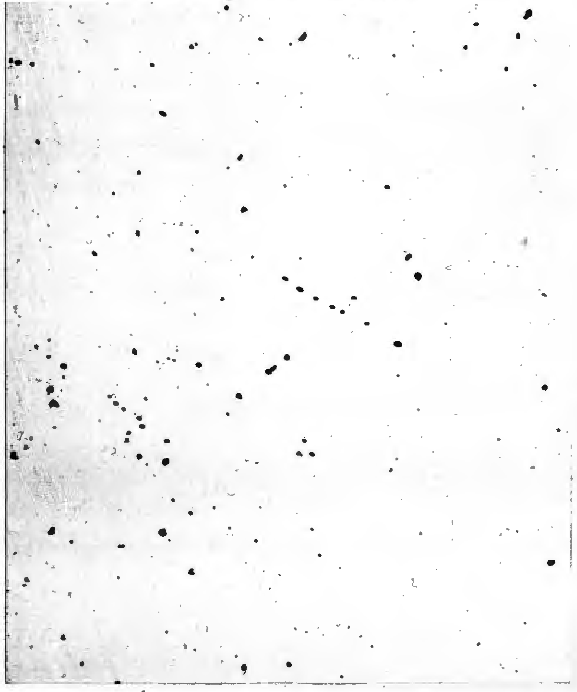

Figure 44. Ingot No. 5, top. As cast. Transverse. 150 X; Unetched

Figure 45. Ingot No. 5, bottom. As cast. Transverse. 150 X; Unetched

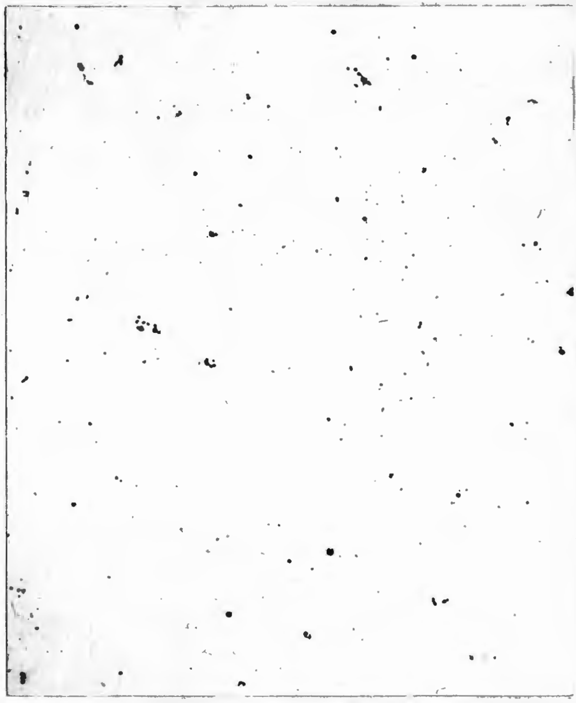

Figure 46. Ingot No. 9, top. As cast. Transverse. 150 X; Unetched

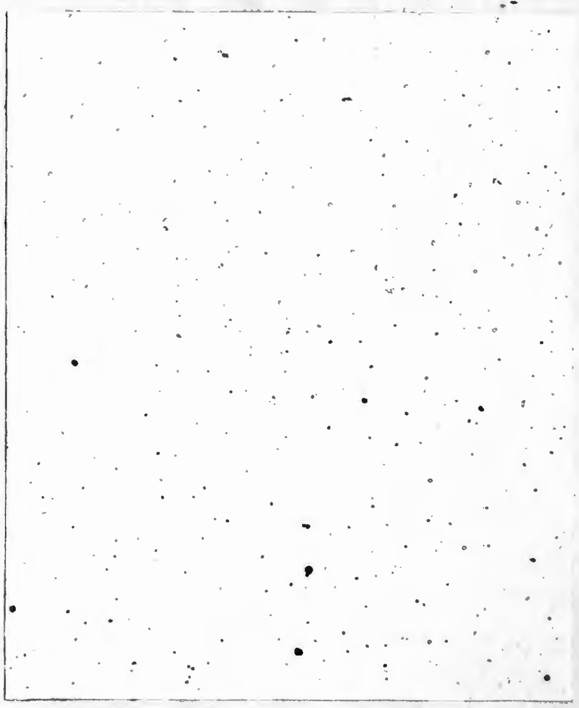

Figure 47. Ingot No. 9, bottom. As cast. Transverse. 150 X; Unetched

Figure 48. Ingot No. 11, top. As cast. Transverse. 150 X; Unetched

Figure 49. Ingot No. 11, bottom. As cast. Transverse. 150 X; Unetched

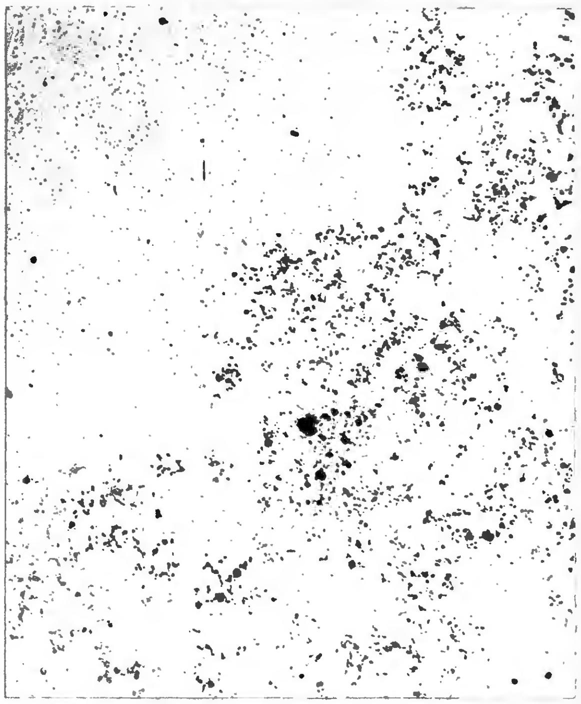

Figure 50. Ingot No. 13, top. As cast. Transverse. 150 X; Unetched

Figure 51. Ingot No. 13, bottom. As cast. Transverse. 150 X; Unetched

Figure 52. Ingot No. 14, top. As cast. Transverse. 150 X; Unetched

Figure 53. Ingot No. 14, bottom. As cast. Transverse. 150 X; Unetched

pipes. Near the pipes, clusters of inclusions appear. The first parts of the ingot to solidify are purer than the original liquid metal, while the last part to solidify, in the region of the pipe, tends to be enriched in certain impurities such as sulfur. Any high-melting, low specific gravity inclusions which were not entrapped in earlier solidification would also appear in the pipe region.

In Figure 54a is shown, at 500 X, the microstructure of an inclusion cluster which appeared near the pipe of ingot 1. These inclusions appeared gray when projected onto the ground glass plate and black in polarized light. The same area is shown in Figure 54b after sulfur printing for 20 seconds in a two per cent sulfuric acid solution. The sulfur printing pitted the inclusions. This is particularly evident in the large round inclusion. This indicates that these inclusions are wüstite with some dissolved FeS which was attacked by the sulfuric acid.

In Figure 55a is shown, at 500 X, the unetched microstructure of an inclusion cluster which appeared in the pipe region of ingot 13. These inclusions appeared light gray when projected onto the ground glass plate, and dark brown, almost black, in polarized light. In Figure 55b is shown the same area after sulfur printing for 20 seconds. The inclusions were heavily attacked by the sulfur printing, indicating that they are relatively pure sulfides. The appearance of these inclusions in polarized light indicates that they are primarily FeS. Pure FeS is black-brown. MnS is green,

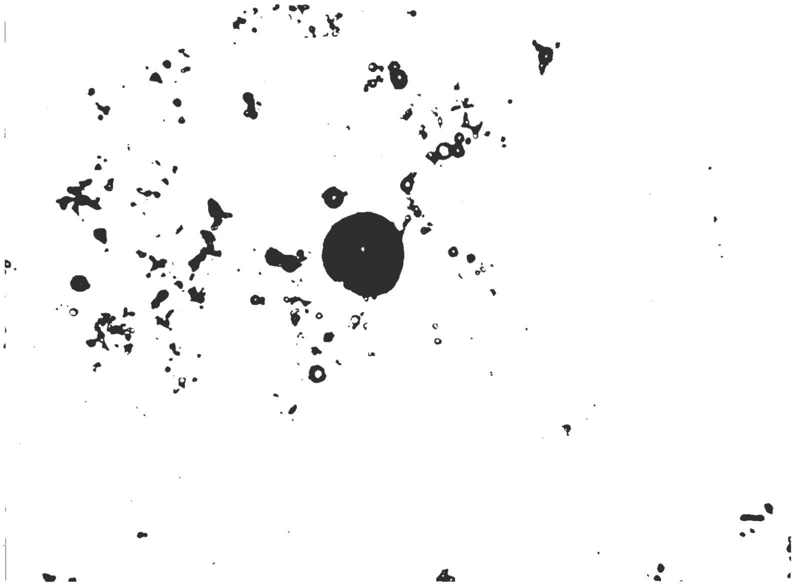

Figure 54a. Ingot No. 1, top. As cast. Transverse section.

500 X; Unetched

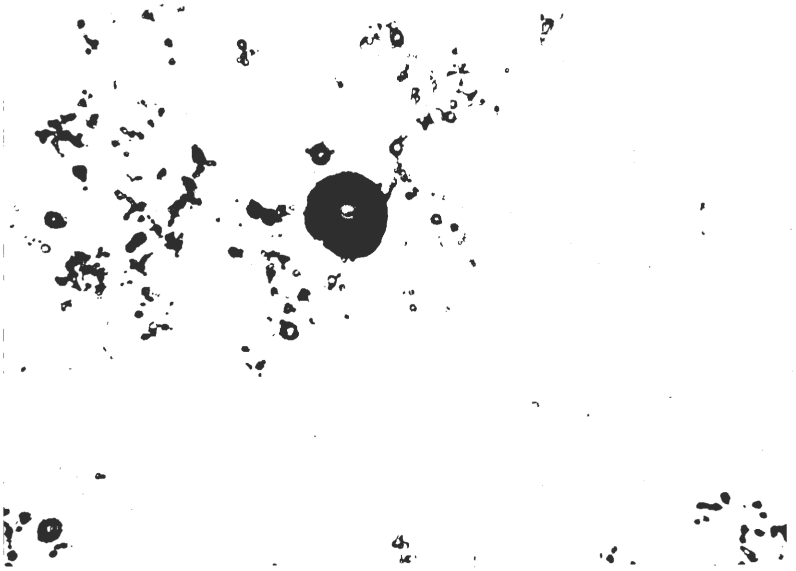

Figure 54b. Ingot No. 1, top (same area as above). As cast. Transverse section.

500 X; 2% H_2SO_4, 20 seconds

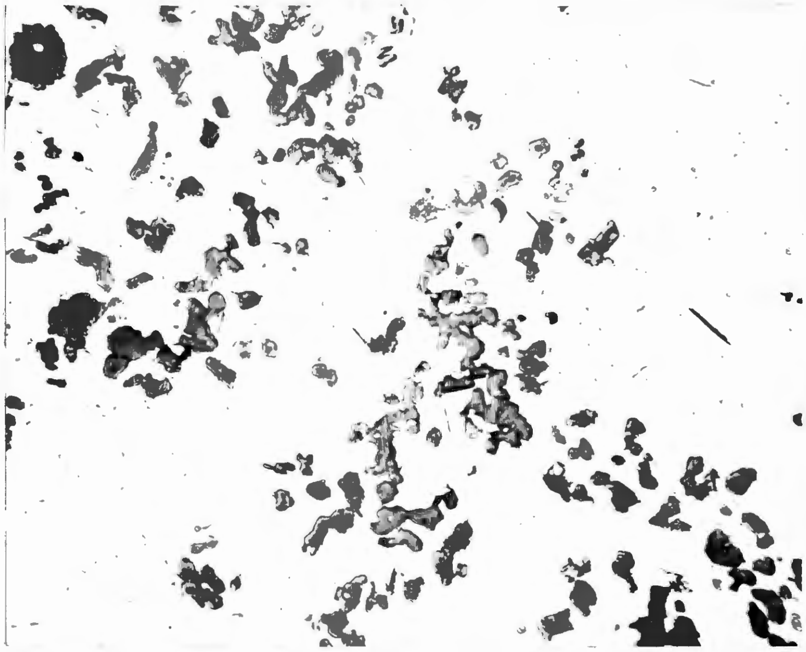

Figure 55a. Ingot No. 13, top. As cast. Transverse section.

500 X; Unetched

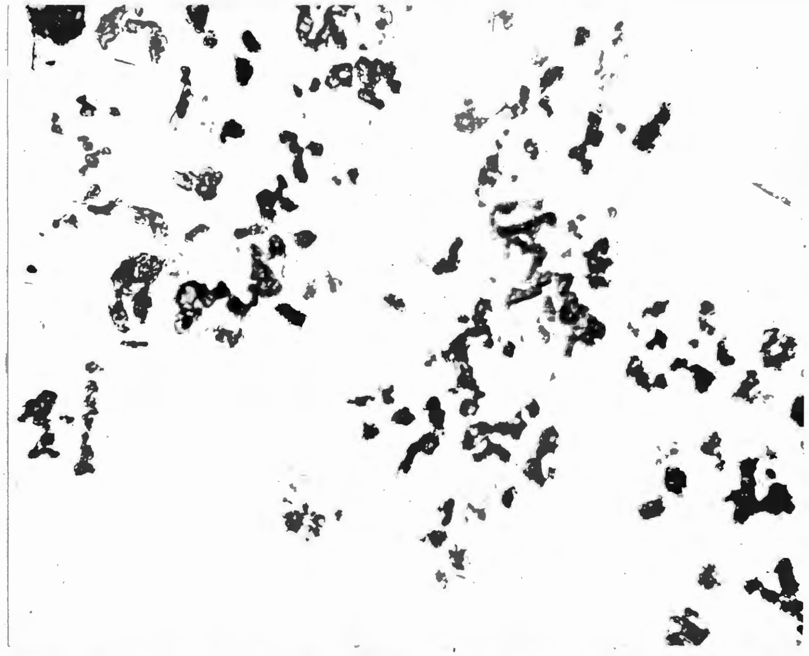

Figure 55b. Ingot No. 13, top (same area as above). As cast. Transverse section.

500 X; 2% H_2SO_4, 20 seconds

Ce_2S_3 is red, and La_2S_3 is red-yellow.

Further examination of this microstructure in polarized light revealed the presence of many very small red and orange inclusions dispersed throughout the matrix. An occasional large orange-red inclusion appeared which was apparently composed of a number of the smaller inclusions. From Table X it is seen that only Ce_2S_3 is red and La_2S_3 is red-yellow. Singleton, op. cit., had observed small red and orange inclusions in steel to which he had added cerium. By electrolytic extraction, he identified these small red and orange inclusions as Ce_2S_3.

Examination of the other ingots to which rare earth metal had been added also showed these red and orange inclusions in varying numbers. Most of these inclusions were well dispersed, with only occasional agglomerates appearing. These agglomerates were more numerous in the ingot tops than in the bottoms. These red and orange inclusions were conspicuously absent in the ingots to which no rare earth metal had been added.

Examination in polarized light of the slag-scum beads from ingots 1, 5 and 14 revealed many of the red and orange inclusions in the slag layer removed after the rare earth metal additions. In other areas they did not appear. This evidence strongly indicates that these inclusions are rare earth sulfides.

The appearance of FeS in the pipe region of ingot 13 indicates that normal sulfur enrichment occurs in the last metal to solidify involving the uncombined sulfur.

The majority of the small dispersed inclusions shown in the other microstructures appear bright white in polarized light. Al_2O_3 is colorless and appears white in polarized light. In view of the aluminum deoxidation, most of these numerous white inclusions are most probably Al_2O_3.

There appeared in all of the ingots, small dispersed bright green inclusions. Ce_2O_3 is gray green and Nd_2S_3 is olive green. The numerous occurrence, however, of these green inclusions in the ingots to which no rare earths were added strongly indicates that they are MnO and MnS which are both green. Armco Steel Corporation gives, as a typical analysis of their ingot iron, a manganese content of 0.028 per cent.

X. CONCLUSIONS

Mischmetal additions to basic-lined induction heats of ingot iron in quantities ranging from 0.1 to 0.5 per cent result in desulfurization--the efficiency of desulfurization increasing with increasing quantities of mischmetal additions. The sulfur drops noted were accompanied by decreased hot shortness for the 0.1 per cent additions while the 0.5 per cent additions resulted in no decrease in hot shortness.

Oxygen contents of more than 0.025 per cent tended to increase hot shortness. Oxygen contents below this amount appeared to have little effect on hot shortness.

The apparent decrease in hot shortness with increasing residual aluminum contents was most probably due to accompanying decreases in oxygen contents.

No conclusions can be made on the relative effects of mischmetals containing 25 and 30 per cent lanthanum, respectively.

The rare earth oxides may have an effect on hot workability, perhaps as nucleating agents; however, results are erratic, probably due to the method of addition.

Copper contents up to 0.081 per cent have no apparent effect on hot shortness.

Decreased hot workability occurring in heats to which 0.5 per cent mischmetal had been added may be a result of embrittling of the gamma-iron as a result of solid solubility.

For heats to which 0.5 per cent mischmetal had been added, a total holding interval of three minutes would have resulted in more complete reaction of the mischmetal with accompanying lower residual rare earth contents.

From a study of inclusions aided by sulfur printing, the reaction mechanism appears to be, that in the absence of excessive oxygen, the rare earth metals react with sulfur in the molten metal. The rare earth sulfides formed, being refractory and having densities lesser than that of iron, float upward to the slag phase where they may be removed. If left for sufficient time in an oxidizing slag, the rare earth sulfides will be oxidized with the sulfur reverting to the melt. If the ingot cooling rate is sufficiently slow, the remaining rare earth sulfides tend to coalesce and float upward during solidification. The sulfides which do not have sufficient time to coalesce appear as fine inclusions in the matrix. In polarized light, these rare earth sulfides appear red or orange.

SUGGESTIONS FOR FURTHER STUDY

Although desulfurization occurred in heats melted in air, heats melted in neutral and reducing atmospheres would also be of interest. Heats could also be studied in which mischmetal is added before deoxidation is carried out. Vacuum melting would enable further study on the effects of oxygen and other occluded gases.

The effect of copper on hot shortness in ingot iron could be studied--both with and without rare earth additions.

Effects of rare earth oxides in ingot iron could be studied by adding the oxides as briquettes.

The holding times between rare earth metal additions and pouring could be studied further, particularly for additions in excess of 0.3 per cent.

Electrolytic extraction of inclusions would enable their identification.

Pure cerium and lanthanum could be added to separate heats for purposes of comparison.

For studying reaction mechanisms, use could be made of radioactive isotopes. Sulfur 35 (half-life 37.1 days, beta decay, 0.167 Mev) could be used to study sulfur reaction mechanisms in conjunction with auto-radiography. Radioactive isotopes of cerium may also be used--perhaps for studying rare earth-oxygen reaction mechanisms. Cerium 139 has a half life of 140 days, cerium 141 a half-life of 33 days, and cerium 144 a half-life of 282 days.

APPENDIX I

High-Frequency Induction Melting

All of the heats were made in a 17-pound, tilting-type, Ajax-Northrup induction furnace. A charge of 11 pounds of Armco iron punchings was used for each heat. Additions and slagging were accomplished by use of low-carbon steel welding rods. The high-frequency power source was a 20-kilowatt Ajax-Northrup, hydrogen-type, mercury spark-gap converter. Such units are described in a number of references. The advantages of induction heating are the speed at which heats can be made, and the close control that can be maintained on composition. A slag cover is not necessary. The furnaces are well adapted for both atmosphere and vacuum melting. The electromagnetic stirring action provides constant stirring of the components.

The packing of the crucibles is much the same for the different types. Magnesia crucibles were used in this investigation. The coil was first insulated with a double layer of mica sheet. Care was taken in inserting the mica to prevent its tearing. Magnesia powder (Normag) was then rammed firmly around the crucible to within one-half inch of the top. Three parts of powdered magnesia were then mixed intimately with one part of western bentonite and just enough water was added to produce a cohesive mass. This paste was then packed around the top of the crucible and dried overnight. Several preliminary heats were made with graphite crucibles packed with graphite powder. Special care was taken in inserting the mica sheet and in ramming the graphite powder to prevent the powder from causing arcing between the coils.

An arc between the coils will not melt the coils for a minute or so, but as a safety precaution, the power was immediately cut in the few instances in which arcing occurred. The packing powders were re-used after grinding and sieving. The magnesia crucibles were used for two heats by covering the furnace with insulating bricks while cooling to prevent cracking from thermal shock.

The making of heats is fairly safe if necessary precautions are taken. High-frequency melting is a two-man operation--both for efficiency and for safety. Operating instructions and safety precautions must be obtained before attempting a heat.

The converter unit is protected from overload by fuses. It is necessary to flush the electrode chamber for 15 minutes before the power is turned on to prevent an explosion when the arc is struck by the electrodes. A mica blowout window prevents serious explosion but mercury may be thrown out. A check of the converter power lines with an ammeter revealed that the maximum power that could be drawn without blowing a fuse was 17 kilowatts. As the power fluctuates one or two kilowatts during operation, a safe operating range was found to be 14-16 kilowatts. The cooling water for both the furnace and the converter (separate) must be turned on prior to operating.

The operator must never, of course, touch the coils or exposed lead wires while the power is on. He should wear protective clothing. Asbestos coats, gloves and leggings afford excellent protection. A plastic face shield will protect the face against stray sparks. The eyes should be protected by welding glasses.

The furnace should be covered with insulating bricks to conserve heat. During the initial meltdown, bridging will occur if too much metal is added at once. Additions should always be made in small pieces to prevent freezing of the top of the melt. Special care should be taken in making some additions to ferrous melts. Aluminum will spark very badly and splash hot metal if added too rapidly. Care must always be taken to prevent water or moisture from coming into contact with the hot metal. This will result in a violent explosion. Preheating of the charge, all additives, and the ingot mold will drive out the moisture. The fact that the mold appears to be dry should never be taken as a guide. It takes little moisture to cause an explosion. Before pouring of the tilting-type furnace, care should be taken to insure that the guides are properly seated in the tilting apparatus. The power must always be cut before pouring.

APPENDIX II

Logs of Heats Made

Heat No. 1-A --Charge: 11 Pounds Armco Iron Punchings

Additions: 75 Grams Aluminum

Time	Event	Temp., °F
1:30	Power on	
2:20	Melt	
2:27	Added	2890
2:31	75 gms aluminum	
2:31.5	Slagged	2900
2:32	Poured	

Heat No. 1 ----Charge: 11 Pounds Armco Iron Punchings

Additions: 100 Grams Aluminum

Time	Event	Temp., °F
8:02	Power on	
9:23	Melt	
9:32	Added	2900
9:38	100 gms aluminum	
9:39	Slagged	2900
9:40	Poured	

Heat No. 3 ----Charge: 11 Pounds Armco Iron Punchings

Additions: 100 Grams Aluminum
5.2 Grams Mischmetal

Time	Event	Temp., °F
12:00	Power on	
1:20	Melt	
1:30	Added	2900
1:36	100 gms aluminum	
1:36.5	Slagged	
1:37	Added 5.2 gms mischmetal	2910
1:38	Slagged	
1:39	Poured	

Heat No. 4 --Charge: 11 Pounds Armco Iron Punchings

Additions: 100 Grams Aluminum
15.0 Grams Mischmetal

Time	Event	Temp., °F
6:45	Power on	
8:10	Melt	
8:17	Added	2900
8:22	100 gms aluminum	
8:23	Slagged	
8:23.5	Added 15.0 gms mischmetal	2890
8:24.5	Slagged	
8:25.5	Poured	

Heat No. 5 --Charge: 11 Pounds Armco Iron Punchings

Additions: 100 Grams Aluminum
25.1 Grams Mischmetal

Time	Event	Temp., °F
12:48	Power on	
2:10	Melt	
2:18	Added	2900
2:23	100 gms aluminum	
2:23.5	Slagged	
2:24	Added 25.1 gms mischmetal	2890
2:25	Slagged	
2:26	Poured	

Heat No. 7 --Charge: 11 Pounds Armco Iron Punchings

Additions: 100 Grams Aluminum
5.3 Grams Lan-cer-amp

Time	Event	Temp., °F
11:25	Power on	
12:40	Melt	
12:48	Added	2900
12:54	100 gms aluminum	
12:54.5	Slagged	
12:55	Added 5.3 gms Lan-cer-amp	2910
12:56	Slagged	
12:57	Poured	

Heat No. 8 --Charge: 11 Pounds Armco Iron Punchings

Additions: 100 Grams Aluminum
15.3 Grams Lan-cer-amp Metal

Time	Event	Temp., °F
3:15	Power on	
4:36	Melt	
4:45	Added	2900
4:50	100 gms aluminum	
4:51	Slagged	
4:51.5	Added 15.3 gms Lan-cer-amp	2900
4:52.5	Slagged	
4:53.5	Poured	

Heat No. 9 --Charge: 11 Pounds Armco Iron Punchings

Additions: 100 Grams Aluminum
25.0 Grams Lan-cer-amp Metal

Time	Event	Temp., °F
12:00	Power on	
1:23	Melt	
1:30	Added	2900
1:35	100 gms aluminum	
1:35.5	Slagged	
1:36	Added 25.0 gms Lan-cer-amp	2910
1:37	Slagged	
1:38	Poured	

Heat No. 10 --Charge: 11 Pounds Armco Iron Punchings

Additions: 100 Grams Aluminum
5.0 Grams Rare Earth Oxide Mixture

Time	Event	Temp., °F
2:28	Power on	
3:50	Melt	
4:00	Added	2910
4:05	100 gms aluminum	
4:06	Slagged	
4:07	Added 5.0 gms rare earth oxide	2900
4:07.5	Rare earth oxide stirred into melt	
4:08.5	Slagged	
4:09	Poured	

Heat No. 11 --Charge: 11 Pounds Armco Iron Punchings

Additions: 100 Grams Aluminum
10.0 Grams Rare Earth Oxide Mixture

Time	Event	Temp., °F
7:15	Power on	
8:40	Melt	
8:51	Added	2900
8:57	100 gms aluminum	
8:57.5	Slagged	
8:58.5	Added 10.0 gms rare earth oxide	2910
8:59	Rare earth oxide stirred into melt	
9:00	Slagged	
9:00.5	Poured	

Heat No. 12 --Charge: 11 Pounds Armco Iron Punchings

Additions: 100 Grams Aluminum
5.1 Grams Lan-cer-amp Metal
10.0 Grams Rare Earth Oxide Mixture

Time	Event	Temp., °F
11:40	Power on	
12:48	Melt	
12:58	Added	2900
1:03	100 gms aluminum	
1:03.5	Slagged	
1:04.5	Added 5.1 gms Lan-cer-amp	2890
1:05	Added 10.0 gms rare earth oxide	
1:05.5	Rare earth oxide stirred into melt	
1:06	Slagged	
1:06.5	Poured	

Heat No. 13 --Charge: 11 Pounds Armco Iron Punchings

Additions: 100 Grams Aluminum
15.1 Grams Lan-cer-amp Metal
10.0 Grams Rare Earth Oxide Mixture

Time	Event	Temp., °F
8:15	Power on	
9:37	Melt	
9:45	Added	2890
9:50	100 gms aluminum	
9:50.5	Slagged	
9:51.5	Added 15.1 gms Lan-cer-amp	2910
9:52	Added 10.0 gms rare earth oxide	
9:52.5	Rare earth oxide stirred into melt	
9:53	Slagged	
9:53.5	Poured	

Heat No. 14 --Charge: 11 Pounds Armco Iron Punchings

Additions: 100 Grams Aluminum
25.1 Grams Lan-cer-amp Metal
10.0 Grams Rare Earth Oxide Mixture

Time	Event	Temp., °F
2:00	Power on	
3:23	Melt	
3:31	Added	2900
3:36	100 gms aluminum	
3:36.5	Slagged	
3:37.5	Added 25.1 gms Lan-cer-amp	2910
3:38	Added 10.0 gms rare earth oxide	
3:38.5	Rare earth oxide stirred into melt	
3:39	Slagged	
3:39.5	Poured	

APPENDIX III

Hot-Rolling and Swaging

After cutting the ingots in half, and taking sections for metallographic examination and sulfur printing, the machined bars were placed in the pre-heated, resistance-type furnace. The bars had been machined to one-inch diameters. The furnace was heated to 870°C in order to remain just below the hot-short region. Five to six hours were required to bring the furnace to temperature. No protective atmosphere was used in the furnace. As considerable oxide forms at this temperature, identification of the bars had to be watched closely. Each bar was heated for 30 minutes prior to rolling.

Guide tables of steel sheet and angle iron were constructed for both the entrance and exit sides of the rolls to both facilitate guiding the bars into the rolls and catching them on the exit side.

Eight passes were made on each bar. Two-high rolling mills of the type used usually have indentations of alternating rounds and ovals. The bars were passed in succession from the 1 1/8-inch oval to the 5/8-inch round. When passing from rounds into ovals, the bars were simply placed on the guide table, lined with the opening in the rolls, and tapped on the trailing end to push them into the moving rolls. More difficulty was encountered in passing from ovals into rounds as the bars had a tendency to twist. This was overcome by tapping the bars into position before starting the rolls. This procedure, however, was not successful in making the second pass--from the 1 1/8-inch oval into the 7/8-inch round. The motor would not drive the rolls with an obstruction of this size. This pass was made by guiding the bars into the moving rolls with tongs. The bars did not twist but extreme care had to be taken to prevent the tongs from being pulled into the rolls.

Two passes could be made before reheating of the bars was necessary. The last pass on each bar was made cold to remove mill-scale and increase the extent of cold working.

The cold swaging was done in six passes. The die sizes used were: 0.650, 0.600, 0.550 and 0.500 inch, respectively. The dies were well oiled before inserting into position to prevent sticking. The bars were passed into the dies by using a pipe with an inside diameter of one inch and a rod with an outside diameter of one inch. The bars were placed in the pipe and thrust into the swaging dies by using the rod as a plunger.

In making the 0.500-inch pass, a ridge usually developed which caused the bars to rotate at the same speed as the dies. The bars are supposed to rotate, but at a speed somewhat slower than the dies. This difficulty was overcome by grasping the revolving bars firmly in gloved hands and restricting the revolving until the ridges completely disappeared. The bars were passed through the 0.500-inch die three times to insure uniform working and symmetry.

As in induction melting, rolling and swaging is a two-man operation. Asbestos gloves were worn to prevent burns. It should be emphasized that extreme caution must be exercised in passing the hot metal into the rolls.

APPENDIX IV

Sulfur Printing

Sulfur printing, or Baumann printing, was originated by Heyn and Bauer in 1906 and was modified by Baumann. The method is described in a number of textbooks and technical papers, as well as in the ASTM Standards. Sulfur printing affords a convenient means of detecting and permanently recording the distribution of sulfur in iron and steel.

The method consists essentially of placing in intimate contact on a prepared metal surface, photographic bromide paper which has been previously soaked in a dilute solution of sulfuric acid in water.

The reaction of the sulfuric acid with the sulfide regions of the iron or steel produces hydrogen sulfide gas, which reacts with the silver bromide in the paper emulsion, forming a characteristic brown to gray-black deposit of silver sulfide. The reactions may be expressed as follows:

$$MeS + H_2SO_4 \rightleftarrows MeSO_4 + H_2S$$

$$H_2S + 2AgBr \rightleftarrows Ag_2S + 2HBr$$

In this investigation, sections were cut from the ingots at approximately one-half inch from the bottoms, and at the tops near the beginning of the pipes. These sections were then ground on a coarse belt grinder. This was followed by grinding through the 2, 1, 0 and 00 emery papers. The sections were washed thoroughly with a soap solution, rinsed with methyl alcohol, and dried under a warm air blast.

AZO F-4 contact printing paper was soaked for five minutes in a two per cent solution of sulfuric acid in water. Any photographic bromide paper would have worked equally as well. Contrary to usual requirements for the handling of photographic paper, the entire operation may be carries out in daylight. A two per cent solution of hydrochloric acid in water works equally as well. The concentrated sulfuric acid used to prepare the solution must be clear or the prints have a tendency to discolor and obliterate the printing of the sulfide regions.

After soaking the photographic paper, the paper was placed emulsion side up on a ground glass plate upon which a paper towel had been placed to insure intimate contact. The excess solution was removed from the emulsion side of the paper with a paper towel and the prepared surface of the specimen was pressed firmly onto the printing paper. Contact was maintained for three minutes for all prints. The prints were then washed for five minutes to remove the remaining acid and fixed in a standard hypo solution. Failure to wash the prints in running water prior to the fixing resulted in the hypo solution quickly becoming too acid to fix properly. After fixing for fifteen minutes, the prints were washed for one hour in running water and dried.

The slag samples and rolled bars were printed in exactly the same manner. Special care was taken in printing the slag specimens to insure that all of the excess acid was removed from the paper emulsion before printing. The slag samples were porous and any acid would have flowed into the pores resulting in false indications of the sulfide regions.

APPENDIX V

Polishing, Etching, and Metallography

The polishing of any metal with the aim of preserving non-metallic inclusions is a tedious task. This is especially true for softer metals such as ingot iron. Not only is there a great tendency for inclusions to be pulled out, but there is also the danger of flow in the polished surface resulting in pseudo-structures.

Care was taken throughout the grinding and polishing to use gentle pressure for each operation. Gentle pressure tends to keep flow and pulling out of inclusions at a minimum. Each step in the grinding and polishing was carried just to completion and no further in an attempt to preserve as many of the inclusions as possible.

The specimens were first ground on the number 120 belt grinder and then on the number 320 belt grinder. The specimens were then ground successively through the 2, 1, 0, 00 and 000 emery papers. At each change of emery paper, the specimens were washed thoroughly and grinding was resumed in a direction perpendicular to the previous grinding.

After grinding on the 000 emery paper, the specimens were washed and polished for approximately four minutes on a billiard-cloth lap wheel with levigated alumina abrasive. The specimens were rotated counterwise to the rotation of the lap wheel.

The specimens were washed thoroughly and polished on a selvyt-cloth lap wheel with Linde B abrasive. Instead of rotating counterwise to the lap, the specimens were held stationary for approximately five seconds and then rotated

90 degrees. The surfaces were usually scratch-free in three or four minutes. Prolonged polishing on either lap wheel resulted in most of the inclusions being pulled out.

Etching for grain boundaries was done with a two per cent nital solution by immersion. Special etching of inclusions was done by immersing the specimens for 10 seconds in a 10 per cent nital solution, and by sulfur printing for 20 seconds as described in Appendix IV. The macroetching was done by immersing the specimens for two minutes in a 10 per cent nital solution.

The photomicrographs were made on a Bausch and Lomb metallograph with a carbon-arc illuminating source. Photographic film was used for the lower magnifications and metallographic plates were used for the magnifications of 500 diameters.

BIBLIOGRAPHY

1. Vogel, R. Uber Cer-Eisenlegierungen. Zeitschrift für anorganische und allgemeine Chemie. Germany. Vol. 99, p. 30 (1917)

2. Allison, F. G., and Rock, M. M. Studies of the macrostructure of cast steel. Chemical and Metallurgical Engineering. Vol. 23, pp. 383-389 (1920)

3. Burgess, G. K., and Woodward, R. W. Manufacturing and properties of steel plates containing zirconium and other elements. National Bureau of Standards, Technical Paper 207. 1921.

4. Spring, L. W. Adds cerium to brass and iron. Foundry. Vol. 50, pp. 542-544 (1922)

5. Gillett, H. W., and Mack, E. L. Experimental production of alloy steels. U. S. Bureau of Mines. Bulletin 199. 1922.

6. Gillett, H. W., and Mack, E. L. Molybdenum, cerium and related alloy steels. N. Y., The Chemical Catalog Co., Inc., 1925. p. 226.

7. Post, C. B., Schoffstall, D. G., and Beaver, H. O. Hot-workability of stainless steel improved by adding cerium and lanthanum. Journal of Metals. Vol. 3, pp. 973-977B (1951)

8. Berry, C. D., and Dorvell, A. A. Effect of cerium on ductility and impact strength of steel. American Foundryman. Vol. 20, pp. 45-46 (Dec. 1951)

9. Knapp, W. E., and Bolckom, W. T. Rare earths improve properties of many ferrous metals. Iron Age. Vol. 169, pp. 129-134 (Apr. 24, 1952)

.0. Knapp, W. E., and Bolckom, W. T. Rare earths improve properties of many ferrous metals. Iron Age. Vol. 169, pp. 140-143 (May 1, 1952)

1. Lillieqvist, G. A., and Michelson, C. G. Properties of cast steels improved with rare earth element additions. Journal of Metals. Vol. 4, pp. 1024-1031 (1952)

.2. Lillieqvist, G. A. The effect of rare earth additions on the properties of cast steels. Metals Review. Vol. 26, p. 8 (Apr. 1953)

13. Post, C. B., and Beaver, H. O. Rare earths in stainless brought up to date. Iron Age. Vol. 171, pp. 148-149 (June 4, 1953)

14. Snellman, M. G. A study of desulphurization of steel with rare earths. Thesis, University of Pittsburg, Pittsburg, Pennsylvania (1953)

15. Russell, J. V. Rare earth additions affect surface quality of low carbon steel. Journal of Metals. Vol. 6, pp. 438-442 (1954)

16. Henke, R. H., and Lula, R. A. Rare earths counteract hot rolling defects in stainless steel. Journal of Metals. Vol. 6, pp. 883-888 (1954)

17. Tisdale, N. F., and Tisdale, N. F. Jr. Fine-grained iron and steel. U. S. Patent 2,683,661, July 13, 1954.

18. Jepson, J. O., and Duwez, P. Partial phase diagram of the iron-cerium system. American Society for Metals. Transactions. Vol. 47, pp. 543-553 (1955)

19. Jackson, W. L. Rare earths in steel castings. Metallurgia. Vol. 54, pp. 233-238 (Nov. 1956)

20. Tisdale, N. F., and Tisdale, N. F. Jr. Composition of rare earth oxides for production of iron and steel. Canadian Patent 530,556, September 18, 1956.

21. Wilson, W. G. Rare earths homogenize ingots. Iron Age. Vol. 182, pp. 78-79 (Oct. 2, 1958)

22. Tageev, V. M., and Smirnov, Yu. D. Prevention of A-segregation in the solidification of steel by treatment with rare earth elements. Brutcher Translation No. 4060 (1958)

23. Perkins, R. A., and Binder, W. O. Improving hot ductility of 310 stainless. Journal of Metals. Vol. 9, pp. 239-245 (Feb. 1959)

24. Singleton, R. H. Determination of the cerium habit in carbon steel. Metallurgical Society, American Institute of Mining and Metallurgical Engineers. Transactions. Vol. 215, pp. 675-679 (1959)

25. Yost, D. M., Russell, H., and Garner, C. S. The rare-earth elements and their compounds. N. Y., John Wiley and Sons, Inc., 1947. 92 p.

26. Handbook of chemistry and physics. 41st Edition, Cleveland, Chemical Rubber Publishing Company. 1959-1960.

27. Wohrman, C. R. Inclusions in iron. Cleveland, American Society for Steel Treating, 1928. 162 p.

28. Sauveur, A. The metallography and heat treatment of iron and steel. 3rd Ed. Cambridge, Mass., The University Press, 1926. pp. 124-125.

29. Hansen, M. Constitution of binary alloys. 2nd Ed. N. Y., McGraw-Hill Book Co., Inc., 1958. pp. 91, 451, 581, 686, 705.

30. Cain, J. R. Influence of sulphur, oxygen, copper, and manganese on the red-shortness of iron. Bureau of Standards. Technologic Paper 261. 1924.

31. Hilty, D., and Crafts, W. Manganese modification of the Fe-S-O system. Journal of Metals. Vol. 6, pp. 959-967 (1954)

32. Asanti, P., and Kohlmeyer, E. Uber die thermischen Eigenshaften der Vebindungen von Kobalt mit Sauerstoff Schwefel. Zeitschrift für anorganische und allgemeine Chemie. Germany. Vol. 265, p. 94 (1950)

33. Cornelius, H. Kupfer im technischen Eisen. Berlin, Julius Springer, 1940 p. 95.

34. Ellis, O. W. Further experiments on the forgeability of steel. American Society for Steel Treating. Transactions. Vol. 21, pp. 673-707 (1933)

35. Sauveur, A. Steel at elevated temperatures. American Society for Steel Treating. Transactions. Vol. 17, pp. 410-448 (1930)

36. Ihrig, H. K. A quantitative hot workability test for metals. Iron Age. Vol. 153-2, pp. 86-89 (Apr. 20, 1944)

37. Ihrig, H. K. The effect of various elements on the hot workability of steel. Metals Technology. Vol. 12, pp. 1-29 (Oct. 1945)

38. Clark, C. L. Evaluating steel forgeability. Iron Age. Vol. 153-2, pp. 52-55 (Mar. 16, 1944)

39. Symposium on hot-working. Iron and Steel Division, American Institute of Mining and Metallurgical Engineers, Transactions. Vol. 167, pp. 735-790 (1946)

40. Carney, D. J. Gases in liquid iron and steel. Gases in metals. Cleveland, American Society for Metals, 1953. pp. 69-118.

41. Kenyon, R. L. Recrystallization and grain control in ferrous metals. Grain control in industrial metallurgy. Cleveland, American Society for Metals, 1949. pp. 74-157.

42. Cushman, A. S., and Gardner, H. A. The corrosion and preservation of iron and steel. 1st Ed. N. Y., McGraw-Hill, 1910. pp. 78-80.

43. Cushman, A. S. The manufacture of pure irons in open-hearth furnaces. American Society for Testing Materials. Proceedings. Vol. 11, pp. 387-416 (1911)

44. Cleaves, H. E., and Thompson, J. G. The metal-iron. 1st Ed. N. Y., McGraw-Hill, 1935. 574 p.

45. Rawdon, H. S. Effect of sulfur in steel. American Society for Testing Materials. Vol. 36, part I, pp. 88-91 (1936)

46. Anderson, C. T., Kimball, R. W., and Cattori, F. R. Effect of various elements on hot-working characteristics and physical properties of Fe-C alloys. Journal of Metals. Vol. 5, pp. 525-529 (1953)

47. Kremers, H. E. Rare earth metals. Rare metals handbook. York, Pa., Maple Press Company, 1954. pp. 329-345.

48. The Metals Handbook, 1948 Edition. American Society for Metals, Cleveland, Ohio.

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