WATERTOWN ARSENAL
WATERTOWN, MASS.
LABORATORY
INDEXED

310/178-10 ✓

(1)
SC

(6)

THE EFFECT OF RARE-EARTH METALS ON CAST STEELS

Sponsored by

(18) WA

WATERTOWN ARSENAL

(19) 310/178-10

Contract No. DA-33-019-ORD-1156 (15)

DTIC
ELECTE
JUN 18 1981
S D
A

Prepared by

STEEL FOUNDERS' SOCIETY OF AMERICA, Rocky River OH

(10) **CHARLES W. BRIGGS**

Technical & Research Director

(12) 61

(11) **April 1954**

This document has been approved for public release and sale; its distribution is unlimited.

333850

4B

NOTE:-This form is to be executed to show proposed distribution, and forwarded in triplicate to the Chief of Ordnance for prior approval of all distributions. Proposed distribution to agencies or individuals whose official interest in the report is not obvious must be justified by explanatory statements on the back of this form.

BINDING AREA FORM NO. ORDBE-342L. (Rev.) 2 Sept. 1947 *BINDING AREA*

COPIES PREPARED 6

EXTRA COPIES REMAINING

WATERTOWN ARSENAL
TECHNICAL REPORT DISTRIBUTION

REPORT NO 310/178-10 TITLE: Steel Founder's Society of America DA...1156
Rpt. dated April 1954.

TO:	NO. OF COPIES	DATE OCO APPROVAL	DATE SENT	TO:	NO. OF COPIES	DATE OCO APPROVAL	DATE SENT
WATERTOWN ARSENAL-ORDBE				OTHER:			
Laboratory File	1						
~~Author:~~ A. Hurlich	1	#2		Returned from OTS were			
OFFICE, CHIEF OF ORDNANCE				sent for retention	2	#31 and #33a	
ORDIR-Artillery							
ORDIM-Ammunition				Cert # 31 New Process			
ORDIT-Automotive				Metals Inc. Newark N.J.			
ORDIS-Small Arms				For retention 9/16/58			
ORDTB-Res. & Materials							
ORDTM-Ammunition Dev.							
ORDTR-Artillery Dev.							
ORDTS-Small Arms Dev.							
ORDTT-Tank Automotive							
ORDTU-Rocket Dev.							
ORDTX-Executive							
ORDTX-AR - Executive Library	1						
ORDNANCE DEPARTMENT AGENCIES							
ORDBA-Frankford Arsenal							
ORDBB-Picatinny Arsenal							
ORDBC-Rock Island Arsenal							
ORDBD-Springfield Armory							
ORDBF-Watervliet Arsenal							
ORDBG-Aberdeen Prov. Ground							
ORDJR-Raritan Arsenal							
ORDMX-Detroit Arsenal							

APPROVING AUTHORITY:
Ltr.:
Date:
From:

THE EFFECT OF RARE-EARTH METALS ON CAST STEELS

Printed in the United States of America

TABLE OF CONTENTS

OUTLINE OF THE PROBLEM

Certain information which was made available during 1952 indicated that the low temperature toughness of alloy cast steels could be improved and critical alloys conserved through the addition of rare-earth metals to cast steels. The information that had been made available was developed in connection with the basic open-hearth steelmaking practice. It seemed advisable that other steelmaking methods be investigated and other steels be studied as to the effect of rare-earth metal additions. In view of this condition a program of research was planned so as to investigate:

(1) Successful practices of employing rare-earth metals to reduce sulfur content and improve the low temperature impact properties of cast steels made in acid lined furnaces as well as basic furnaces.

(2) The determination of the usefulness of the rare-earths in their various forms, such as metals, oxides, and so forth.

(3) The investigation of the effect of rare-earth metals on the properties and hardenability of various low-alloy cast steels with and without the presence of boron.

The research was planned in two phases: (a) a laboratory investigation to determine the type and amount of rare-earth metals to use; and (b) to produce low-alloy cast steels with rare-earth additions in production size steel melting furnaces by different melting methods. Phase (a) was carried on at Battelle Memorial Institute and phase (b) was undertaken by seven member companies of Steel Founders' Society. The research began in February 1953.

SUMMARY OF CONCLUSIONS OF THE RESEARCH REPORT

1—Additions of rare-earth metals to cast steel produced under basic slags will result in some desulfurization of the steel. Approximately 0.006 percent sulfur or less is removed by the addition of 3 pounds of misch metal per ton of steel. About 40 percent of the original sulfur content can be removed by adding 5 pounds per ton of misch metal. The latter quantity of rare-earth metal is undesirable as low toughness values also result.

2—Cast steels produced with acid slags are not desulfurized by the additions of rare-earth metals.

3—The presence of rare-earth metals in cast steels results in change in the shape, color, and composition of the sulfide inclusions. It is possible to form Types I, II, IV, or combination of these types, with Type III inclusions from an aluminum-killed steel which contains only Type III inclusions. The type of inclusions formed is proportioned to the sulfur content of the steel and the amount of rare-earth metals added.

4—Excellent ductility and Charpy V-notch impact properties result in the formation of Type I inclusions by addition of rare-earth metals. The amount of misch metal necessary to form Type I inclusions varies somewhat depending on whether they were laboratory or production heats. The reason for this is apparently the percent recovery of the rare-earth metals in the steel.

5—No sulfur reduction, change in shape of the sulfide inclusions, improvement in ductility or toughness resulted from the addition of rare-earth oxides or fluorides.

6—Rare-earth metal additions are equally effective in all types of low-alloy cast steels. Ductility and impact properties are improved at various hardness levels provided Type I inclusions are predominant throughout the steel.

7—The presence of rare-earth metal in cast steel does not influence the hardenability of the steel.

8—Large additions of misch metal in relation to the sulfur content are responsible for a concentration of Type IV inclusions in heavy sections and precipitation of gas porosity along the cope surface of the casting.

PREFACE

to the

RESEARCH REPORT

Many members of the Steel Casting Industry have heard discussions regarding the advantages resulting through the use of rare-earth metals in cast steels. A number of foundries have tried to use rare-earth metals in some of their production steels without too much success. In fact it has been generally stated throughout the industry that the only advantage results through their application to basic open-hearth cast steels.

However the very excellent low temperature impact values that were regularly being obtained from the basic open-hearth operation were very noticeable to Army Ordnance engineers and it was their hope that similarly high values could be obtained from other foundries supplying steel castings to the Ordnance Department. It was evident that further research on the subject of rare-earth metal additions to cast steel was advisable on an industry-wide scope. Therefore in the fall of 1952 Watertown Arsenal approached Steel Founders' Society regarding a basic study of the effect of rare-earth metals in cast steels.

The Technical Research Committee of the Society prepared a general plan of research and a government contract was signed in February of 1953 and completed in January 1954.

The research report is very detailed and the continued reference to tables and illustrations results in difficult reading. It should also be pointed out that many inferences are drawn regarding the mechnical property test differences which are not shown to be statistically significant. This is probably unavoidable in view of the numerous phases that were to be covered and the minimum amount of test data collected. Therefore the report may be considered as an excellent basis for thought and further action rather than conclusive proof. The information presented is pertinent but there are limitations concerning the conclusions arising out of the lack of reproducibility of test results.

It is suggested that the foundryman first review the Summary of the Conclusions of each section of the report and then study the general conclusions to Parts I and II of the report as well as reading Part III of the report, before he studies the report in its entirety.

The Technical Research Committee wishes to express its appreciation to the Battelle Memorial Institute staff under the direction of Mr. F. W. Boulger for its part in the research activities. Their task was an especially difficult one as they had to produce certain results speedily so that their results could be the basis of the procedure for the production of commercial steels by the cooperating member companies.

The Committee also wishes to thank the members of the staffs of the seven member companies that produced the production heats of low-alloy cast steels containing rare-earth metals, oxides, and fluorides. They had difficult schedules to follow with exacting test requirements. They cooperated to the maximum and fulfilled all requirements. The Technical Research Committee appreciates their accepting the assignment and their support and interest in the research. The contributing companies are as follows:

American Steel Foundries

Burnside Steel Foundry Company

The Commercial Steel Casting Company

Continental Foundry & Machine Company

Dodge Steel Company

The Hartford Electric Steel Corporation

The National Roll & Foundry Company

The Society expresses gratitude to Watertown Arsenal for initiating the studies and providing the necessary funds. Their confidence in the Society's research activities is appreciated. Special acknowledgment is made to Mr. Paul V. Riffin of the Arsenal Metallurgical Staff for his coordinating activities.

Charles W. Briggs
Technical and Research Director
By direction of the
Technical Research Committee

H. D. Phillips, *Chairman*

E. H. Berry
C. K. Donoho
F. X. Hohn
C. B. Jenni
G. A. Lilliequist
H. A. Schwartz
R. A. Willey
C. H. Wyman
V. E. Zang

FINAL REPORT
ON
RESEARCH PROJECT NO. 36

THE EFFECT OF RARE-EARTH METALS IN CAST STEELS

PART I—LABORATORY STUDIES AT BATTELLE MEMORIAL INSTITUTE

BY

F. W. BOULGER, M. C. UDY, M. J. WAHLL AND
R. H. FRAZIER

PART II—THE PRODUCTION OF COMMERCIAL CAST STEELS CONTAINING RARE-EARTH ADDITIONS

PART III—SUMMARY, DISCUSSIONS, AND CONCLUSIONS

BY

CHARLES W. BRIGGS

STEEL FOUNDERS' SOCIETY OF AMERICA
IN COOPERATION WITH
Member Foundries of the SFSA
AND
Battelle Memorial Institute

THE EFFECT OF RARE-EARTH METALS ON CAST STEELS

PART I

LABORATORY STUDIES AT BATTELLE MEMORIAL INSTITUTE

INTRODUCTION

The rare-earth metals have atomic numbers from 57 to 71, and are similar in chemical properties. The addition agents used in this study were alloys or mixtures containing principally cerium, lanthanum, neodymium, and praseodymium as active materials. The composition of the alloys and mixtures of the rare-earth metals investigated is given in Table 1.

Misch metal is an alloy of the rare-earth metals in much the proportions they occur in nature or in monazite sands from which thorium has been recovered. The addition of this alloy to steel was tried as early as 1918(1). Although claims of desulfurization and increased ductility were made, there was not much further work done at the time. The use of misch metal as an addition to steel was discouraged by reports(2) that it caused dirty steel, unless special precautions were used, thereby lowering the mechanical properties. It should be noted that these early additions of misch metal to steel were on the order of twenty times the size of additions now recommended.

The revival of interest in the use of the rare-earth elements as additions to cast steel began in 1951(3,4,5). It is reported that rare-earth metal additions have a beneficial effect on ductility and impact properties, improve the high temperature properties of carbon and low-alloy steel and are beneficial in the production procedures of making steel castings, such as sulfur reduction, changes in inclusion type, improved fluidity, and so forth.

Some foundries attempting to adopt the rare-earth metal addition practice have not found the beneficial effects indicated and, therefore, these research studies were devised to develop the facts regarding the addition of rare-earth metals to cast steels.

The work was designed to answer, insofar as possible, four major questions:

(1) Do rare-earth metals remove sulfur from cast steel?

(2) How do rare-earth metals improve mechanical properties of cast steel?

TABLE 1

Approximate Compositions of Rare-Earth-Metal and Rare-Earth-Element Addition Agents Used

Rare-Earth Addition Agent	Supplier	Composition, percent					
	Rare-Earth Metals						
		Ce	**La**	**Nd**	**Pr**	**Total**	**Fe**
Misch metal	General Cerium Company	54	24	13	6	97	2
Misch metal Lan-Cer-Amp No. 1	American Metallurgical Products Company	45	29	15	8	97	1
	Cerium Fluoride						
		Ce	**F**				
Cerium fluoride	Lindsay Light & Chemical Company	71	29(1)				
	Rare-Earth Oxide Plus Reductant Compounds						
		Rare-Earth Oxides	**Ca**	**B**	**Si**	**O**	**Other**
T-Compound	Molybdenum Corporation of America	68.0	3.8(2)	6.2(2)		12.0(4)	10% $NaNO_3$
Limed T-Compound	Molybdenum Corporation of America	61.5	3.4(2)	5.6(2)		10.5(4)	9% $NaNO_3$ 10% CaO
Remox-C Compound	Mallinckrodt Chemical Works	51.0	9.55(3)		13.45(3)	9.0(4)	17% $NaNO_3$

(1) As CeF_3; (2) As CaB_6; (3) As $CaSi_2$; (4) As rare-earth oxides

(3) To what extent can rare-earth metals replace critical alloys?

(4) What rare-earth-metal addition practices are preferable?

Desulfurization of steel depends on time, temperature, state of deoxidation, and composition of metal and slag. Therefore, the effects of these factors on sulfur content were investigated to provide answers for the first question.

Mechanical properties of cast steel, especially toughness and ductility, may be improved by the rare-earth elements through removing sulfur, by preventing temper brittleness, by changing the type of inclusions, or by some other alloying effect. Therefore, the answer to the second question was sought by examining the mechanical properties of cast steels in which desulfurization was accomplished by rare-earth-metal additions, and also the properties of steels in which rare-earth-metal additions were too small, or for some other reason, failed to cause sulfur removal. Heat treatments designed to show up susceptibility to temper brittleness were used. Inclusion types were determined metallographically. Hardenability tests were also made to indicate possible alloying effects.

An answer to the third question was sought by varying the composition of rare-earth-treated steels with respect to Mn, Cr, Ni, and Mo, and comparing the mechanical properties of the resulting steels. Rare-earth-treated steels containing boron added by various commercial boron addition agents were also studied. The possibility of interference with rare-earth-metal effects by such elements as C, N, Ti, and V was also investigated.

The fourth question was answered by making comparable steels using two different misch metals, three different mixes containing rare-earth-metal oxides with reductants, and a rare-earth fluoride. All of these addition agents are commercially available, and claims have been made for their beneficial effects in cast steel. The amount of desulfurization, the inclusion types, and the mechanical properties resulting from the different additions were compared.

The laboratory research program was supplemented by a separate commercial melting and testing program. Information on this phase of the study is found in Part II of this report.

Melting and Casting Practices

The results of the laboratory studies are based on data obtained from fifty-one 275-pound heats of steel made in the laboratory induction furnace. Seven heats were made in silica crucibles, the rest in magnesia crucibles. All but two of the heats contain about 0.23 percent carbon, but fall into eleven groups so far as other alloying elements are concerned. The nominal compositions of the cast steels are listed in Table 2. Table A-1 in the Appendix lists the compositions of all of the individual heats. Complete chemical analyses of all heats were not considered necessary because the melting practices were carefully controlled. Spot checks indicated that actual compositions were close to the intended compositions.

TABLE 2

Nominal Base Composition of Eleven Groups of Cast Steel Used in the Investigation

Nominal Composition, weight percent							
C	Mn	Si	Mo	Cr	Ni	S	P
			Grade "B" Steel				
0.23	0.70	0.40				0.045	0.020
			Manganese-Molybdenum Steels				
0.23	1.25	0.40	0.10			0.045	0.020
0.23	1.25	0.40	0.10			0.020	0.020
			Manganese-Chromium-Molybdenum-Nickel Steels				
0.23	1.25	0.40	0.40	0.50	0.25	0.035	0.020
0.23	1.25	0.40	0.20	0.50	0.25	0.035	0.020
0.23	1.25	0.40	0.20	0.50	—	0.035	0.020
0.23	1.50	0.40	0.40	0.50	0.25	0.035	0.020
0.23	1.50	0.40	0.20	0.50	0.25	0.035	0.020
0.23	1.25	0.40	0.50	0.50	0.50	0.035	0.020
0.23	1.50	0.40	0.40	1.00	0.25	0.035	0.020
0.23	1.50	0.40	0.20	1.00	0.25	0.035	0.020

Sheared ingot iron and a part of the ferrosilicon and ferromanganese were charged to a preheated crucible and the power was applied. Meltdown times average about 51 minutes. Pyrite and ferromolybdenum were added at meltdown, when necessary to produce the desired compositions. The alloys were added with the power turned on to insure adequate mixing. For most of the heats additions were made according to a definite time schedule.

The time intervals for additions of the ferroalloys was about ¾ minute, depending on the time required for solution. The additions following aluminum deoxidation were made at 30-second intervals. Similarly, the time from the furnace addition of the rare-earth material to pouring was considered very important. This period, which was controlled carefully, was three minutes for most heats. Special melting practices were used when investigating factors affecting desulfurization or certain additions containing rare-earth elements.

The rare-earth metals were added to the liquid steel as lumps approximately one inch in diameter. They were wired to steel rods and plunged deep into the molten metal. Powdered addition agents were placed inside small iron cans and also submerged in the bath.

Ordinarily, the melts were tapped at 2875 degrees F directly from the furnace into the molds. The type mold varied with the purpose for which the heat was made. The SFSA standard double-leg keel blocks were cast in dry-sand molds for mechanical tests. Prior to use, the molds were ignited with white gasoline to insure complete dryness. The five keel blocks poured from each heat were poured within 1½ minutes of the tapping time. Three-inch-diameter ingots, weighing 8 pounds, were cast in dry-sand molds when desulfurization or inclusion data were of primary interest.

The bath temperatures and pouring temperatures were measured with an optical pyrometer. Occasional checks with immersion thermcouples agreed with the pyrometer measurements within 15 degrees F.

Heat Treatment Methods

The legs were torch cut from the keel blocks and heated two hours at 1750 degrees F and air cooled and cut to stock sections. The stock for tensile and Charpy bars was subsequently heat treated in 1-inch and ½-inch-thick sections, respectively. The heat treatments consisted of holding them for one hour at 1650 degrees F and then quenching them in water at 80 degrees F until they reached a temperature of about 100 degrees F. The stock was then tempered for two hours at the temperature required to produce the desired hardness. Most of the stock sections were quenched in water from the tempering treatment. A few duplicate pieces were furnace cooled to establish tendencies for temper brittleness. Tempering temperatures used for all specimens were such as to produce approximately 260 B.H.N.

Stock from seven heats containing larger alloy contents was heat treated by a practice intended to simulate cooling rates in 4-inch and 6-inch sections. Assemblies of the type illustrated in Figure 1 were used for this purpose. Bars machined from the keel-block legs were mounted in a picture frame and ground to insure smooth, flat surfaces. The smooth surface finishes resulted in intimate contact and good heat transfer between the plates and test stock. Circumferential, double-pass welds were then made to join the picture frame and the cover plates. The dimensions of the cover plates and the picture frame were chosen so that cooling during quenching occurred through the cover plates.

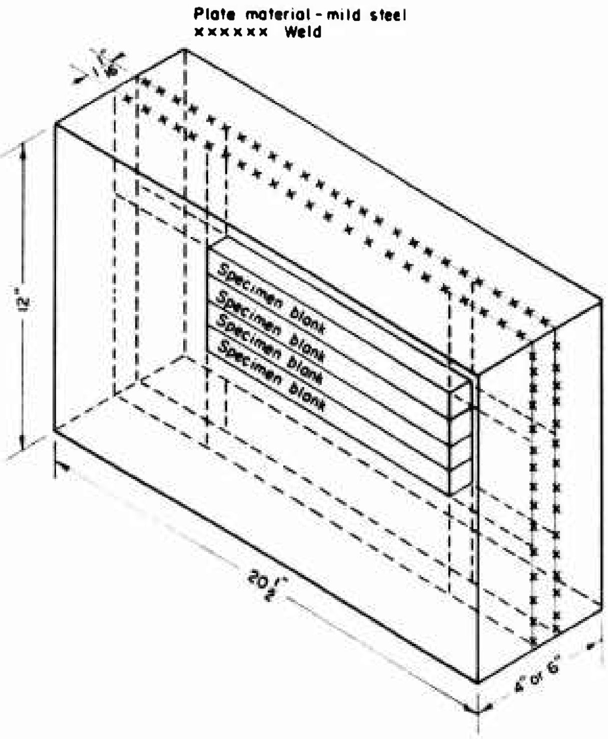


Figure 1—Assembly for heat treating specimen blanks within 4- and 6-inch-thick steel plates.

The assemblies, simulating heavy homogeneous plates, were heated so that the center one-inch section was maintained at 1650 degrees F for one hour and then quenched in water. A thermocouple embedded three inches deep from one end of the assembly was used as the control couple. The plates were flush quenched in a large tank of circulating water having a temperature of 80 degrees F. Quenching periods were 20 to 40 minutes for the 4-inch and 6-inch assemblies, respectively. The composite plates were tempered at 1150 degrees F and then quenched in water. The tempering periods were 4 and 6 hours for the 4-inch and 6-inch-thick assemblies, respectively. These heating periods were intended to produce two-hour tempering treatments on the specimens at the center of the heavy assemblies.

SECTION I — DESULFURIZATION

Under some conditions, the addition of rare-earth metals to liquid steel results in desulfurization. Earlier work for the Steel Founders' Society of America indicated that the amount of the addition, the sulfur content of the melt, and the bath temperature all affected the extent of sulfur removal (1). Fourteen heats were made to verify the tentative conclusions reached earlier. The sulfur contents of the heats which shed light on the mechanisms of defulsurization with rare earths are given in Table 3. All of the steels were aluminum-killed and treated with 5 pounds of rare-earth metals per ton of steel.

Acid Steels

It will be observed from Table 3 that desulfurization was attempted in five acid steels. There was, apparently, a drop in the sulfur content directly after the rare-earth metal addition. However, shortly thereafter a sulfur reversion occurred and the steel picked up sulfur. It appeared, therefore, that a basic slag was necessary to trap the rare-earth sulfides which float out of the desulfurized bath. This point was checked by placing a molten basic slag on the steel about two minutes after the rare-earth metals had been added to the steel in the silica crucible. Although some sulfur reversion had occurred while the steel was in the silica crucible, desulfurization started again when the metal was covered with the molten basic slag.

In a control heat made in an acid crucible without rare-earth metals (9889) there was a slight drop in sulfur content after the molten basic slag was added. This slag probably would have been a more effective desulfurizer if the bath had been turbulent.

Basic Steels

The rare-earth metal treatment of steel in a basic crucible resulted in sulfur reductions upward of 50

TABLE 3

Data Showing the Influence of Various Factors on Desulfurization of Steel with Rare-Earth Metals

Elapsed Time After Adding Rare-Earth, minutes	Heat:	9805	9806	9889	9881	9880	9277	9797	9796	9890(1)	9890(1)	9794	9795	9800	9807	9877
	Type:	Acid	Acid(2)	Acid(2)	Acid	Acid	Basic	Basic	Basic	Basic	Basic	Basic	Basic	Basic	Basic	Basic
	°F:	2850	2850	2850	2850	2850	3050	3050	2950	3050	2850	2850	2860	2850	2860	2860
	Al. lb/ton:	2	2	2	2	2	2	2	0	2	2	2	2	2	2	2
	Rare-Earth, lb/ton:	5	5	0	5	5	5	5	5	5	5	5	5	5	5	3
		Sulfur Content at Time Indicated, percent														
Before		0.043	0.039	0.037	0.039	0.037	0.043	0.044	0.059	0.039	—	0.042	0.043	0.042	0.042	0.033
1/2		0.026	0.029	—	—	—	—	—	—	0.027	—	0.038	—	—	—	—
3/4		—	—	0.036	—	—	0.022	—	—	—	—	—	—	—	—	—
1		—	—	0.037	—	—	—	0.039	0.051	0.027	—	—	0.016	—	—	—
1-1/2		—	—(2)	—(2)	—	—	—	—	—	0.031	—	0.041	—	—	—	—
2		—	0.035	0.034	—	—	0.028	0.038	0.050	—	—	—	0.014	—	—	—
2-1/2		0.030	0.034	0.032	—	—	—	—	—	0.034	—	—	—	—	—	—
3		—	0.031	0.035	0.035	0.034	0.033	0.038	—	0.031	—	0.023	0.015	0.021	0.036	0.022
4		—	0.027	0.034	—	—	—	—	0.054	—	—	—	—	—	—	—
5		0.037	—	0.032	—	—	0.035	—	—	—	—	—	—	—	—	—
6		—	0.032	—	—	—	—	—	—	—	—	—	—	—	—	—
10		0.036	—	—	—	—	0.038	—	—	—	0.034	0.021	—	—	—	—
12		—	—	—	—	—	—	—	—	—	0.035	—	—	—	—	—
14		—	—	—	—	—	0.040	—	—	—	0.033	—	—	—	—	—
16		0.039	—	—	—	—	—	—	—	—	0.033	0.021	—	—	—	—
20		0.039	—	—	—	—	0.041	—	—	—	—	0.025	—	—	—	—
25		0.040	—	—	—	—	0.039	—	—	—	—	0.024	—	—	—	—
30		0.041	—	—	—	—	0.040	—	—	—	—	0.024	—	—	—	—

Note: All but three steels contain 1.25 percent Mn and 0.10 percent Mo. Heats 9800 and 9881 contain 0.70 percent Mn. Heat 9877 contains 1.50 percent Mn, 0.40 percent Mo, 1.0 percent Cr, 0.25 percent Ni, and 0.0045 percent B.

(1) After holding five minutes at 3050°F, Heat 9890 was held eleven minutes at 2850°F.

(2) After holding for two minutes a basic slag was placed on the crucible. Slag: SiO_2-20, CaF_2-20, and CaO-60 percent.

percent. Desulfurization was over in approximately three minutes of holding time and longer holding times were not beneficial. The fact that desulfurization occurred rapidly agrees with earlier data.

Desulfurization was only temporary when steel was maintained at a high temperature of 3050 degrees F (Heat 9277). This indicates that high bath temperatures hinder desulfurization and that low bath temperatures should be employed when the rare-earth metals are added. Figure 2, which summarizes the data for three steels melted in basic crucibles, supports this conclusion.

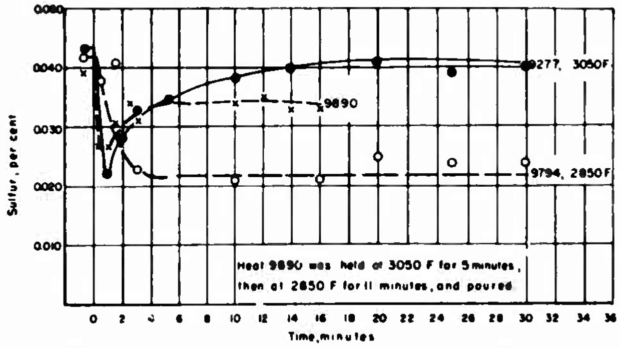


Figure 2—Effect of time and temperature on desulfurization of basic aluminum-killed steels treated with 5 pounds of rare-earth metal per ton added at 0 minutes

Desulfurization Considerations

The behavior of these laboratory heats is consistent with the theory that rare-earth elements in steel baths react rapidly with sulfur to form sulfides which are only slightly soluble. The solubility of the sulfides should, and apparently does, decrease with decreasing temperature. Consequently, the equilibrium sulfur content of a melt containing a particular amount of rare-earth elements is lower at lower temperatures. Since the sulfides in excess of the solubility precipitate and float out, lower temperatures favor desulfurization. The data indicate that another factor has an important influence on the final sulfur content. Sulfur reversion from the slag can occur, probably because some of the rare-earth sulfides are converted to oxides or nitrides by reaction with air. This is more likely to occur at higher temperatures.

The laboratory experiments indicated that the sulfur content of the bath tends to increase during prolonged holding. It is believed that sulfur reversion is less likely to occur in practice where the bath is covered with a protective blanket of slag.

The desulfurization considerations are graphically explained in Figure 3 which compares the changes in sulfur content resulting from additions.

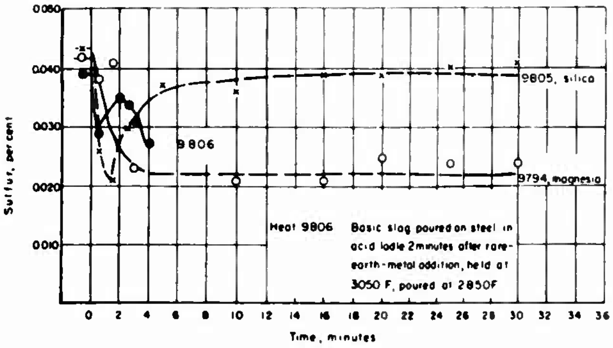


Figure 3—Influence of time and environment on desulfurization at 2850°F on aluminum-killed steel with 5 pounds per ton of rare-earth metal added at 0 minutes

Figure 3 compares the changes in sulfur content resulting from adding five pounds of misch metal to aluminum-killed steels in acid and basic crucibles. In both cases the sulfur content was quickly lowered nearly 50 percent from 0.043 to about 0.023 percent. Since this was true for both acid and basic crucibles, it apparently resulted from a homogeneous reaction in the metal bath. After about 1¾ minutes, however, sulfur reversion occurred in the silica crucible but not in the basic vessel.

The test results of Table 3 indicate that desulfurization at 2850 degrees F was practically complete within three minutes after the addition of the rare-earth metals. With this point as a base, other basic heats were made with variations in the amount of rare-earth metals added. Figure 4 shows the influence on the size of the rare-earth metal additions on the amount of sulfur removed from the steel. The data for thirty-one heats indicate that additions of three pounds or less of misch metal per ton of steel were not very effective in removing sulfur.

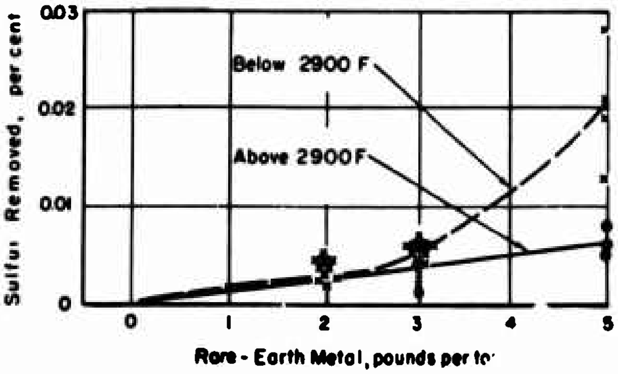


Figure 4—Effect of temperature on desulfurization of basic aluminum-killed steels originally containing about 0.04 percent sulfur

Summary on Desulfurization

1. Cast steels produced in acid-lined crucibles are not desulfurized by the additions of rare-earth metals, oxides, or fluorides.
2. Rare-earth metal additions, to steel produced in basic crucibles, resulted in desulfurization upward of 50 percent of the original sulfur content.
3. High steel temperatures hinder desulfurization. Maximum desulfurization results, with rare-earth metal additions, at steel temperatures of approximately 2850 degrees F.
4. Desulfurization is complete within three minutes following the addition of rare-earth metals.
5. An addition of five pounds of rare-earth metal per ton of steel is necessary to remove 40 to 50 percent of the original sulfur present.
6. Rare-earth containing oxides and fluorides had but little desulfurization effect on molten cast steels produced even in basic crucibles.

SECTION II

INFLUENCE OF RARE-EARTH METALS ON SULFIDE INCLUSIONS

The influence of the original sulfur level on the tendency for desulfurization by rare-earth metal, Figure 5, was taken from the earlier work of SFSA. The chart shows that it is easier to remove sulfur from high-sulfur steels. Desulfurization is usually slight until the addition exceeds three pounds per ton, even though it is a little more marked in steels with higher sulfur contents.

On the average, the addition of three pounds of rare-earth metal per ton of steel in the laboratory removed 10 percent of the original sulfur. Additions of five pounds or more of the metal per ton of steel removed about 40 percent of the original sulfur. At the lower sulfur levels, however, additions larger than five pounds per ton of steel produced no additional desulfurization. Perhaps this implies that the solubility of the sulfides in steel at 2850 degrees F was the factor limiting desulfurization.

In the earlier studies it was noted that neither rare-earth fluroides nor oxides acted as desulfurizers in the laboratory experiments. However, Table 4 indicates that some sulfur was removed (Heat 9895) by an addition agent made from the oxides of the rare-earth elements and a reducing agent. Also, the Ce/La ratio of misch metal does not significantly affect its ability to remove sulfur from steel. Likewise, the addition of cerium fluoride removed no sulfur. As would be expected, no desulfurization occurred in the steels (Heats 143, 144) made in acid crucibles.

Since the rare-earth elements combine with oxygen as well as sulfur, their ability to remove sulfur should be impaired by a higher oxygen level in a steel bath. Equal additions of misch metal lowered the sulfur content of the silicon-killed heat (9807) only 0.006 percent, as contrasted to 0.028 and 0.021 percent sulfur removed from the aluminum-killed steels. (9795 and 9800, Table 3).

Sulfur analyses on the experimental steels indicate that minor amounts of N, V, Ti, and B do not interfere with the desulfurizing action of misch metal. Furthermore, variations in chromium contents up to one percent, in molybdenum contents

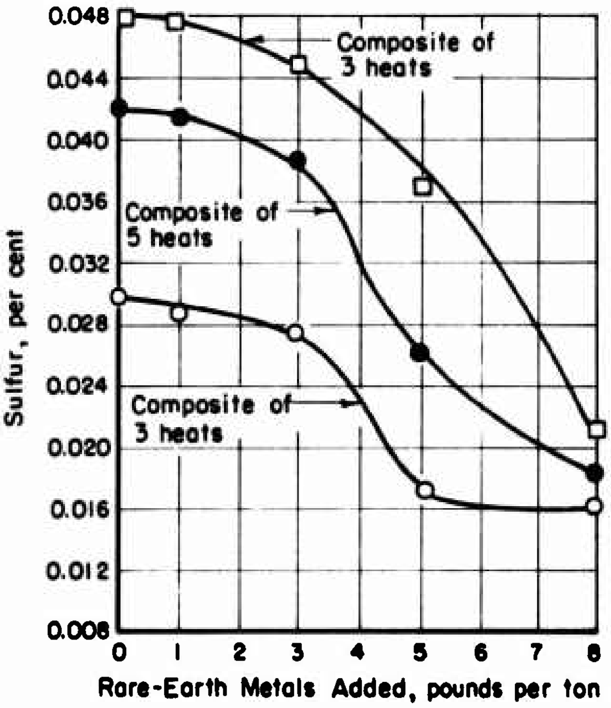


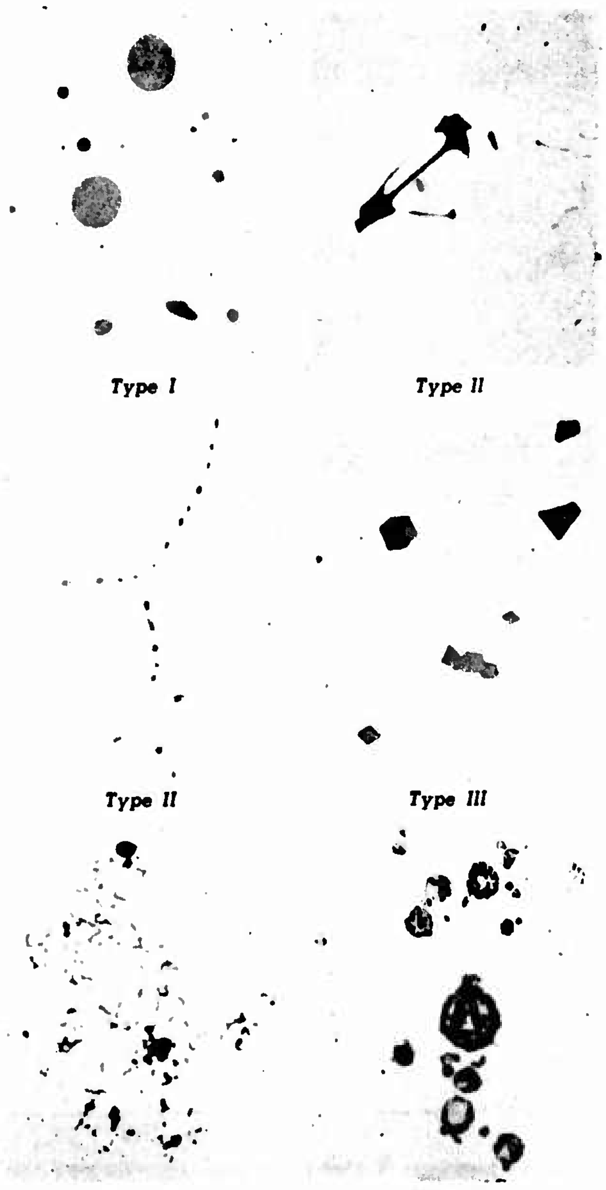
Figure 5—Desulfurization of basic aluminum-killed steels poured below 2900°F. Each curve is a composite for several similar Mn-Mo cast steels

TABLE 4 — Influence of Commercial Rare-Earth Addition Agents on Sulfur Content of Aluminum-Killed Laboratory Steels

Heat	Crucible	Addition Agent	Sulfur Content, percent		
			Melt	Final	Amt. Removed
9804	Magnesia	Lan-Cer-Amp No. 1	.033	.027	.006
9894	Magnesia	Misch metal, General Cerium Co.	.028	.024	.004
9895(1)	Magnesia	T-Compound	.029	.023	.006
9896	Magnesia	T-Compound	.030	.028	.001
9897	Magnesia	Cerium fluoride	.027	.028	None
143(1)	Silica	Limed T-Compound	.039	.037	.002
144	Silica	Remox-C Compound	.036	.035	.001

Note: The steels contained approximately 0.23 percent C, 1.2 percent Mn, 0.4 percent Si, 0.4 percent Mo, 0.50 percent Cr, 0.25 percent Ni. All were treated with 2 pounds of aluminum per ton. The time between the addition of the rare-earth agent at 2860°F and pouring was three minutes. The additions were equivalent to 3 pounds of rare-earth elements per ton of steel.

(1) The additions were made before aluminum in the case of these two heats.


Type I *Type II*

Type II *Type III*

Type IV *Type IV*

Figure 6—System used for classifying sulfide inclusions in steels discussed in this report (500X-1/5 reduction)

from 0.1 to 0.5 percent, and in manganese in the range between 0.7 and 1.5 percent, do not seem to have any influence on the desulfurizing power of rare-earth metals.

Increasing additions of rare-earth-containing materials to molten steel changes the size, shape, and color of sulfide inclusions. Such attributes are important because they reflect the composition of the sulfides and the state of deoxidation of the steel. Furthermore, the quantity and shape of inclusions present in a steel influence its mechanical properties. For simplicity, the characteristic sulfides in the experimental steels were classified according to the system shown in Figure 6. These photomicrographs typify the size and shape of sulfide inclusions, but are not intended to be representative of the quantity found in steels.

The terms Type I, Type II, and Type III inclusions are well known and have been used for classifying sulfide inclusions in cast steels for many years. As illustrated in Figure 6, Type I sulfides are irregularly spaced spheroidal particles which vary in size. They are predominantly manganese sulfides but are sometimes duplexed with oxides or with iron sulfide. They always contain some iron and are generally dove gray in color. They are characteristic in silicon-killed steels.

Type II sulfides are characteristic of steels deoxidized with titanium or with critical amounts of zirconium or aluminum. Type II sulfides occur as intergranular films or as chains of small round particles delineating grain boundaries. Sulfides with this distribution have the most harmful effect on the toughness and ductility of cast steels. Type III sulfides are angular in shape and characteristic of steels containing aluminum or zirconium in amounts in excess of the quantities required for deoxidation. Presumably, they contain some of the deoxidizing element.

The term Type IV sulfide is used in this report to denote the kind of inclusions found in some steels treated with rare-earth-containing materials. They were usually small, irregularly shaped, and occurred in clusters or clouds. Occasionally, large duplexed inclusions were found. These contained a brownish-yellow phase in the gray sulfide matrix. The colored areas are believed to be relatively pure rare-earth sulfides. Presumably, such inclusions were ready to float out of the melt but were trapped during solidification.

Metallographic examinations were made of castings produced from all heats. The classification typical of the sulfide inclusions found in the specimens is indicated in Table 5. The inclusions found in steels which had not been treated with rare-earth agents were as would be expected from the preceding discussion. That is, silicon-killed steels contained round Type I sulfides.

An addition of five pounds of misch metal per ton of steel had no effect on the sulfides typical of silicon-killed steels (Heat 9807, Table A-2 Appendix). Earlier work showed that smaller additions also have no effect on sulfides in such steels.

TABLE 5

Effect of Rare-Earth Addition Agents on Shape of Sulfide Inclusions in Aluminum-Killed Laboratory Steels

Addition Agent		Number of Steels With Inclusion Type Indicated				
Type	Amount, lb/ton	Type III	Type II	Type I and Type II	Type I	Type IV
Aluminum only	2	47	0	0	0	0
Oxides and fluorides of rare-earth elements	3(a)	5	0	0	0	0
Rare-earth metal (misch metal)	1	0	1	0	0	0
Rare-earth metal (misch metal)	2	0	0	3	7	0
Rare-earth metal (misch metal)	3	0	0	0	12	0
Rare-earth metal (misch metal)	5(b)	0	0	2	18	6
Rare-earth metal (misch metal)	8(b)	0	0	3	4	12

Note: The chemical analyses of the steels summarized here varied in the range indicated in Table A-1.

(a) These additions contained the equivalent of 3 pounds of rare-earth elements per ton of steel.

(b) Some of these data are from Table 2 of the report listed as Reference 1 because this study covered only ten steels given misch-metal additions of 5 pounds per ton and none of 8 pounds per ton.

Table 5 summarizes the effects on sulfide-inclusion shape of adding rare-earth-containing materials to the aluminum-killed steels. Some data from a previous SFSA report (1) are included to supplement the information on the effects of additions amounting to five pounds or more per ton of steel. The data in this table refer to steels processed in the laboratory and cast about three minutes after the special addition. The compositions of the steels covered a fairly wide range. However, it is well established that the common alloying elements have no effect on sulfide shapes, except when they act as deoxidizers or combine with sulfur.

The size of the misch-metal addition controls its effect on the shape of sulfides in aluminum-killed steels (Table 6). The effects of adding one or two pounds of misch metal per ton of steel were not completely consistent in these experiments. Usually they changed the angular Type III sulfides to Type I, but some film sulfides (Type II) were present in one-third of the heats treated with small amounts of misch metal. Twelve heats were treated with three pounds of rare-earth metal per ton of steel. In every case, angular sulfides were avoided and the steels were characterized by globular, Type I sulfides.

Figure 7 illustrates the effect of progressively larger additions of misch metal on the sulfides in

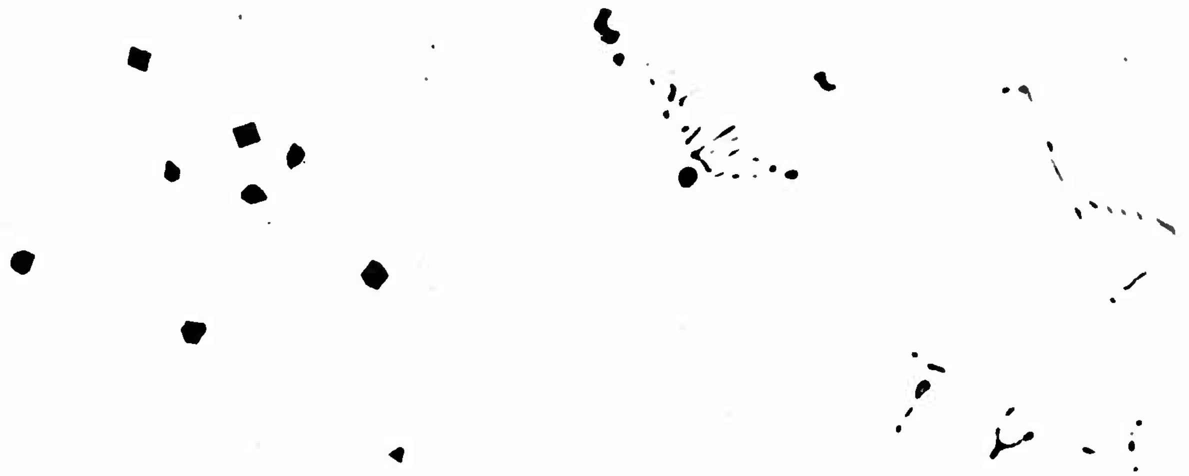
TABLE 6

Inclusion Classification and Spectrographic Aluminum Contents of Some Aluminum-Killed Steels Treated with Misch Metal

Heat	Sample Number(1)	Misch-Metal Addition, lb/ton	Total Aluminum, percent	Sulfide-Inclusion Type
9798	A	0	0.086	III
9802	M-1	1	0.092	III
9802	A	1	0.080	II
9804	M-1	3	0.096	III
9804	A	3	0.074	I
9796	A	5	0.070	I, II
9800	A	5	0.072	I
9795	A	5	0.077	I
9880	A	5	0.077	I, II

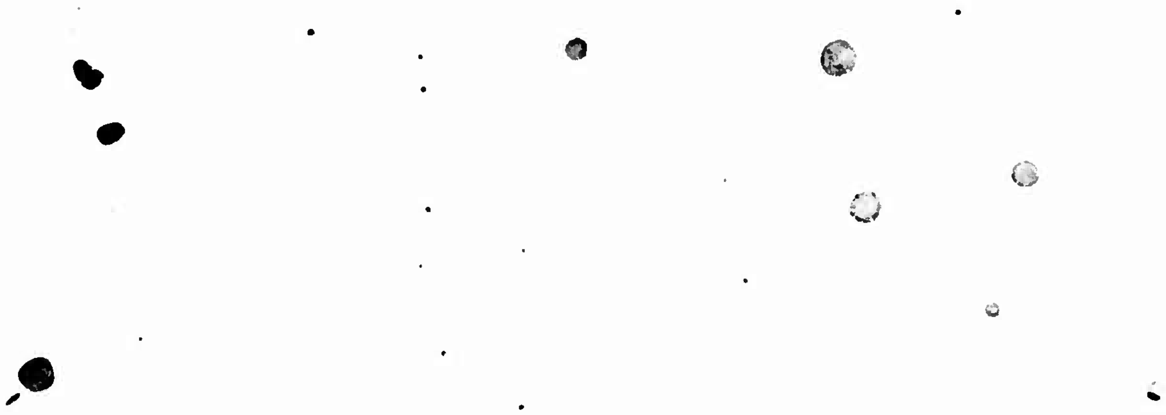
Note: All steels were deoxidized with two pounds of aluminum per ton (0.10 percent).

(1) "A" indicates sample analysis was taken from keel block 3 minutes after the addition of misch metal, or 3 minutes after aluminum in the case of Heat 9798. M-1 indicates the sample was taken 1/4 minute before the misch-metal addition.



No Misch Metal

1 lb/ton Misch Metal



2 lbs/ton Misch Metal

3 lbs/ton Misch Metal

Figure 7—Sulfide inclusions typical of cast steels deoxidized with 2 pounds of aluminum and then treated with 0 to 3 pounds of misch metal per ton of steel (500X)

the experimental steels. All of these heats were deoxidized with aluminum before being treated with misch metal. A marked change in inclusion shape results from the rare-earth-metal additions. If the addition is too small, sulfides of the kind shown for the one-pound addition sometimes occur.

The photomicrographs show the kind of sulfides normally produced by the additions indicated. However, three of the steels treated with two pounds of misch metal per ton of steel exhibited both Type I and Type II sulfides, Figure 8. The steels used for this illustration contained some titanium which was introduced as part of the boron addition. The presence of titanium in sulfides changes their color. This accounts for the light gray color of the film and chain sulfides which is particularly noticeable in the lower photomicrograph. These inclusions were tan rather than gray in reflected light.

Most of the steels treated with three or five pounds of misch metal per ton of steel contained Type I sulfides. It is unusual to find this desirable type of nonmetallic inclusion in steels containing more than 0.02 percent aluminum. Therefore, aluminum analyses were made on some steels to establish whether the Type I sulfides resulted from misch metal instead of losses in aluminum.

The results of spectrographic analyses for aluminum are given in Table 6. They show that all of these steels contained aluminum in the range normally associated with angular Type III sulfides. As expected, the three samples of steel not treated with misch metal contained inclusions of that type. The sample treated with only one pound of misch metal per ton of steel (9802A) contained film sulfides as illustrated in Figure 7. This indicates that some of the rare-earth elements dissolved in the

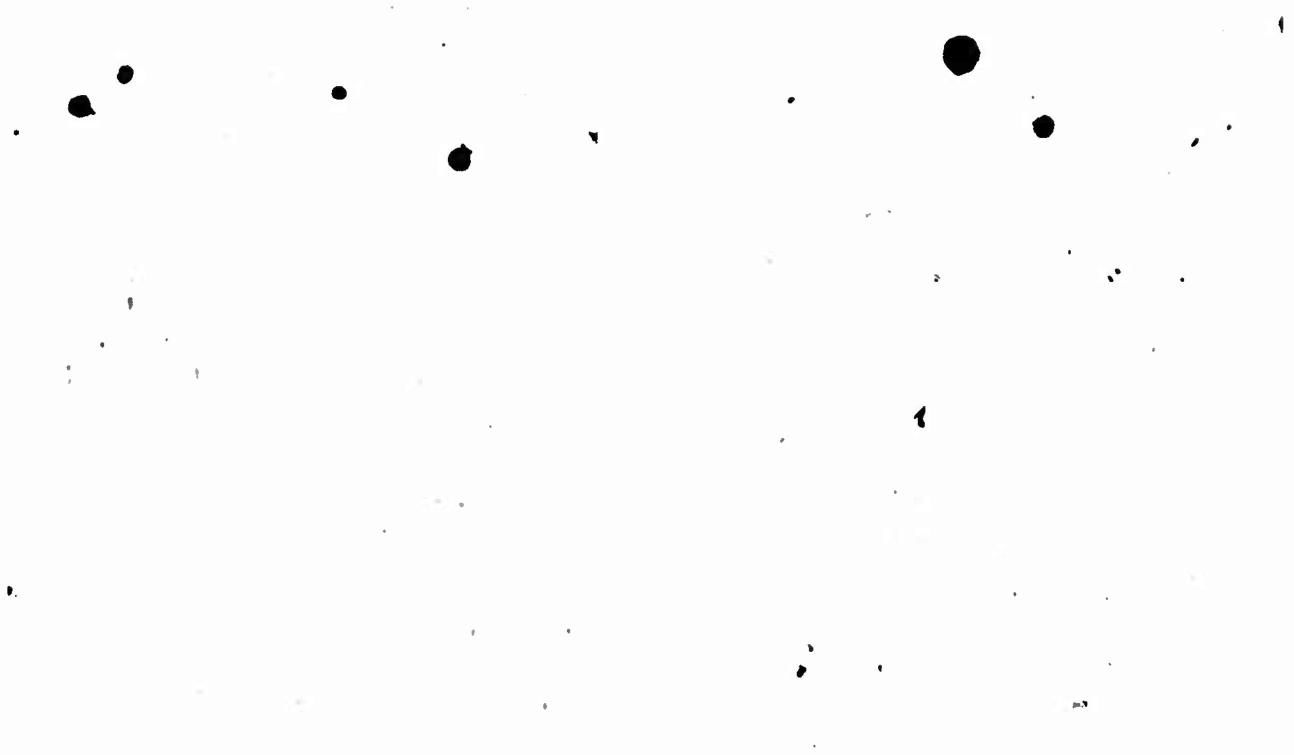
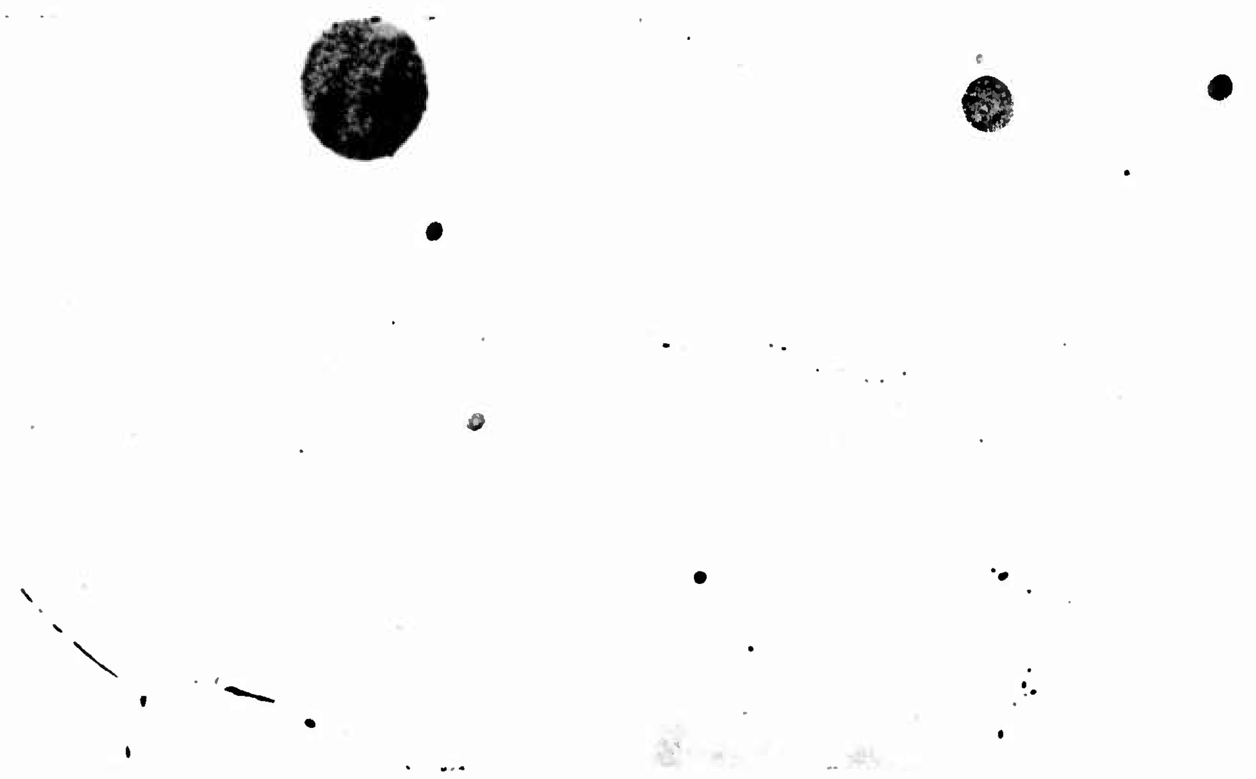


Figure 8—Mixed types of sulfide inclusions found in some aluminum-killed steels treated with two pounds of misch metal per ton of steel (500X)



Basic Furnace *Acid Furnace*

Figure 9—Mixed types of sulfide inclusions found in two aluminum-killed steels treated with five pounds of misch metal per ton of steel (500X)

manganese sulfides and changed their shape to Type II. This change in shape occurred despite the presence of comparatively large amounts of aluminum in the steel.

Four-fifths of the aluminum-killed steels of Table 5 treated with three or five pounds of misch metal per ton of steel contained only Type I sulfides. The analytical data for three of such steels (9800A, 9804A, 9795A) indicate that they contained aluminum in amounts which usually produce Type III sulfides. Hence, it is safe to conclude that the change in inclusion shape resulted from the solution of misch metal, not from oxidation or loss of aluminum.

Two steels (9880A and 9796A, Table 6) were unusual because they contained mixtures of Type I and Type II sulfides, although they had been treated with five pounds of misch metal per ton. Representative inclusions found in these two heats are shown in Figure 9. The inclusions fit the same classification, even though one steel was made by basic practice and the other by acid practice. This illustrates the fact that the type of crucible did not influence the response of the steel to additions of misch metal insofar as inclusion characteristics were concerned.

TABLE 7

Classification of Sulfide Inclusions Found in Aluminum-Killed Steels Cast at Different Times After Adding Misch Metal

	Heat 9277	Heat 9794	Heat 9890	Heat 9805
Type of curcible	Mg O	Mg O	Mg O	Si O_2
Misch-metal addition, lb/ton	5	5	5	5
Inclusion type before misch metal	III	III	III	III
Inclusion type 3 minutes after adding misch metal	I	IV	I	IV
Inclusion type 30 minutes after adding misch metal	II	II	II	II

Large additions of misch metal produce duplexed sulfides termed Type IV inclusions. Most of the laboratory steels treated with eight pounds and about one-third of those treated with five pounds of misch metal per ton contained inclusions of that kind. These statements refer to samples of laboratory steels cast less than five minutes after receiving the addition of rare-earth metal. Prolonged holding caused changes in composition which resulted in a change in the type of sulfide inclusions. Table 7 and Figure 10 show that these progressive changes depend on the time of holding in the furnace after the addition of rare-earth metal. Long holding times result in the formation of Type II inclusions.

Lanthanum and Cerium Effect

Table 8 gives the results of spectrographic analyses for lanthanum and cerium for some of the experimental steels listed in Table 8. The data agree with earlier results in showing conclusively that the cerium-lanthanum ratio in the steel is higher than in the addition agent. The fact that proportionately larger amounts of lanthanum were lost proves that it is a stronger deoxidizer and desulfurizer than cerium. This is of academic rather than practical importance, because comparatively pure cerium produces the same effects as misch metal (1).

Additional cerium and lanthanum analyses are given in Table 9 together with the inclusion classification. It is quite difficult to obtain reliable analytical values for the rare-earth elements. Neverthe-

TABLE 8

Analysis For Cerium and Lanthanum in Some Experimental Steels

Sample Number	Misch Metal, lb/ton	Analysis, percent				Analysis Ratio		Inclusion Type
		S	Ce	La	Ce + La	Ce/La	(Ce + La)/S	
9794M	5	0.024	0.040	0.005	0.045	8	1.9	IV
9795A	5	0.015	0.020	0.002	0.022	10	1.5	I
9800A	5	0.021	0.025	0.03	0.028	8	1.3	I
9802A	1	0.028	0.020	0.003	0.023	7	0.7	II
9803A	2	0.031	0.025	0.003	0.028	8	0.9	I
9804A	3	0.027	0.025	0.003	0.028	8	1.0	I
9880A	5	0.034	0.032	0.012	0.044	2.7	0.8	II
9796A	5	0.054	0.027	0.009	0.036	3.0	0.7	II

Note: All steels were deoxidized with 2 pounds of aluminum per ton. All heats except 9796 and 9880 were made in basic crucibles. The Ce/La ratio of the misch metal used for the addition was 1.5 to 1.

Sulfur 0.042 per cent *Sulfur 0.038 per cent* *Sulfur 0.024 per cent*

Before Misch Metal *½ Minute after Misch Metal* *30 Minutes after Misch Metal*

Figure 10—Effect of holding time on inclusion characteristics of steels treated with 5 pounds of misch metal per ton of steel after aluminum deoxidation. (500X-reduced ½)

less, the data in Tables 8 and 9 seem to indicate the approximate quantities of cerium and lanthanum required to change the shape of sulfide inclusions in aluminum-killed cast steels.

The effect of a particular amount of rare-earth elements on inclusions is influenced by the sulfur content of the steel. That is, the ratio of rare-earth elements to the sulfur content gives a better correlation with inclusion type than the analytical values for cerium and lanthanum. The (Ce + La)/S ratios for five of the seven steels with Type IV sulfides exceeded 1.6. The exceptions were steels containing no acid-soluble aluminum. On the other hand, fourteen of the nineteen aluminum-killed steels with (Ce + La)/S ratios of less than 1.6 were characterized by Type I sulfides. Four steels in this group, having ratios between 0.6 and 0.8, contained Type II sulfides. Apparently, the inclusions in these steels did not contain enough lanthanum and cerium to complete the change from Type III to Type I sulfides.

It appears that excessive quantities of rare-earth elements cause the formation of Type IV sulfides and insufficient amounts produce Type II sulfides in steel. Proper amounts produce spheroidal Type I sulfides in aluminum-killed steels; additions of two to five pounds of misch metal usually produce this desirable effect. The amounts of cerium and

TABLE 9

Analysis For Cerium and Lanthanum in Some Experimental Manganese-Molybdenum Steels

Heat	Crucible	Aluminum Added, lb/ton	Rare-Earth-Metal Added, lb/ton	Analysis, weight percent Ce	La	S	Analysis Ratios Ce/La	(Ce+La)/S	Inclusion Type
7640-4	Magnesia	0	5.2(1)	0.030	0.005	0.024	6.0	1.5	I
-5	Magnesia	0	11.6	0.055	0.0065	0.015	8.5	4.1	IV
7965	Magnesia	0	8.1(1)	0.030	0.0045	0.036	6.7	1.0	I, II
8094-2	Silica	0	2.4(4)	0.030	0.009	0.040	3.3	1.0	I
-3	Silica	0	5.2	0.020	0.006	0.037	3.3	0.7	IV
-4	Silica	0	11.6	0.100	0.031	0.043	4.4	2.9	IV
-5	Silica	0	11.6	0.013	0.001	0.044	15.0	0.4	I
8242-5	Magnesia	1	8(1)	0.020	0.0055	0.026	3.6	1.0	IV
8243-5	Magnesia	1	8(3)	0.030	0.010	0.041	3.0	1.0	I
8316-3	Magnesia	1	3(1)	0.030	0.0085	0.046	3.5	0.8	I
-4	Magnesia	1	5	0.020	0.0035	0.032	5.7	0.7	I
-5	Magnesia	1	8	0.018	0.004	0.013	4.5	1.7	IV
8317-3	Magnesia	3	3(1)	0.060	0.020	0.042	3.0	1.9	I
-4	Magnesia	3	5	0.050	0.015	0.035	3.3	1.9	I
-5	Magnesia	3	8	0.040	0.006	0.010	6.7	4.6	IV
8318-2	Magnesia	1	1(1)	0.030	0.0075	0.063	4.0	0.6	II, III
-4	Magnesia	1	5	0.030	0.005	0.044	6.0	0.8	I
-5	Magnesia	1	8	0.030	0.0085	0.039	3.5	1.0	I
8785(4)	Silica	1.5	2(2)	0.025	—	0.029	—	0.9	I
8786(4)	Silica	1.5	2(3)	0.010	0.003	0.028	3.3	0.5	I
8789(4)	Magnesia	1.5	2(2)	0.018	—	0.028	—	0.6	I
8790(4)	Magnesia	1.5	2(3)	0.010	0.003	0.029	3.3	0.5	I
8791(4)	Magnesia	1.5	2(1)	0.010	0.002	0.028	5.0	0.5	I

Note: Data taken from Reference 1.

(1) Added as General Cerium Company's misch metal containing 54 percent Ce and 24 percent La.

(2) Added as 95 percent cerium alloy.

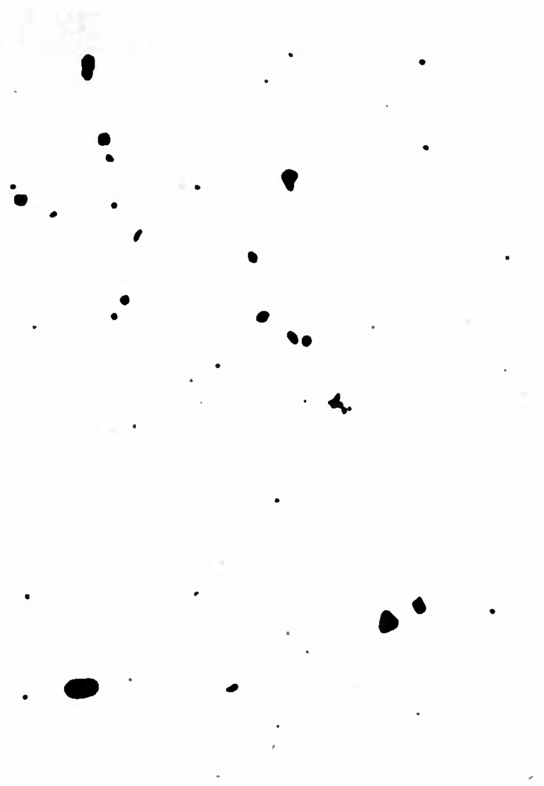
(3) Added as Lan-Cer-Amp containing 45 percent Ce and 29 percent La.

(4) After the misch-metal additions, 3 pounds per ton Ca-Si-Mn alloy was added. Each heat was tapped into a ladle at 3000 degrees F and poured at about 2850 degrees F.

lanthanum necessary to produce these changes are larger for steels with higher sulfur contents. To a lesser extent, the aluminum content of a steel seems to have the same effect as sulfur. This seems reasonable if a certain percentage of rare-earth elements in the sulfide phase is required for Type I sulfides.

The data for the steels made in the laboratory indicate that the size of the misch metal addition should be proportioned to the sulfur content of the metal. This follows from the observation that the inclusion type depends more on the (Ce+La)/S ratio than on the absolute amounts of the rare-earth elements present in the steel. An average of 18 percent of the misch metal addition was recovered in the steel in these experiments. Also, most of the laboratory steels contained about 0.035 percent sulfur. Under these conditions, the desirable globular Type I sulfide inclusions were formed in steels treated with 3 pounds of misch metal per ton of steel. The recoveries in these steels resulted in (Ce+La)/S ratios between 1.0 and 1.6. If the recoveries had been better or the sulfur contents of the liquid steel had been lower, the ratios would have been higher. In such an event, undesirable Type IV sulfide characteristics of steels with (Ce+La)/S ratios exceeding 1.6 would probably have been formed.

Five of the heats for this program were treated with nonmetallic addition agents containing rare-earth elements. One was made with cerium fluoride, the others with agents containing rare-earth oxides and a reducing material. No changes in the shape of the sulfide inclusions occurred in these experiments, and the variations in sulfur contents noted are not considered significant. Figure 11 shows the appearance of the sulfide inclusions typical of the steels treated with addition agents other than misch metal. The inclusions are angular, similar to those found in aluminum-killed steels containing no rare-earth elements.



(1) *5 pounds per ton T-Compound*
(2) *2 pounds per ton Aluminum*

Summary on Inclusions as Formed by Rare-Earth Metals

1. Increasing additions of rare-earth metals to aluminum-killed molten steel change the size, shape, and color of the sulfide inclusions in the steel.
2. Addition of rare-earth metals in amounts up to 5 pounds per ton to silicon-killed steel has no effect on the typical sulfides of these steels.
3. The addition of misch metal per ton of steel to aluminum deoxidized steels of 0.035 sulfur content changes the Type III sulfides as follows:

   1 lb/ton of steel—Type III to Type II

   2 lb/ton of steel—Type III to Types I and II

   3 lb/ton of steel—Type III to Type I

   5 lb/ton of steel—Type III to Types I and IV

   8 lb/ton of steel—Type III to Type IV
4. The amount of misch metal addition should be proportioned to the sulfur content of the melt because the inclusion type depends on the $(\mathrm{Ce}+\mathrm{La})/\mathrm{S}$ ratio in the steel.

(1) *2 pounds per ton Aluminum*
(2) *5 pounds per ton T-Compound*

(1) *2 pounds per ton Aluminum*
(2) *4.2 pounds per ton Cerium Fluoride*

Figure 11—Sulfide inclusions in cast steels treated in the order, quantity and type of additions as indicated. (500X)

5. Inclusion types formed on the basis of the (Ce+La)/S ratio are as follows:

   Ratios between 1.0 and 1.6 form Type I inclusions

   Ratios about 1.0 form Type II inclusions with Types I or III inclusions present

   Ratios above 1.6 form Type IV inclusions

6. The (Ce+La)/S ratio depends on the quantity of sulfur present in the steel and on the quantity of rare-earth metals entering the steel. Laboratory studies indicated a range of 8 to 60 percent of the rare earth metals additions were recovered in the steel. However, from a commercial point of view the Ce+La recoveries probably would be somewhere in the range of 10 to 25 percent of the total pounds of rare-earth metals added per ton of steel.

7. It should be pointed out that throughout these studies there is a varying percent recovery of rare-earth elements in the molten steel. There are several reasons for this variation. In some cases the sulfur is eliminated from the steel as rare-earth sulfides; in other cases, the analyses of the rare-earth elements may be in error. A small error in these cases has an important effect on the (Ce+La)/S ratio.

   Also, in a number of cases two types of inclusions may be found in the same steel. It has been observed in the studies that both Type I and Type II inclusions may be present in a steel, yet a similar steel produced in apparently the same manner results in only Type I inclusions. The region of 0.6 to 1.0 (Ce+La)/S ratio is very susceptible to the combination of both Types I and II inclusions being present in the same steel.

8. A very general rule which should work in a majority of the cases, and which can be easily remembered is based on the sulfur content and the quantity of rare-earth metals to add in order to produce the favorable Type I inclusion. This rule is as follows:

Sulfur Content of Steel	Pounds/ton of Rare-Earth Metals to add to produce Type I Inclusions
0.025 to 0.040	3
Greater than 0.040	4
Less than about 0.020	2

9. No change in the shape of the sulfide inclusions occurred upon the addition of non-metallic addition agents containing rare-earth elements.

SECTION III

INFLUENCE OF RARE-EARTH METALS ON MECHANICAL PROPERTIES OF CAST STEELS

Sulfur Content vs. Impact Properties

V-notch Charpy tests were made on heats produced primarily for studying desulfurization by additions of misch metal. The Charpy data were useful for deciding upon melting practices to be used for subsequent heats and for interpreting later data. Table 10 gives average Charpy values based on triplicate tests at temperatures between 80 and -100 degrees F.

The Charpy values for the six steels listed first in the table are in the order of their sulfur contents. Higher sulfur contents usually result in lower notched-bar values. In this group, the effects of variations in sulfur content apparently outweighed the effects of differences in sulfide shape. This influence of sulfur level on Charpy values was used in interpreting data for other heats which differed slightly in sulfur content.

Heats 9795, 9796, and 9797 were made under similar conditions except for melting and pouring temperatures. The best Charpy values were obtained on the heats poured at 2850 degrees F. This temperature produced the lowest sulfur content after the misch-metal addition, and the Charpy properties were controlled largely by the sulfur contents of the steels; consequently 2850 degrees F was the temperature chosen for producing steels made later in the program. The unusually poor Charpy properties of the 0.059 percent sulfur heat (9796), which had the highest sulfur content in the group, should be noted. The harmful effect of sulfur was probably accentuated by the presence of film sulfides in this casting. A (Ce+La)/S ratio of less than 0.6 was apparently obtained because of the high sulfur content.

The differences attributable to composition were not so pronounced as might be expected because the specimens were heat treated in ½-inch sections. The low-alloy steel would not harden through in some larger sections where the higher alloy steel would respond satisfactorily.

TABLE 10

Effect of Melting Practice, Sulfur Content, and Sulfide-Inclusion Type on Charpy Impact Properties of Experimental Steels

Heat	Pouring Degrees F	Crucible	Additions, lb/ton		Analysis, percent			Sulfide-Inclusion Type	V-Notch Charpy Values at Temperature Indicated, ft-lb							
			Al	Misch Metal	Mn	Melt S	Final S		+80°F	+32°F	0°F	—20°F	—40°F	—60°F	—80°F	—100°F
9796	2950	Magnesia	2	5	1.25	0.059	0.054	I, II	17.0	—	16.0	—	16.5	13.0	11.5	9.0
9798	2850	Magnesia	2	0	1.25	0.044	0.044	II	28.5	—	23.5	22.5	21.5	—	15.0	—
9797	3050	Magnesia	2	5	1.25	0.044	0.038	I	36.0	—	34.0	31.5	27.0	—	19.0	15.0
9880	2850	Silica	2	5	1.25	0.037	0.034	I	61.5	56.0	40.5	29.5	30.5	—	18.5	—
9799	2850	Magnesia	2	0	1.25	0.020	0.020	III	45.5	—	42.5	33.0	26.5	—	19.5	—
9795	2850	Magnesia	2	5	1.25	0.043	0.015	I	72.0	—	63.5	—	41.5	—	32.0	27.5
9807	2850	Magnesia	0	5	1.25	0.042	0.036	I	56.5	—	36.5	29.0	25.0	19.5	—	—
9881	2850	Silica	2	5	0.70	0.039	0.035	I	46.0	40.5	38.0	—	31.0	—	18.5	—
9800	2850	Magnesia	2	5	0.70	0.042	0.021	I	58.0	41.0	33.0	22.5	17.5	—	—	—

Note: The Charpy values are averages for three V-notch specimens. Composition of the steels is given in Table A-1. The two heats listed at the bottom of the table contained 0.70 percent manganese, the others contained 1.25 percent manganese and 0.10 percent molybdenum. Heat 9796 held 30 minutes at 2950° F before pouring keel blocks; Heat 9797 held 80 minutes at 3050° F before pouring keel blocks. The others were held 3 minutes and poured at 2850° F.

The steels which were made in silica crucibles, had good Charpy properties. For their sulfur content, they were equal to the steels made in magnesia crucibles.

Figure 12 shows the relationship between the sulfur content of the steels listed in Tables 10 and 12 and their average Charpy values at -40 degrees F. It appears that decreasing the sulfur content of these steels by 0.010 percent increased the Charpy at this temperature about 7 foot-pounds.

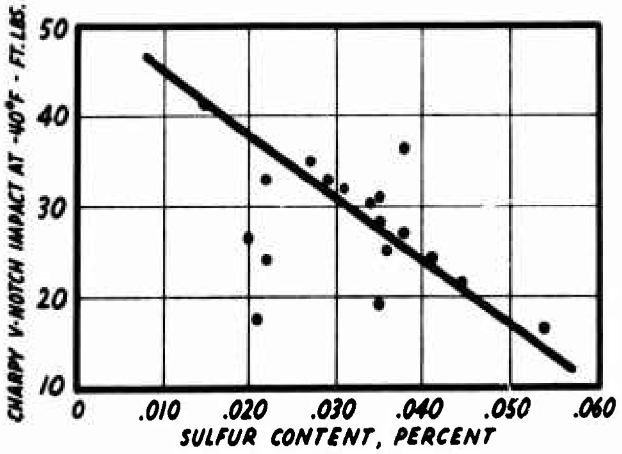


Figure 12—The relation between sulfur content and Charpy V-notch impact values of the experimental steels at -40°F. Data taken from Tables 11 and 13

Temper Brittleness

When castings are heat treated in comparatively heavy sections, the cooling rate from the tempering treatment is necessarily slow. If a slow rate of cooling results in poor toughness, the steel is said to be temper brittle. Since this behavior is undesirable, the influence of rare-earth-metal additions on the susceptibility to temper brittleness was investigated.

Table 11 gives the history and Charpy data for ten sets of samples used for studying temper brittleness. The cooling rate for the furnace-cooled samples was quite slow, approximately 5 hours from 935 degrees to 80 degrees F. The compositions of these heats are given in Table A-1 of the Appendix. All of the steels, except Heat 9800, contained 0.10 percent molybdenum, an element which retards or prevents temper brittleness. The base composition used in this investigation did not exhibit temper brittleness, even without an addition of misch metal. Consequently, the fact that the other heats did not exhibit temper brittleness does not give much information about the effects of rare-earth elements. The results of Table 11 were taken as an indication that misch-metal additions do not significantly increase the tendency for temper brittleness. Nevertheless, all steel used for the other mechanical tests was quenched from the tempering temperature. It should be pointed out that Heat 9800 should have been the most susceptible to temper brittleness. No temper brittleness was noted as shown in Table 11.

TABLE 11

Impact Tests Made to Determine the Susceptibility of Experimental Steels to Temper Brittleness

Heat	Specimen(3)	Misch-Metal Addition, lb/ton	Inclusion Type After Misch Metal	Sulfur, percent	Brinell Hardness	Charpy Impact Values(4) at Various Temperatures, ft-lb							
						+80°F	+32°F	0°F	—20°F	—40°F	—60°F	—80°F	—100°F
9798(1)	A	0	II	0.044	268	28.5	—	23.5	22.5	21.5	—	15.0	—
9798(1)	F	0	II	0.044	269	25.0	24.5	17.5	—	20.0	—	14.5	9.0
9799(1)	A	0	III	0.020	269	45.5	—	42.5	33.0	26.5	—	19.5	—
9799(1)	F	0	III	0.020	268	44.0	—	41.0	34.0	26.0	—	18.5	—
9795(1)	A	5	I	0.015	265	72.0	—	63.5	—	41.5	—	32.0	27.5
9795(1)	F	5	I	0.015	268	67.5	—	54.0	—	40.5	27.0	16.5	11.0
9880(1)	A	5	I	0.034	269	61.5	56.0	40.5	29.5	30.5	—	18.5	—
9880(1)	F	5	I	0.034	269	69.0	60.0	50.0	—	31.0	31.0	—	16.0
9800(2)	A	5	I	0.021	265	58.0	41.0	35.0	22.5	17.5	—	—	—
9800(2)	F	5	I	0.021	265	67.0	—	—	—	36.0	—	21.5	—

(1) Nominal composition: 0.23 percent carbon, 1.30 percent manganese, 0.10 percent molybdenum; aluminum-killed. killed.

(2) Nominal composition: 0.23 percent carbon, 0.70 percent manganese; aluminum killed. No molybdenum present.

(3) Letter "A" represents water quenching from tempering treatment. Letter "F" represents furnace cooling from tempering treatment, five-hour cooling time.
Tempering temperature 935° F for all steels except Heat 9800, which was tempered at 850° F.

(4) Charpy values are averages for three V-notch specimens.

Notched-bar Impact Properties

One of the principal objects of this study was to establish the effects of rare-earth metals on the mechanical properties of cast steels. The data in Table 11 show the effect of such additions on the Charpy V-notch impact properties of steels containing 1.3 percent manganese and 0.1 percent molybdenum.

The best notched-bar properties of the group (9795) received an addition of five pounds of misch metal per ton of steel which lowered the sulfur content from 0.043 to 0.015 percent and changed the sulfide inclusions to Type I globules. This steel, with 0.02 percent cerium plus lanthanum by analysis, had Charpy values of 72 and 41.5 foot-pounds at 80 degrees F and -40 degrees F, respectively. These energy values can be contrasted with those of 28.5 and 21.5 foot-pounds for the untreated steel (9798) tested at the same temperature. The Charpy properties of the steel containing rare-earth elements are also better than those which contained low sulfur but no misch metal. Consequently it appears that the benefits of the misch-metal treatment were greater than would be expected from desulfurization alone.

Steel made in a silica crucible and treated with misch metal (9880), also had better notched-bar properties than comparison heats without misch metal (9798 and 9899) In this case, too, the improvements are independent of desulfurizing effects, though misch metal caused the sulfide inclusions to have a globular shape.

Perhaps a note of caution is appropriate at this point. As indicated in Section II, the addition of five pounds of misch metal per ton of steel usually results in the presence of Type IV sulfide inclusions. Earlier work (1) showed that steels with such inclusions have very poor ductility in tension. For this reason and for economy, such large additions of misch metal are not recommended. The good properties of Heats 9795 and 9880 are attributed to the fact that they contained Type I sulfides and retained quantities of rare-earth elements more typical of additions of three pounds per ton of steel than of the five pounds per ton actually added.

Charpy tests were also made on a number of low-alloy, Ni-Cr-Mo steels. The results obtained from nine heats which had the same base composition are summarized in Table 12. All of these steels were made in magnesia crucibles and deoxidized with two pounds of aluminum per ton of steel.

The two steels prepared without misch metal additions had poorer Charpy properties than the four heats which received additions of misch metal. The differences were numerically larger at room temperature, but large enough to be significant at temperatures down to -80 degrees F. The ductility of the tensile specimens was also improved, but neither yield nor tensile strength seems to have been affected by the rare-earth-metal treatments. Also, the benefits of the misch-metal additions could be detected at hardness levels of either 265 or 300 Brinell (9811, 9812). Part of the improvement in this case is attributed to the removal of some sulfur.

TABLE 12

Effects of Various Additions of Misch Metal on Toughness and Ductility of Steel
(Composition: 0.23 percent carbon, 0.40 percent molybdenum, 0.50 percent chromium and 0.25 percent nickel)

Heat	Mish Metal, lb/ton	S, %	Inclusion Type	Brinell Hardness	Elongation in 2 In., %	Reduction of Area, %	Yield Strength (0.2% Offset), 1000 psi	Tensile Strength, (1) 1000 psi	V-Notch Charpy Value(2), ft-lb		
									+80°F	—40°F	—80°F
9801	0	0.041	II	260	15.6	33.0	100.0	113.3	26.5	24.0	18.5
9802	1	0.031	II	262	15.5	36.0	108.5	120.1	30.0	32.0	23.0
9803	2	0.029	I	260	18.0	45.1	107.6	118.5	41.0	31.0	23.0
9804	3	0.027	I	267	18.6	47.9	111.2	122.7	35.5	35.0	24.5
9811(3)	0	0.035	III	268	18.2	40.3	109.7	122.2	38.0	28.0	19.0
9812(3)	3	0.022	I	268	21.0	56.2	108.8	121.2	72.0	33.0	25.0
9811	0	0.035	III	300	—	—	—	—	33.0	19.0	14.0
9812	3	0.022	I	302	—	—	—	—	55.0	24.0	—

Note: All steels were made in magnesia crucibles and deoxidized with two pounds of aluminum per ton of steel.

(1) The tensile specimens were heat treated in 1-inch square sections. The values are averages of two tests. The stock was water quenched from 1625° F, tempered 2 hours at 1100° to 1150° F and water quenched.

(2) The Charpy specimens were heat treated in 1/2-inch sections; the values are averages of three tests. The specimens were hardened from 1625° F and tempered 2 hours at 1100 to 1150° F. The higher-hardness-level specimens were tempered at 1050° F. All specimens were water quenched from the tempering temperatures.

(3) Heats 9811 and 9812 contained about 0.2 percent more manganese than the others.

TABLE 13

Mechanical Properties of Experimental Steels Treated with Different Rare-Earth Addition Agents

Heat	Addition Agent	Sulfur Content, %	Inclusion Type	Brinell Hardness	Elongation in 2 In., %	Reduction of Area, %	Yield Strength, 1000 psi	Tensile Strength, 1000 psi	V-Notch Charpy Value, ft-lb							
									+80°F	+32°F	0°F	—20°F	—40°F	—60°F	—80°F	—100°F
9801	None	0.041	II	255	15.6	33.0	100.0	113.3	26.5	—	—	25.0	24.0	22.0	18.5	16.0
141	None	0.038	III	263	14.0	29.8	114.4	123.4	42.0	—	—	—	36.5	41.5	34.0	23.0
9808	(1)	0.031	I	256	20.0	52.1	94.2	109.8	54.5	—	—	—	47.5	34.0	26.5	15.0
9804	(1)	0.027	I	269	18.6	47.9	111.7	127.7	35.5	—	—	—	35	32.5	24.5	18.5
9894	(2)	0.024	I	268	—	—	—	—	76.5	—	—	—	71.5	38.0	33.5	32.5
9895	(3)	0.023	III	267	—	—	—	—	39.5	38.5	30.0	—	22.0	18.5	14.0	—
9896	(3)	0.029	III	266	—	—	—	—	45.0	44.5	40.0	28.0	24.0	—	—	—
9897	(4)	0.028	III	258	—	—	—	—	51.5	48.5	49.5	49.0	37.0	—	25.0	19.0
143	(5)	0.037	III	268	16.7	43.0	114.3	128.2	37.5	—	36.5	30.0	24.5	25.5	17.0	—
144	(6)	0.035	III	267	17.1	42.6	115.8	129.6	37.5	—	—	—	39.5	39.0	36.0	24.5

Note: Compositions are given in Table A-1. They contain approximately 0.23 percent C, 1.3 percent Mn, 0.4 percent Mo, 0.5 percent Cr, and 0.2 percent Ni. All were deoxidized with two pounds of aluminum per ton of steel. Heats 143 and 144 were made in silica crucibles, the others in magnesia crucibles. Charpy values are averages of three tests, and tensile data are based on two tests. Tempering temperatures are given in Table A-2.

(1) Heats 9804 and 9808 were treated with 3 pounds per ton of Lan-Cer-Amp No. 1, a misch metal made by the American Metallurgical Products Company.

(2) Heat 9894 was treated with 3 pounds per ton of misch metal made by the General Cerium Company.

(3) Heats 9895 and 9896 were treated with 5 pounds per ton of T-Compound made by Molybdenum Corporation of America. This addition is equivalent to 3 pounds per ton of misch metal. In Heat 9895, the steel was deoxidized after the T-Compound addition. In Heat 9896, the steel was deoxidized before the T-Compound addition.

(4) Heat 9897 was treated with 4.2 pounds per ton of CeF_3 made by the Lindsay Light and Chemical Company. This addition is equivalent to 3 pounds per ton of misch metal.

(5) Heat 143 was treated with 5.5 pounds per ton of limed T-Compound made by Molybdenum Corporation of America. This addition is equivalent to 3 pounds per ton of misch metal.

(6) Heat 144 was treated with 6 pounds per ton of Remox-C Compound made by the Mallinckrodt Chemical Works. This addition is equivalent to 3 pounds per ton of misch metal.

The data for this series of steels show that misch-metal additions which improved the mechanical properties also changed the inclusions to Type I sulfides.

Influence of Rare-earth Oxides and Fluorides

Some nonmetallic agents containing rare-earth elements were used in the laboratory experiments in addition to misch metal. Mixtures of rare-earth oxides with a calcium-silicon or a calcium-boride alloy as the reducing agent were used for four heats. Another heat was made with cerium fluoride. The quantities of these materials added to the melts corresponded to three pounds of misch metal per ton of steel. The approximate compositions of the addition agents are given in Table 1.

The mechanical properties of heats made with the six types of rare-earth-containing addition agents used during this investigation are given in Table 13. All steels were similar in alloy composition and were poured at temperatures about 2870 degrees F.

The heats which were treated with misch metal, had Charpy and tensile ductility properties better than the untreated control heat. Superior notched-bar properties were evident at temperatures down to -60 degrees F. Part of the superiority, especially at room temperature, of the steels treated with misch metal is attributed to their lower sulfur contents. The misch-metal additions also produced Type I sulfides.

The data in Table 13 indicate that none of the oxide or fluoride additions changed the shape of the sulfide inclusions. Nevertheless, Heat 144, made in silica crucible, had particularly good notched-bar properties at low temperatures. This melt was treated with a mixture of rare-earth oxides and calcium silicon, but the good properties cannot be attributed to any special addition.

A limed T-compound containing calcium boride as the reducing agent was added to three heats. These heats had the poorest notched-bar properties of the group in tests at -40 degrees F. The room-temperature Charpy values, however, were better than those of the untreated steels.

It was suspected that some boron in the T-Compound would be retained in the steel. This would be expected to occur in aluminum-killed steels because aluminum has a stronger affinity for oxygen than does boron. Spectrographic analyses indicated that Heat 9895 contained 0.003 percent boron and Heat 9896 contained 0.0015 percent boron. Both quantities are sufficient to increase hardenability.

The data in Table 14 indicate that misch metal is superior to the other addition agents (Heat 9894). Misch metal appears to be better because it removed more sulfur from the melts than the other additions and because it changed the shape of the sulfide inclusions. For these reasons, misch metal was used for introducing rare-earth elements to most of the experimental steels.

Influence of Minor Elements on the Response of Cast Steels to Rare-Earth Additions

A variety of materials are used for adding boron to increase the hardenability of steel. The different addition agents contain small quantities of other elements, as indicated in Table 14. It was suspected that some of these elements might interfere with the beneficial effects of misch metal. Table 15 presents data on mechanical properties of fifteen heats made to study this possibility. The possibility that the presence of misch metal might prevent the effect of boron on hardenability was also considered worthy of investigation. This point is discussed in another section.

Good ductility properties and impact properties were obtained on steels treated with the boron

TABLE 14

Compositions of Boron-Containing Materials Used in this Investigation

Trade Name	Composition, percent(1)							
	B	Ti	Zr	Al	Si	Mn	C	Fe
Ferroboron	16.3	—	—	(0.5)	4.3	—	—	Balance
Borosil	2.92	—	—	—	38.58	—	0.94	Balance
Carbortam	1.74	15.78	—	(1-2)	2.65	(0.1-0.2)	5.88	Balance
Grainal X-79	0.44	(20)	(4)	(13)	—	—	—	Balance

(1) Parentheses indicate the nominal amounts of these elements.

TABLE 15

Influence of Titanium, Nitrogen, Carbon, Vanadium, and Various Boron Addition Agents on Charpy Properties of Experimental Steels

Heat	Misch-Metal Addition[1], lb/ton	Inclusion Type	Composition, percent		Boron Agent	Brinell Hardness	Elongation in 2 In., percent	Reduction of Area, percent	Yield Str., 1000psi	Tensile Str., 1000psi	V-Notch Charpy Value, ft-lb							
			S	Special Element							+80°F	+32°F	0°F	—20°F	—40°F	—60°F	—80°F	—100°F
9810	3	I	0.028	0.005 B	Ferroboron	260	18.8	50.5	112.3	124.6	52.5	—	49.5	50.0	31.0	28.5	22.5	—
9813	3	I	0.028	0.006 B	Ferroboron[2]	268	20.0	53.5	107.6	121.8	58.0	46.5	—	—	21.0	—	—	—
9891	2	I, II	0.025	0.005 B	Carbortam	255	19.8	50.1	105.3	119.5	53.0	—	—	46.0	34.5	27.5	22.5	—
9892	2	I	0.029	0.005 B	Borosil	253	20.3	51.3	103.4	117.3	52.5	52.5	55.0	42.0	32.5	—	27.0	24.5
9893	2	I, II	0.026	0.005 B, 0.17 Ti	Grainal X-79	262	13.6	25.8	103.1	115.9	6.0	—	—	—	3.0	—	—	—
9884	0	III, II	0.028	0.09 Ti	None	264	13.6	25.3	103.3	114.6	12.5	10.5	—	—	6.5	—	4.0	—
9885	2	I, II	0.026	0.08 Ti	None	267	17.1	37.6	112.0	123.0	14.5	—	7.6	—	6.3	—	—	—
9898	0	III	0.026	0.003 B	Carbortam	254	17.0	38.3	107.8	120.9	46.0	47.0	43.5	39.5	30.5	17.5	20.5	—
9899	2	I	0.022	0.0045 B, 0.016 N	Carbortam	253	20.8	57.0	107.1	120.4	68.5	—	58.5	—	40.0	30.5	27.0	24.0
9882	0	III	0.026	0.017 N	None	253	19.1	45.6	108.5	127.8	39.0	—	38.0	—	25.0	22.5	19.0	10.0
9883	2	I	0.023	0.017 N	None	268	18.9	47.9	106.5	120.2	53.5	—	—	—	34.5	29.5	22.5	—
142	2	I, II	0.035	None	None	269	10.2	32.5	118.7	132.7	34.5	—	—	—	30.0	32.5	30.0	19.5
9879	2	I	0.029	0.11 V	None	255	21.9	49.1	97.2	110.0	47.0	44.0	47.0	37.5	30.5	24.0	20.0	18.0
9887	0	III	0.030	0.44 C	None	253	21.7	39.4	94.2	112.9	37.5	—	—	—	35.5	33.0	25.0	21.5
9886	2	I	0.027	0.40 C	None	254	18.4	36.6	109.6	126.2	52.5	—	—	—	50.5	45.5	32.5	28.0

Note: These steels were made in magnesia crucibles and were aluminum killed; most of them contained approximately 0.23 percent C, 1.3 percent Mn, 0.5 percent Mo, 0.5 percent Cr, and 0.5 percent Ni. Steels 9810 and 9813 have slightly less Mn, Mo, and Ni.

(1) The misch metal was obtained from American Metallurgical Products Company.

(2) Ferroboron added after rare-earth-metal addition.

TABLE 16

Mechanical Properties of Quenched and Tempered Cast Steels With Various Alloy Contents and Misch Metal Additions

Heat	Nominal Composition, percent Mn	Mo	Cr	Ni	B	Actual S	Final Inclusion Type	Yield Str., 1000psi	Tensile Str.,(1) 1000psi	Brinell H'dness	Elongation in 2 In., %	Reduction of Area, %	V-Notch Charpy Values(2), ft-lb +80°F	+32°F	0°F	—20°F	—40°F	—60°F	—80°F	—100°F
Heated as 1-Inch Thick Sections																				
9804	1.25	0.40	0.50	0.25	—	0.027	I	111.7	122.7	269	18.6	47.9	35.5	—	—	—	35.0	32.5	24.0	18.5
9808	1.25	0.40	0.50	0.04	—	0.027	I	94.2	109.8	256	20.0	52.1	54.5	—	—	—	47.5	34.0	26.5	15.0
9809	1.25	0.20	0.50	0.25	0.0045	0.028	I	110.4	120.9	256	17.5	47.5	50.0	—	—	48.0	41.0	37.0	27.5	19.0
9810	1.15	0.40	0.50	0.25	0.006	0.028	I	112.2	124.6	262	18.8	50.5	52.5	—	49.5	50.0	31.0	28.5	22.5	—
9811	1.50	0.40	0.50	0.25	—	0.035	III	109.7	122.2	268	18.2	40.3	38.0	—	36.0	30.0	28.0	24.5	19.0	—
9812	1.50	0.40	0.50	0.25	—	0.022	I	108.8	120.9	268	21.0	56.2	71.5	—	59.5	44.5	33.0	27.5	25.0	—
9813	1.50	0.40	0.50	0.25	0.0045	0.028	I	107.6	121.8	268	20.0	53.5	58.0	46.5	28.0	20.0	21.0	—	—	—
9875	1.50	0.20	0.50	0.25	0.0045	0.031	I	108.7	122.1	268	19.0	46.2	49.5	36.0	33.5	—	15.5	—	—	—
9876	1.50	0.40	1.00	0.25	—	0.026	I	106.6	121.2	268	20.0	51.6	59.5	44.5	30.5	25.0	21.0	—	—	—
9877	1.50	0.40	1.00	0.25	0.0045	0.022	I	104.9	120.1	268	19.5	53.6	57.0	35.5	25.0	—	18.5	13.5	—	—
9878	1.50	0.20	1.00	0.25	0.0045	0.028	I	102.2	116.4	257	19.2	49.7	34.5	17.5	15.5	—	10.0	—	—	—
9888	1.25	0.20	0.50	0.25	—	0.026	I	100.0	114.9	255	19.8	56.4	60.5	—	50.0	49.0	32.0	26.0	—	—
9894	1.25	0.40	0.50	0.25	—	0.024	I	—	—	268	—	—	76.5	—	—	—	71.5	38.0	33.5	32.5
Heat Treated as 4-Inch Thick Sections																				
9811			(See above analysis)					86.6	102.7	208	20.5*	33.3	47.0	32.0	23.5	—	16.5		—	
9812								84.4	100.2	214	20.5*	34.7	52.5	27.5	23.0	17.0	12.0		—	
9813								88.4	104.3	221	23.2*	34.6	35.5	22.0	—	—	12.5		—	
9875								90.3	107.5	228	24.0*	30.0	46.5	41.0	25.0	—	19.5		10.5	
Heat Treated as 6-Inch Thick Sections																				
9875			(See above analysis)					88.4	104.0	197	26.7*	25.1	48.5	36.5	23.0	—	13.0		9.0	
9876								89.5	103.6	208	25.0*	25.6	44.5	36.0	31.5	22.0	17.5		7.5	
9877								89.6	106.5	228	23.2*	32.5	47.5	22.0	—	—	10.5		—	
9878								85.1	101.6	214	25.0*	32.0	24.5	11.0	—	—	5.5		—	

Note: All heats made in basic-lined crucibles and deoxidized with 2 pounds per ton of aluminum. All but Heat 9811 were treated with three pounds of misch metal per ton of steel. Specimens quenched from 1625° F and tempered 2 hours.

Note: The plates were held one hour after the center of the assemblies shown in Figure 1 reached 1650° F. The 4-inch-thick assembly was quenched for 20 minutes and the 6-inch-thick assembly for 40 minutes in running water. The small tensile bars used for the tests conformed to ASTM standards for 1.25-inch gage length specimens.

(1) Tensile values are average of two tests.

(2) Charpy values are average of three tests.

* Elongation in 1.25 inches %.

alloys: ferroboron, Carbortam, and Borosil. These property data indicate that boron does not influence the response of cast steels to additions of misch metal. The heat to which Grainal 79 was added (9893) had poor ductility values and the V-notch Charpy value was only 6 foot-pounds. The low values are the result of the presence of titanium-rich Type II sulfides and had nothing to do with the rare-earth addition. Chemical analysis indicated that the steel contained 0.17 percent titanium.

Also, the presence of 0.09 percent titanium induced brittleness (Table 16, Heats 9884, 9885) and the Charpy impact values were reduced to one-fourth their normal level. These steels contained some film sulfides.

Most of the induction-furnace steels used for this investigation contained approximately 0.005 percent nitrogen. However, three high-nitrogen heats were made to determine whether this element affected the influence of misch-metal additions. This was considered a matter of practical importance because many electric-furnace steels contain above 0.01 percent nitrogen.

The addition of two pounds per ton of misch metal to steel containing 0.017 percent nitrogen improved the Charpy properties (9882, 9883). The effect on the tensile properties was not significant. The comparatively high nitrogen content did not interfere with the effect of misch metal on the shape of the sulfide inclusions. Also, the data indicate that a relatively high nitrogen content is not deleterious in aluminum-killed steels treated with rare-earth metals (9899, 9883).

Comparison of the data indicates that vanadium does not interfere with the action of misch-metal additions. Besides, misch-metal additions produced the normal changes in steels containing 0.4 percent carbon.

Effect of Alloy Composition and Misch Metal on the Properties of Cast Steels

Twelve of the experimental heats can be compared to secure some information about the influence of alloying elements on the mechanical properties of cast steels treated with misch metal. The steels listed in Table 16 represent two levels of manganese, molybdenum, chromium, and nickel contents. All but one of these heats was treated with three pounds of misch metal per ton of steel and six of them contained boron. The data in Table 16 are for specimens tempered to approximately 265 Brinell. Charpy values for seven of the steels tempered to 300 Brinell are listed in Table 17.

The presence of 0.25 percent nickel in most of the experimental steels probably had little, if any, effect on their mechanical properties (9808, 9804, 9894).

Variations in managanese content in the alloy steels from 1.15 to 1.50 percent had no consistent influence on the mechanical properties.

Raising the chromium content from 0.50 to 1.00 percent had no effect on the room-temperature properties of the experimental steels. The data indicate that the higher chrominum content may have impaired the low-temperature impact properties slightly. This condition was reported when the steels were tempered to 300 Brinell as shown in Table 17.

TABLE 17

V-Notch Charpy Properties of Experimental Steels Heat Treated to Approximately 300 Brinell in ½-Inch Sections

	Nominal Composition, percent				Sulfur,	Inclusion	Brinell	Charpy Values at Indicated Temperature, ft-lb						
Heat	Mn	Mo	Cr	B	%	Type	Hardness	+80°F	+32°F	0°F	—20°F	—40°F	—60°F	—80°F
9811(1)	(1.50)	(0.40)	(0.50)	—	0.035	III	297	33.5	—	26.0	22.5	18.5	27.5	14.0
9812	1.42	(0.40)	(0.50)	—	0.022	I	302	55.5	46.5	36.0	29.5	24.0	22.0	—
9813	1.57	(0.40)	(0.50)	(0.0045)	0.028	I	302	39.5	23.5	20.5	21.0	15.5	—	—
9875	(1.50)	(0.20)	(0.50)	(0.0045)	0.031	I	300	39.5	24.5	19.0	—	15.0	14.0	—
9878	(1.50)	(0.20)	(1.00)	(0.0045)	0.028	I	297	12.5	—	—	—	4.5	—	—
9876	(1.50)	(0.40)	1.04	—	0.029	I	302	36.0	19.5	16.0	—	12.5	—	—
9877	1.46	(0.40)	(1.00)	(0.0045)	0.022	I	297	39.5	22.5	15.5	15.5	10.5	—	—

Note: All steels were deoxidized with two pounds of aluminum and contain 0.23 percent C and 0.25 percent Ni. Boron was added as ferroboron. Charpy values are averages of three tests. Actual compositions are given without parentheses while intended compositions are enclosed in parentheses.

(1) Not treated with misch metal. All other heats were treated with 3 pounds per ton of misch metal.

The data, on the whole, however, is too inconclusive to make any definite statements.

The steels containing 0.40 percent molybdenum usually exhibited better mechanical properties at room temperature than comparable steels with 0.20 percent molybdenum. However, the low temperature tests showed no consistent influence of molybdenum. The only significance that can be given to the properties of the one-inch sections in Tables 16 and 17 is that steels treated with rare-earth metals show better properties.

Heavy Sections Simulated

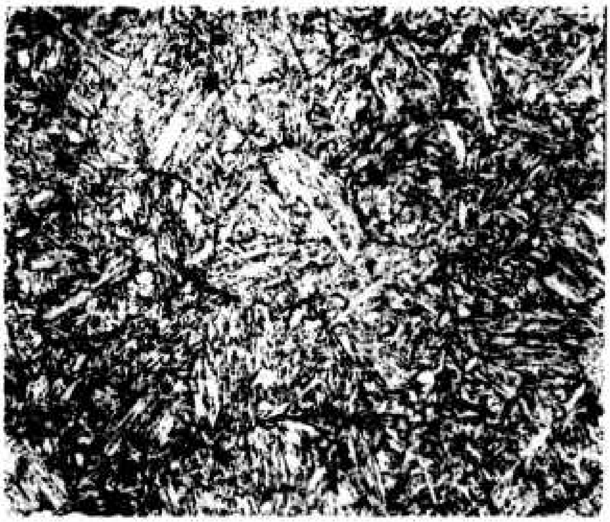
Seven of the experimental steels in Table 16 studied in the one-inch section were also heat treated under conditions approaching those typical of the center of 4-inch or 6-inch plates. This stock was welded inside cover plates, using the arrangement illustrated by Figure 1. The tensile and V-notch Charpy data for specimens heat treated in this way are also given in Table 16.

The plate assemblies were tempered at 1150 degrees F, a temperature which would develop a hardness of approximately 260 Brinell in light sections of the same steels. The surface hardness of homogeneous 4- and 6-inch plates of these compositions would be expected to be about 250 Brinell. However, the data in Table 18 show that most of the specimens taken from the center of the assemblies had Brinell hardnesses of approximately 215 after tempering. The lower hardness level shows that the specimens were not completely martensitic after quenching. The differences in microstructure resulting from heat treating a Mn-Cr-Mo cast steel as different sections are shown in Figure 13.

TABLE 18

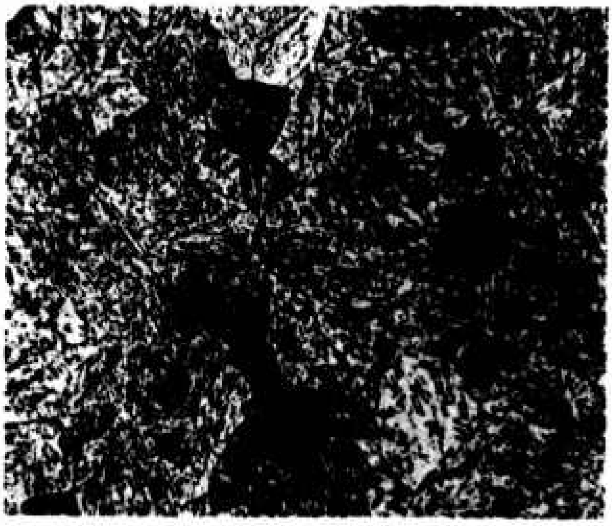
Approximate Cooling Rates at Different Locations on the Special Hardenability Specimen Shown in Figure 16

Cooling Rate Near 1300° F	Distance from the Air-Cooled End of the Hardenability Bar	Other Equivalent Positions
5.1°F per second	1/2 inch	1-7/8 inches on End-quench bar
3.0°F per second	1-3/4 inches	Center of 6-inch steel plate cooled in still water
2.0°F per second	2-1/2 inches	Center of 8 inch plate cooled in still water
1.1°F per second	3-1/4 inches	Center of 10-inch steel plate cooled in still water



½-inch Section - 268 BHN

4-inch Section - 228 BHN



6-inch Section - 197 BHN

Figure 13—The effect of section size during heat treatment on the microstructure of a Mn-Cr-Mo cast steel (Heat 9875) as water quenched from 1650°F and tempered at 1150°F. Nital Etch. (500X)

Despite their lower hardnesses, specimens heat treated as heavy sections had poorer ductility and toughness than those heat treated in light sections. This is shown by the data for Charpy tests at room temperature and by the reduction-of-area values for the tensile specimens. The elongation values of tensile specimens taken from the assemblies were quite high. This is attributed principally to the fact that they were obtained over a 1.25-inch gage length, rather than to a result of hardness level or heat-treating practice.

Comparison of Heats 9811 and 9812 indicates that the addition of misch metal to the latter steel conferred no marked benefits. Heat 9812 did have slightly better reduction of area and room-temperature Charpy values, but the differences are probably not significant.

Heat 9875 was the only steel heat treated as a 6-inch plate which did not contain one percent chromium. Consequently, it had a slightly lower hardness than the others. The Charpy properties of the steel do not appear to be unusual.

Heat 9876, which was free of boron, gave the best Charpy values at -40 degrees F of the four steels heat treated as 6-inch-thick plates. Heats 9875 and 9811 had the best low-temperature properties of those heat treated in the 4-inch-thick assembly. These three materials were the only ones giving Charpy values of 15 foot-pounds or more at -40 degrees F. All but one of the seven heats exceeded this Charpy value when heat treated to 265 Brinell in light sections.

Effect of Rare-Earth-Metal Additions on Grain Size

Fracture grain sizes were determined on a series of steels while increasing the size of the Lan-Cer-Amp additions from 0 to 3 pounds per ton of steel. These specimens were broken with a brittle fracture at liquid nitrogen temperature after water quenching and tempering with the results representing the heat treated grain size. This limited study showed that apparently rare-earth-metal additions have no effect on the heat-treated grain size of aluminum-killed steels.

Summary of the Influence of Rare-earth Metals on the Mechanical Properties of Cast Steels

1. High sulfur contents in low-alloy cast steels, with or without the presence of rare-earth metals, are responsible for low impact values.
2. Best Charpy V-notch impact values are obtained from heats poured at 2850 degrees F. This temperature produced the lowest sulfur content after misch-metal additions.
3. Steels made in silica crucibles had as good impact properties, for their sulfur content, as steel made in basic crucibles.
4. Rare-earth metal additions to alloy steel do not alter the temper brittleness propensities of the steels.
5. Impact properties of cast steels containing rare-earth elements are better than those not treated with rare-earth metals provided the sulfur content is similar.
6. The excellent toughness properties obtained with the addition of rare-earth metals are attributed to the fact that the steels contain Type I inclusions. Large additions of rare-earth metals (5 lbs/ton and greater) produce Type IV sulfide inclusions and result in poor ductility values.
7. Rare-earth metal additions are equally effective in all types of low-alloy cast steels. Ductility and impact properties are improved at various hardness levels. The reason for this is that the inclusions are altered to Type I sulfides; however, part of the improvement may be, in certain cases, the removal of some sulfur (basic heats).
8. The shape of sulfide inclusions was not changed by rare-earth oxide or fluoride additions to cast steels.
9. The addition of boron or vanadium or high nitrogen contents to cast steels does not influence the response of cast steels to additions of misch metal.
10. Low-alloy cast steels of excellent properties can be improved by the addition of rare-earth metals.
11. The impact and ductility properties of rare-earth treated cast steels heat treated to simulate heavy 4- and 6-inch sections are inferior to those of 1-inch sections.
12. Apparently rare-earth-metal additions have no effect on the heat-treated grain size of aluminum-killed steels.

SECTION IV

HARDENABILITY OF CAST STEELS WITH RARE-EARTH METAL ADDITIONS

There is considerable evidence that a slack-quenched steel will have poorer notched-bar properties than a fully hardened steel after both are tempered to the same hardness. Since hardenability can affect the toughness of steel in this way, the influence of rare-earth elements on hardenability is of interest. Therefore, end-quench hardenability tests were made on 29 of the experimental steels.

Four Mn-Cr-Mo steels containing 0, 1, 2, and 3 pounds per ton of misch metal are compared in Figure 14. The untreated steel had slightly lower hardenability than the comparison heats. This suggests that the addition of misch metal increased their hardenability. However, the hardness data for the four heats fall in a narrow band indicating that the differences are small and perhaps they resulted from slightly different recoveries of alloying elements. At any rate, most of the other heats failed to show any effect of rare-earth elements on hardenability. In fact, some steels which were not treated with rare-earth metal had slightly higher hardnesses at distances greater than ½ inch from the quenched end. Slight differences in alloy contents, which were not determined, could account for these results.

Hardenability data were also obtained on cast steels which contained more carbon (0.40 percent) than the rest of the experimental steels. The steel which was treated with misch metal showed but little hardness difference from that of the non-treated steel.

Carbortam, a proprietary boron agent, was added to two cast steels, one of which was also treated with misch metal. Both steels had equivalent hardenabilities.

An additional three heats received equal additions of misch metal, but were treated with different boron alloys. The steel which was treated with Carbortam, had slightly better hardenability than the steel treated with Borosil, while the steel treated with Grainal No. 79 had the poorest hardenability of the group. Chemical analysis of this steel indicated that it contained 0.005 percent boron, an amount usually sufficient to insure good hardenability. Apparently the Grainal was partially effective because this steel did have better hardenability than other steels which were not treated with boron and contained only a little less molybdenum and nickel.

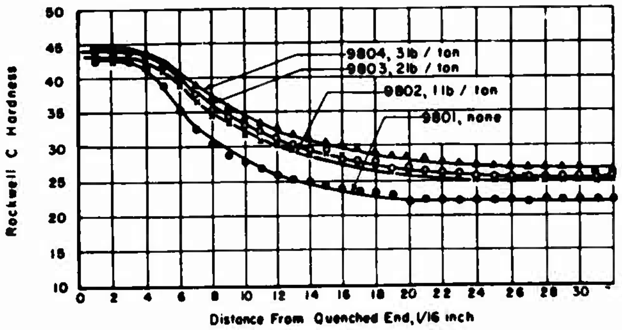


Figure 14—End-quench hardenability data for steels treated with amounts of misch metal indicated

Perhaps the titanium content, which was 0.17 percent, accounts for the poorer hardenability. Titanium, which was recovered from the boron addition agent, could combine with part of the carbon in the steel and make it inactive.

Even though the end-quench test data were not influenced by the presence of misch metal in steel, they did disclose the expected effects of other elements on hardenability. Increasing the molybdenum content from 0.20 to 0.40 percent increased the hardenability. Similarly, increasing the chromium content from 0.5 to 1.0 percent increased the depth of hardening. Also, increasing the manganese level from 1.2 to 1.5 percent increased the hardenability.

It seems safe to conclude, therefore, that the presence of misch metal in cast steel does not influence hardenability, nor does it seem to influence the effect of boron on hardenability.

Two heats were treated with T-Compound instead of misch metal. This material contains calcium boride, which is intended to reduce the rare-earth oxides to a metallic alloy which will dissolve in the melt. Figure 15 shows that the steel which had been treated with misch metal had lower hardenability than either of the heats made with T-Compound. However, chemical analysis showed that the steels treated with T-Compound contained 0.003 percent and 0.0015 percent boron. Boron was introduced into the steel from the calcium boride present in the rare-earth addition agent. Figure 15 indicates that the steel which had the larger boron content, gave the higher hardnesses at most locations on the end-quench.

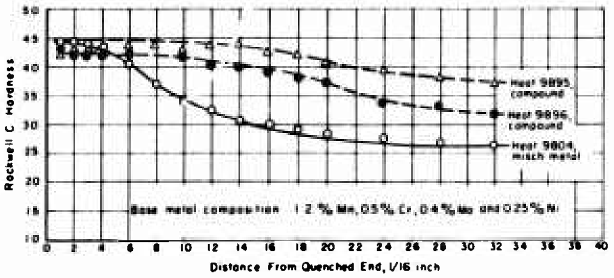


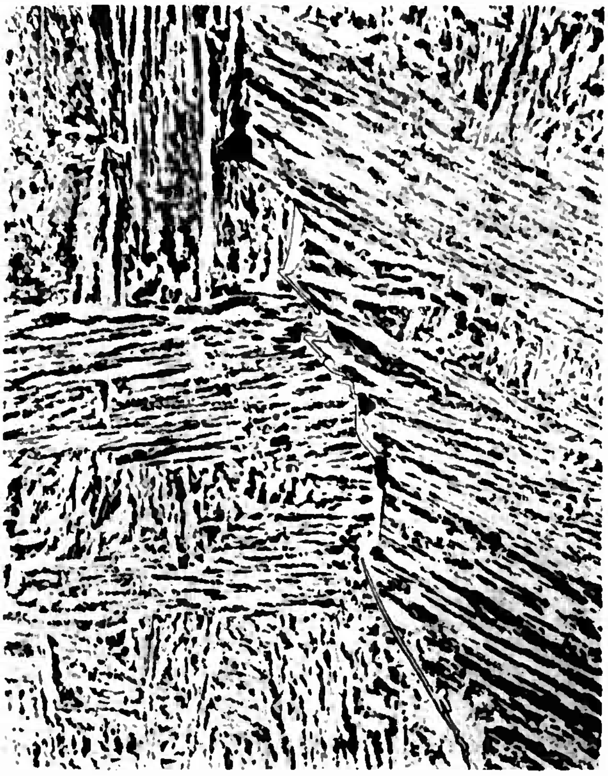
Figure 15—End-quench hardenability data for steels treated with misch metal or with a compound containing rare-earth oxides and calcium boride

The fact that boron was recovered in these two experimental steels is considered important for several reasons. The data show that the hardenability of steels can be unintentionally increased because of the boron effect accompanying a treatment ostensibly intended to add only rare-earth elements. The adventitious addition of boron to steel in this fashion could result in undesirably high boron contents if the steel were also treated with another boron agent.

In another experimental steel 0.013 percent boron was introduced from the calcium boride present in the rare-earth oxide addition agent. That heat was treated with eight pounds of compound per ton of steel. A boron content as high as 0.013 percent results in intergranular films of iron boride, as shown in Figure 16. This intergranular phase embrittles steel.

Since boron was recovered in an effective form in these aluminum-killed steels, it appears that calcium boride did not fulfill its function. That is, it apparently did not react with the rare-earth oxides to form misch metal. Probably, any reduction of the oxides which may have occurred resulted from reaction with the steel bath.

Hardenability tests were not suitable for evaluating the hardenability of some deep-hardening steels prepared for the research study. Therefore, a nonstandard hardenaility test was also used for studying seven of the steels. Figure 17 shows the special test block and specimen assembly used for this purpose. This asembly was heated like an end-quench specimen, then removed from the furnace and cooled in still air. Hardness traverses were then made on the specimen, using the precautions normally followed with end-quench bars.



Addition of rare-earth compound, 8 pounds per ton of steel; boron content: 0.013 per cent

Figure 16—Intergranular film of iron boride in an aluminum-killed steel treated with a material containing rare-earth oxides and calcium boride (500X)

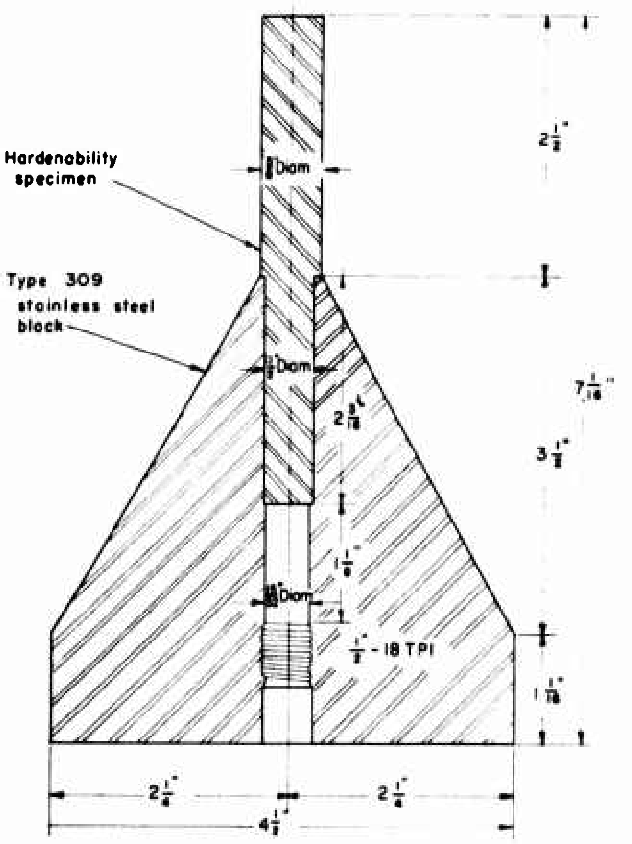


Figure 17—Special air-cooled hardenability specimen and block

The cooling rates near 1300 degrees F in the special hardenability bar overlap those of the slowly cooled end of an end-quench bar and correspond to the center of a 10-inch plate quenched in still water. This does not mean that the cooling rates through other temperature ranges are the same for these positions. This type of specimen and block was developed and used in previous studies at Battelle.(2) The cooling rates in the temperature region around 1300 degrees F at different locations on the special hardenability specimen are given in Table 18. These data were obtained in the earlier work and confirmed during the present investigation.

The data obtained with the special hardenability specimen indicate the hardnesses which would be developed by quenching at the center of heavy sections. The hardness data are summarized in Table 19. They permit comparisons of steels representing several variations in composition.

Results on Cr-Mo steels indicate that misch-metal treatments will not influence the center hardness of deep-hardening steels heat treated in heavy sections. This confirms the end-quench test data, which are applicable to steels quenched in lighter sections.

The highest hardnesses at all positions on the special hardenability specimens were obtained on 1.00 percent chromium, 0.40 percent molybdenum steels. This is to be expected, because they had the highest levels of molybdenum and chromium investigated. The fact that one steel contained boron and the other was free of boron did not influence the hardness of the special specimens. This also was expected, since boron has no appreciable effect on the hardness of samples cooled slowly enough to form significant amounts of pearlite. Consequently, the data show that the hardenability of the base composition was too low and the cooling rates on the special bar too slow for boron to be effective.

Since alloying elements such as chromium raise both martensitic and bainitic hardenability, the data in Table 19 show some influence of this element. Raising the chromium level from 0.5 to 1.0 percent increased the Rockwell C hardness of the special hardenability bar about four units.

Changing the molybdenum level from 0.20 to 0.40 percent did not significantly affect the hardness of the slow-cooled hardenability bar. These data agree with common opinions that molybdenum has little effect on the bainite nose of the transformation curve.

Summary of the Influence of Rare-earth Metals on the Hardenability of Cast Steels

1. The presence of rare-earth metal in cast steel does not influence the hardenability of the steel, nor does it influence the effect of boron on the hardenability.

TABLE 19

Summary of Hardness Data for Hardenability Specimens of Seven Deep-Hardening Experimental Steels

	Heat 9811	Heat 9812	Heat 9813	Heat 9875	Heat 9876	Heat 9877	Heat 9878
			Composition				
Molybdenum, percent	(0.40)	(0.40)	(0.40)	(0.20)	(0.40)	(0.40)	(0.20)
Chromium, percent	(0.50)	(0.50)	(0.50)	(0.50)	(1.04)	(1.00)	(1.00)
Boron(1), percent	—	—	0.006	0.006	—	0.006	0.055
Misch metal	None	Yes	Yes	Yes	Yes	Yes	Yes
			Hardness, Rockwell C, at Position Indicated				
1/16 inch; Standard bar	44	43	43	44	44	44-1/2	44
1/2 inch; Standard bar	41	39	43	43	44-1/2	44	43
1 inch; Standard bar	35	31	42-1/2	42-1/2	42-1/2	43-1/2	42
2 inches; Standard bar	29-1/2	28	35-1/2	36-1/2	37	38-1/2	36-1/2
1/4 inch; special bar	27-1/2	28	28-1/2	30-1/2	32-1/2	32-1/2	31-1/2
1 inch; special bar	27-1/2	28	27	29-1/2	32-1/2	32	31-1/2
1-3/4 inches; special bar	27-1/2	27-1/2	28	28-1/2	32-1/2	32	30-1/2
2-1/2 inches; special bar	27-1/2	28	29-1/2	29-1/2	33-1/2	33	32
3-1/4 inches; special bar	28	28	29	30-1/2	33-1/2	33	31-1/2

Note: Parentheses enclose intended compositions of elements in the steel which were not analyzed.

(1) Boron added as ferroboron.

2. The hardenability of cast steels can be unintentionally increased by the addition of rare-earth compounds containing calcium boride. The function of the calcium boride is to add rare-earth elements to the steel; however, boron is added instead.
3. Rare-earth additions will not influence the center hardness of deep-hardening steels heat treated in heavy sections.

SUMMARY OF THE CONCLUSIONS, PART I

Part I of the report presents a laboratory investigation of the effects of adding materials containing rare-earth elements on the properties of cast steel. Most of the experimental steels were treated with rare-earth metals (misch metal); however, some received additions of cerium fluoride or mixtures containing rare-earth oxides.

Sulfur Removal — Under certain conditions, treating a steel bath with rare-earth metal results in the removal of sulfur. Desulfurization is favored by larger additions, by lower temperatures, by strong deoxidation, and by a basic melting condition. Approximately 0.006 percent sulfur, or less, was removed by the addition of three pounds of misch metal per ton of steel to the laboratory-produced steels. An equivalent addition of rare-earth oxides with a reducing agent apparently removed an equal amount of sulfur from one heat. However, no significant amount of sulfur was removed from another steel treated with this material nor from steel treated with cerium fluoride.

Additions amounting to five pounds of misch metal per ton of steel removed upward of 50 percent of the original sulfur content from the experimental steels. However, such large additions are undesirable because they produce low toughness values. The laboratory work indicates that the desulfurization reaction is essentially complete in three minutes. The experiments indicate that misch-metal additions can remove sulfur temporarily from acid steel but reversion occurs rapidly in the absence of a basic slag.

High temperatures hinder desulfurization. Maximum desulfurization results, with rare-earth metal additions, at steel temperatures of approximately 2850 degrees F.

Inclusion Types — The presence of rare-earth elements in cast steels can change the shape and color, and presumably the composition, of the sulfide inclusions. Changes occurred in those steels treated with misch metal but not in those treated with oxides or fluorides. The influence of misch-metal additions on the sulfides was the same regardless of whether the steels were made in acid or in basic crucibles. It appears that the sulfur level influences the response of a steel to a particular amount of rare-earth elements. Consequently the ratio $(Ce+La)/S$ appears to be a more useful value than just the total amounts of lanthanum and cerium determined by analysis.

Depending on the amount of aluminum present, aluminum-killed steels ordinarily contain either film or angular sulfide inclusions. In these experiments, the addition of two or three pounds of misch metal per ton of aluminum-killed steel resulted in globular sulfides. Globular inclusions as contrasted to other inclusion types have a less harmful effect on ductility and toughness of cast steels. Chemical analyses indicate that the globular sulfides of Type I are typical of aluminum-killed steels containing lanthanum and cerium in amounts approximating the sulfur content. That is, such steels have $(Ce+La)/S$ ratios of 1.0 to 1.5. The data in this report indicate that such steels have better tensile, ductility, and notched-bar properties than aluminum-killed steels not treated with misch metal. Apparently the improvement results from the presence of the rare-earth elements in the steels.

The size of the misch-metal addition or, more probably the amount retained in the steel, is important. In this investigation, additions of one pound per ton of steel did not produce globular sulfides nor did they improve the mechanical properties of the steel. Chemical analyses of such steels indicated that they were characterized by $(Ce+La)/S$ ratios of 0.8 or less. Apparently, such quantities of rare-earth elements are not beneficial.

Large additions of misch metal appear to harm the properties of cast steels. Many of the steels treated with five pounds or more of misch metal per ton of steel were characterized by the presence of many small, irregularly shaped inclusions which occurred in clouds or clusters. Such steels exhibited much poorer ductility than would be expected for their sulfur contents. Chemical analyses of five out of seven such steels indicated that the sum of their lanthanum and cerium contents exceeded 1.6 times their sulfur contents.

A general guide as to inclusion types formed on the basis of the (Ce + La)/S ratio is as follows:

Ratios between 1.0 and 1.6 form Type I inclusions.

Ratios below 1.0 form Type II inclusions with Type I or III present.

Ratios above 1.6 form Type IV inclusions.

The above ratios must be considered as only very general and probably applicable only 75 percent of the time. This conservative view-point may be readily understood when it is realized that the (Ce + La)/S ratio depends upon the quantity of sulfur present in the steel, and on the quantity of rare-earth metals entering the steel. Laboratory studies indicated that an average of all studies showed that approximately 18 percent of the misch metal addition was recovered in the steel.

It should be pointed out that throughout the laboratory studies there is a varying percent recovery of rare-earth elements in the molten steel. This condition resulted in the formation of both Types I and II inclusions in the same steel. However, a similar steel produced in apparently the same manner, results in only Type I inclusions. The region of 0.6 to 1.0 (Ce + La)/S ratio is very susceptible to a combination of Types I and II inclusions being present in the steel.

A very general rule which should work in the majority of cases, and which can be easily remembered for production use by foundrymen, is based on the sulfur content and the quantity of rare-earth metals to add to produce the favorable Type I inclusions. This rule is as follows:

Sulfur Content of Steel	Pounds/ton of Rare-Earth Metals to add to Produce Type I Inclusions
0.025 to 0.040	3
Greater than 0.040	4
Less than about 0.020	2

Mechanical Properties — High sulfur contents in low-alloy cast steels, with or without the presence of rare-earth metals, are responsible for low-impact values. However, the best Charpy V-notch impact properties are obtained from heats poured at 2850 degrees F, since this temperature produced the lowest sulfur content after misch-metal additions.

The impact properties of low-alloy cast steels containing rare-earth elements are better than those not treated with rare-earths, provided the sulfur content is similar. The reason for this condition is that the rare-earth additions produce Type I inclusions which improve toughness values.

Rare-earth metal additions are equally effective in all types of low-alloy cast steels in the improvement of ductility and impact properties at various hardness levels.

The presence of rare-earth elements in cast steels has no direct effect on hardenability. The experiments showed, however, that boron could be recovered from the oxide addition agents which contain boron. Boron introduced in this way, of course, did increase hardenability. The experimental work indicates that additions of misch metal do not interfere with the hardening effects of boron and other elements.

The experimental low-alloy steels studied did not exhibit temper brittleness. Hence, any effect of rare-earth elements on this tendency was not established.

Variations in carbon, nitrogen, vanadium, manganese, chromium, and molybdenum contents did not interfere with the effects expected from additions of misch metal. However, the situation seems to be different for titanium. This element has a strong affinity for sulfur and produces film-type sulfide inclusions. Additions of two pounds of misch metal per ton of steel did not prevent the occurrence of film sulfides in steels containing 0.07 and 0.17 percent titanium. The cast steels containing such amounts of titanium had very poor tensile, ductility, and impact properties regardless of misch-metal treatment.

PART II

THE PRODUCTION OF COMMERCIAL CAST STEEL CONTAINING RARE-EARTH ADDITIONS

INTRODUCTION

Six steel foundry companies cooperated in the production of eight commercial heats of low-alloy cast steel containing rare-earth additions. Two additional heats without rare-earth additions were made as a comparison base.

All the usual commercial melting practices employed in the steel casting industry were investigated to ascertain the effect of the rare-earth additions. The following steelmaking methods were employed: acid electric (2 foundries), acid open-hearth (2 foundries), basic electric and basic open-hearth.

Steel Composition and Production

A Mn-Cr-Mo composition was selected for the foundries to produce. The composition was as follows:

Carbon, percent	0.25 to 0.30
Manganese, percent	1.25 to 1.50
Chromium, percent	0.40 to 0.50
Nickel, percent	0.25 maximum
Molybdenum, percent	0.40 to 0.50
Silicon, percent	0.25 to 0.50
Phosphorus, percent	0.04 maximum Basic
	0.05 maximum Acid
Sulfur, percent	0.04 maximum Basic
	0.05 maximum Acid

The foundries were instructed to use LanCerAmp No. 10 as the source of the rare-earth addition. An amount of 3 pounds of LanCerAmp per ton of steel was suggested as a ladle addition.

Five of the nine steels were made with boron additions as well as rare-earth metal additions. Boron was added in the form of Carbortam in four of the heats and as Borosil in the fifth steel. Instructions to the foundries stated that an addition of .0045 percent boron was to be added.

The foundries were also advised that they could employ ferro-boron or Borosil if the nitrogen content of the steel to be produced was under .008 percent. Only one foundry, the basic open-hearth producer, availed itself of this alternative.

Each foundry was asked to make the steel in accordance with its best commercial practice. However, the deoxidation practice was specified. The steel was deoxidided in the ladle with additions of alloys in the following order:

Aluminum	0.10 percent or 2 pounds per ton
Calcium	0.10 percent or 11 pounds per ton of 18-16-56 CaMnSi alloy
†Lanceramp No. 10	3 pounds per ton
†Boron	.0045 percent or 6.0 pounds per ton of Carbortam (contained boron of 1.5 percent)

---

† Could be added together.

The foundries were asked to avoid excessively high temperatures at the time the additions were made. It was suggested that the steel temperature be kept below 2950 degrees F. It was also suggested that the deoxidizers be added to a slag-free steel when the ladle was about half full. The calcium alloy was enclosed in a suitable steel container and plunged beneath the surface of the molten steel to avoid excessive oxidation losses. The rare-earth metal, LanCerAmp No. 10, is packaged in a metal container by the manufacturer.

Temperature readings were taken at the time of tapping of the heat. The pouring temperature of the test bars was recorded with a platinum-platinum rhodium thermocouple, in a quartz tube, placed under the pouring cup of the 9 x 11 x 4 inch coupon.

Tests

Chemical analyses of the steels were determined by the cooperating foundries. The compositions obtained are listed in Table 21.

All foundries were requested to construct patterns for the SFSA standard keel block coupon of 1-inch legs (ASTM A370-53T) and another keel block of 4-inch legs (Figure 18).

Studies were scheduled on: (1) the properties of a Mn-Cr-Mo steel without rare-earth additions; (2) the properties of Mn-Cr-Mo steel with rare-earth metals added; (3) the properties of Mn-Cr-Mo steel with boron and rare-earth metals added, and (4) the properties of Mn-Cr-Mo steel with rare-earth oxide added. A total of 23 one-inch coupon legs and 2 four-inch coupon legs was required for test specimen purposes.

TABLE 21

COMPOSITION OF THE COMMERCIAL CAST STEELS PERCENT

Type	C	Mn	Cr	Mo	Ni	Si	P	S	B	Rare-Earth Additions(2)
Desired	.25-.30	1.25-1.50	.40 .50	.40-.50	.25 max	.25-.50	.040 max.(4) .050 max.(5)	.040 max.(4) .050 max.(5)	—	
AE-1	.27	1.26	.46	.45	.16	.39	.020	.032	None	None
AE-2	.25	1.20	.58	.49	.10	.45	.024	.034	None	None
AE-5	.26	1.36	.48	.43	.19	.42	.020	.032	.0045(1)	3 lb/ton
AE-6	.28	1.30	.50	.50	.08	.54	.023	.037	.0045(1)	3 lb/ton
AOH-2	.28	1.59	.59	.46	.08	.46	.033	.033	.0045(1)	3 lb/ton
BE	.26	1.37	.53	.47	.19	.44	.012	.012	.0045(1)	2 lb/ton
BOH	.27	1.32	.49	.41	.08	.37	.013	.010	.0040	3 lb/ton
AE-3	.24	1.17	.53	.62	.15	.38	.019	.031	None	3 lb/ton
AOH-1	.25	1.28	.46	.41	.17	.41	.034	.043	None	3 lb/ton
AE-4	.29	1.49	.46	.43	.16	.39	.020	.035	None	6 lb/ton(3)

(1) Addition of .0045% contained Boron.
(2) LanCerAmp #10 - American Metal-Products Co.
(3) Rare-earth oxide (Remox-C) Mallinckrodt Chemical Works.
(4) Basic steel.
(5) Acid steel.

All test coupon legs, after their removal from the keel block, were given a normalizing treatment at 1700 degrees F for one or two hours, depending on the section thickness, followed by air cooling. The test legs were then heated to 1600 degrees F held for 30 minutes and quenched in water until the casting temperature was 250 to 300 degrees F. The legs were then tempered at once to a temperature which would produce a hardness of 260 BHN. Time at the holding temperature was 30 minutes and the legs were then quenched in water. All heat treatment was done at the foundries which produced the test blocks.

Tensile, impact, and hardenability specimens were then machined. The position of the impact specimens in the 4-inch section is shown in Figure 18. All impact specimens, after being machined, were forwarded to Battelle Memorial Institute for checking for dimensions, the machining of the notch, and testing. Tensile and hardenability testing was done by the individual foundries.

The one-inch leg coupons were poured at the beginning of the heat after the pouring of an initial casting and at the end of the heat. The 4-inch leg coupons were cast only at the start of pouring the heat.

SECTION I

PROPERTIES OF RARE-EARTH TREATED PRODUCTION CAST STEELS

Base Control—Steel

Two acid electric Mn-Cr-Mo cast steels produced at different foundries acted as the control heats. The tensile and ductility properties were normal for the hardness values of water-quenched and tempered low-alloy steels (Table 22). The Charpy V-notch impact values for the 1-inch section at both +70 and —40 degrees F were good. A value of 28 foot-pounds is required for 260 BHN at —40 degrees F. The impact specimens from the 4-inch section were taken 1 inch below the surface. However, such values were rather poor at —40 degrees F. The heat treatment temperature was the same as that given the 1-inch sections. The Brinell hardness values were about 26 numbers less than recorded for the 1-inch section.

The hardenability curves for the base steels are reproduced in Figure 19. While the D_I values vary somewhat the curves are very similar.

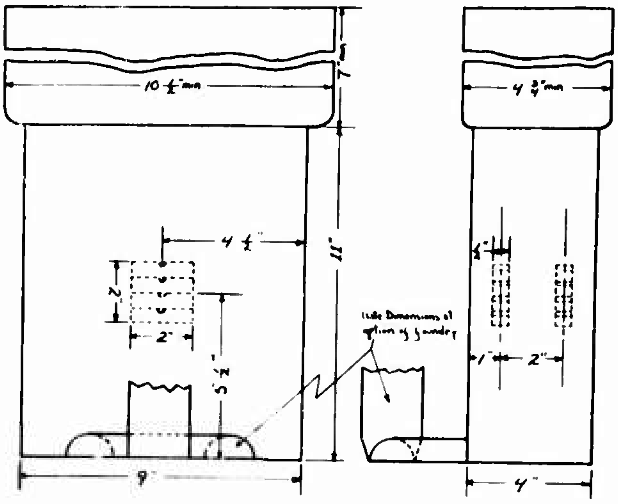


Figure 18—Position of the impact specimens in the 4-inch coupon

TABLE 22 — MnCrMo (CONTROL HEATS)

Chemical Content, Percent at P_1

	C	Mn	P	S	Si	Ni	Cr	Mo	Heat wt. pounds
AE-1	.27	1.26	.020	.032	.39	.16	.46	.45	6400
AE-2	.25	1.20	.024	.034	.45	.10	.58	.49	7800

Tensile Properties - 1-inch Section
Normalized, Water Quenched, Tempered to 260 BHN

		Tensile Strength (1000 psi)	Yield Strength (1000 psi)	El. in 2" (%)	Red. of Area (%)	BHN	D_1 Values	Pouring Temp. °F	Pouring Time after Tap min.
AE-1	P_1†	125.8	110.6	17.8	43.5	270	6.2	2805	16
	P_2‡	136.7	111.0	17.3	46.0	269	—	—	
AE-2	P_1	135.2	117.7	17.0	42.5	269	7.5	2770	10
	P_2	135.1	115.7	17.8	42.8	269	—	—	

Charpy V-Notch Impact Properties for 1-inch Sections
(Normalized, Water Quenched, Tempered to 260 BHN)

		Ft.-lbs. +70°F	Ft.-lbs. —40°F	Rockwell(R_C) Hardness	BHN	Structure	Inclusion Type
AE-1	P_1	44.0	38.0	27.0	263	Temp. Martensite	III
	P_2	45.0	40.0	27.0	259	Temp. Martensite	III
AE-2	P_1	53.5	43.0	26.8	262	Temp. Martensite	III
	P_2	51.8	42.3	26.8	262	Temp. Martensite	III

Charpy V-Notch Impact Properties for 4-inch Sections
(Normalized, Water Quenched, Tempered at same temperature as 1-inch sections)

		Ft.-lbs. +70°F	Ft.-lbs. —40°F	Rockwell(R_C) Hardness	BHN	Structure	Inclusion Type
AE-1	P_1	19.0	5.0	20.6	228	Temp. Bainite + some Martensite	III
AE-2	P_1	18.0	5.0	23.0	244	Temp. Martensite + Temp. Bainite	III

† P_1 - Pouring Position. Start of Pour of heat.
‡ P_2 - Pouring Position. End of Pour of heat.

TABLE 23 — MnCrMo + RARE-EARTH METAL

Chemical Content, Percent at P_1

	C	Mn	P	S	Si	Ni	Cr	Mo	Rare Earth lb/ton	Heat wt. pounds
AE-3	.24	1.17	.019	.031	.38	.15	.53	.62	3†	6800
AOH-1	.25	1.28	.034	.043	.41	.17	.46	.41	3†	19100

† - Lanceramp No. 10

Tensile Properties - 1-inch Section
Normalized, Water Quenched, Tempered to 260 BHN

		Tensile Strength (1000 psi)	Yield Strength (1000 psi)	El. in 2" (%)	Red. of Area (%)	BHN	D_1 Values	Pouring Temp. °F	Pouring Time after Tap min.
AE-3	P_1	126.5	107.0	16.5	38.2	265	7.6	2863	13
	P_2	129.9	119.6	16.0	38.2	273	—	—	—
AOH-1	P_1	121.3	96.6	17.5	36.0	262	4.3	2790	15
	P_2	122.5	93.1	19.0	43.2	262	—	—	—

Charpy V-Notch Impact Properties for 1-inch Sections
(Normalized, Water Quenched, Tempered to 260 BHN)

		Ft.-lbs. +70°F	Ft.-lbs. —40°F	Rockwell(R_C) Hardness	BHN	Structure	Inclusion Type
AE-3	P_1	36.0	34.0	27.0	263	Temp. Martensite	III + I + some II
	P_2	38.0	32.0	29.0	273	Temp. Martensite	III + I + some II
AOH-1	P_1	50.0	33.0	24.0	247	Temp. Martensite	III + I
	P_2	41.0	40.0	24.0	247	Temp. Martensite	III + I

Charpy V-Notch Impact Properties for 4-inch Sections
(Normalized, Water Quenched, Tempered at same temperature as 1-inch sections)

		Ft.-lbs. +70°F	Ft.-lbs. —40°F	Rockwell(R_C) Hardness	BHN	Structure	Inclusion Type
AE-3	P_1	16.0	5.0	20.0	226	Temp. Bainite + some Martensite	II + I
AOH-1	P_1	28.0	7.0	24.8	253	Temp. Martensite + Temp. Bainite + Ferrite	III + I

TABLE 24 — MnCrMo + RARE-EARTH OXIDE

Chemical Content, Percent at P_1

	C	Mn	P	S	Si	Ni	Cr	Mo	Rare Earth Oxide lb/ton	Heat wt. pounds
AE-4	.29	1.49	.020	.035	.39	.16	.46	.43	6†	6800

† - Remox—C

Tensile Properties - 1-inch Section (Avg. 2 specimens)
Normalized, Water Quenched, Tempered to 260 BHN

		Tensile Strength (1000 psi)	Yield Strength (1000 psi)	El. in 2" (%)	Red. of Area (%)	BHN	D_i Values	Pouring Temp. °F	Pouring Time after Tap min.
AE-4	P_1	128.1	108.8	16.3	38.9	269	6.5	2850	16
	P_2	131.0	111.8	16.8	40.2	265	—	—	—

Charpy V-Notch Impact Properties for 1-inch Sections (Avg. 3 specimens)
(Normalized, Water Quenched, Tempered to 260 BHN)

		Ft.-lbs. +70°F	Ft.-lbs. —40°F	Rockwell(R_c) Hardness	BHN	Structure	Inclusion Type
AE-4	P_1	42.0	39.0	28.5	271	Temp. Martensite	III + oxides
	P_2	43.0	37.0	27.0	263	Temp. Martensite	III + oxides

Charpy V-Notch Impact Properties for 4-inch Sections (Avg. 3 specimens)
(Normalized, Water Quenched, Tempered at same temperature as 1-inch sections)

		Ft.-lbs. +70°F	Ft.-lbs. —40°F	Rockwell(R_c) Hardness	BHN	Structure	Inclusion Type
AE-4	P_1	21.0	4.0	21.0	229	Temp. Bainite + some Martensite	III + oxides

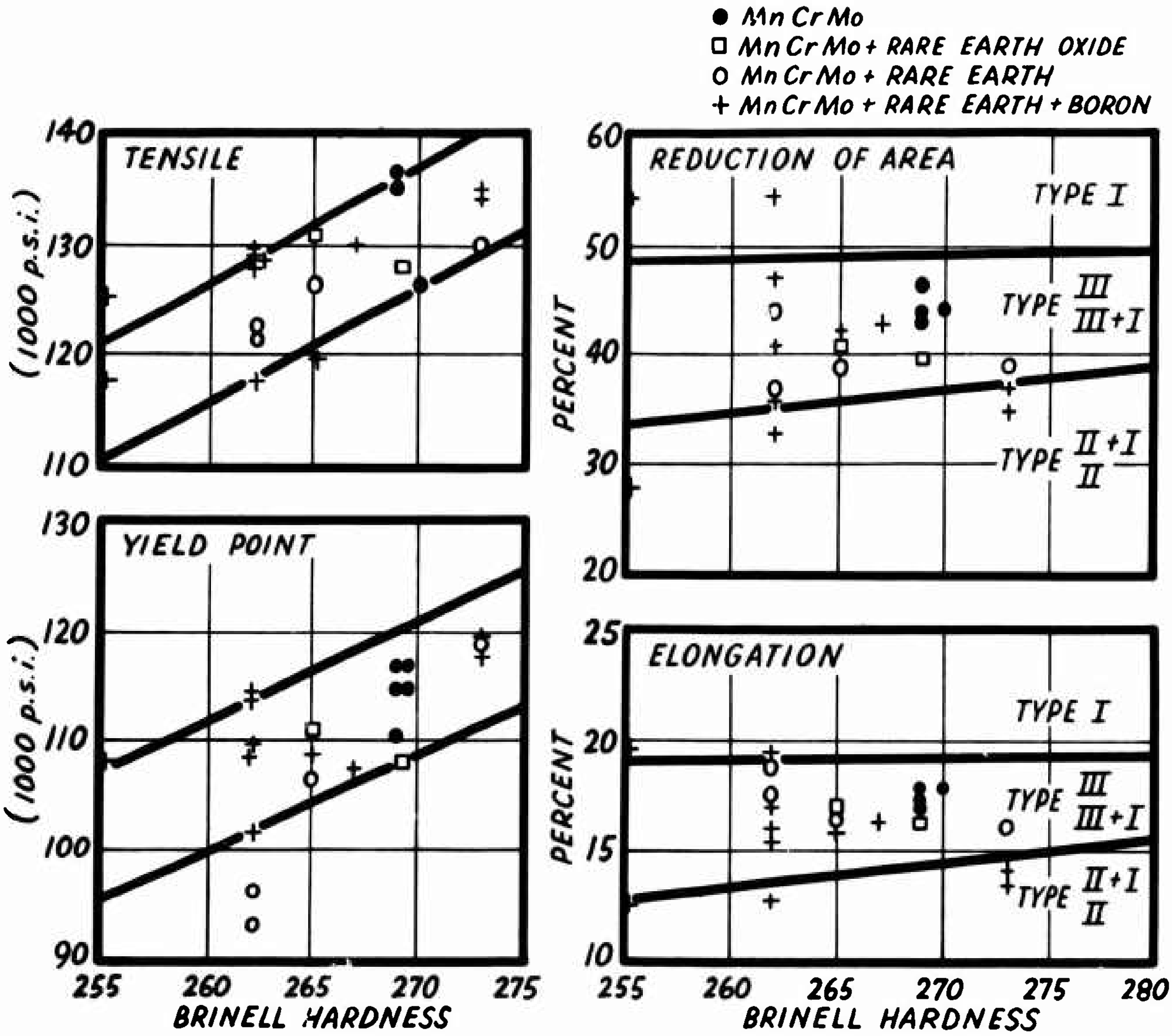


Figure 21—Tensile properties for the production heats of Manganese-Chromium-Molybdenum cast steels on the basis of hardness

TABLE 25

MnCrMo + RARE EARTH METALS + BORON

Chemical Content, Percent at P_1

	C	Mn	P	S	Si	Ni	Cr	Mo	Rare Earth† lb/ton	Heat wt. pounds
AE-5	.26	1.36	.020	.032	.42	.19	.48	.43	3	6800
AE-6	.28	1.30	.023	.037	.54	.08	.50	.50	3	7700
AOH-2	.28	1.59	.033	.033	.46	.08	.59	.46	2.8	22000
BE	.26	1.37	.012	.012	.44	.19	.53	.47	2	14000
BOH	.27	1.32	.013	.010	.37	.08	.49	.41	3	54000

† Lanceramp No. 10

Tensile Properties - 1-inch Section
Normalized, Water Quenched, Tempered to 260 BHN

		Tensile Strength (1000 psi)	Yield Strength (1000 psi)	El. in 2" (%)	Red. of Area (%)	BHN	D_1 Values	Pouring Temp. °F	Pouring Time after Tap min.
AE-5	P_1	129.9	108.2	16.3	42.3	267	7.4	2833	19
	P_2	119.9	109.4	15.8	41.4	265	—	—	—
AE-6	P_1	125.6	108.5	12.5	27.2	255	7.2	2770	8
	P_2	127.9	110.5	15.3	31.9	262	—	—	—
	P_{11}‡	129.5	100.3	17.0	40.4	262	—	—	—
AOH-2	P_1	134.9	119.9	14.0	36.1	273	9.1	2765	22
	P_2	134.7	118.0	13.5	34.1	273	—	—	—
BE	P_1	118.5	102.4	19.5	54.0	262	7.2	2820	7
	P_2	117.4	101.8	19.8	54.0	255	—	—	—
BOH	P_1	120.4	115.3	12.8	34.9	262	8.2	2788	10
	P_2	128.7	115.4	17.0	46.6	262	—	—	—

Charpy V-Notch Impact Properties for 1-inch Sections
(Normalized, Water Quenched, Tempered to 260 BHN)

		Ft.-lbs.		Rockwell(R_c)			Inclusion
		+70°F	—40°F	Hardness	BHN	Structure	Type
AE-5	P_1	40.0	33.0	26.0	259	Temp. Martensite	III + I + some II
	P_2	41.0	36.0	24.8	253	Temp. Martensite	III + I + some II
AE-6	P_1	25.0	13.0	23.0	244	Temp. Martensite	II
	P_2	26.0	15.0	25.3	256	Temp. Martensite	II
	P_{11}‡	36.0	18.0	25.3	256	Temp. Martensite	IV
AOH-2	P_1	28.0	14.0	28.0	269	Temp. Martensite	II
	P_2	25.0	11.0	24.5	251	Temp. Martensite	II
BE	P_1	61.0	42.0	24.8	253	Temp. Martensite	I
	P_2	67.0	41.0	25.0	255	Temp. Martensite	I
BOH	P_1	57.0	49.0	28.5	271	Temp. Martensite	III + I
	P_2	70.0	69.0	27.0	263	Temp. Martensite	III + I

‡ 7 lb/ton Lanceramp No. 10. Sulfur content of steel .017 percent.

Charpy V-Notch Impact Properties for 4-inch Sections
(Normalized, Water Quenched, Tempered at same temperature as 1-inch sections)

		Ft.-lbs.		Rockwell(R_c)			Inclusion
		+70°F	—40°F	Hardness	BHN	Structure	Type
AE-5	P_1	20.0	5.0	21.0	229	Temp. Bainite + some Martensite	II + some I
AE-6	P_1	13.0	5.0	22.0	237	Temp. Martensite + Temp. Bainite	III + IV
AOH-2	P_1	14.0	9.0	30.0	283	Temp. Martensite + Temp. Bainite	II
BE	P_1	25.0	6.0	20.0	226	Temp. Martensite + Temp. Bainite	I
BOH	P_1	49.0	28.0	23.3	245	Temp. Martensite + Temp. Bainite	III + I + IV

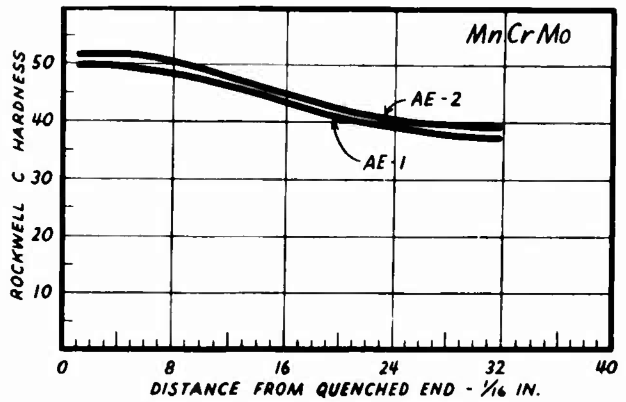


Figure 19—End-quench hardenability curves at position P_1 for production heats of Manganese-Chromium-Molybdenum cast steels. Base control steels

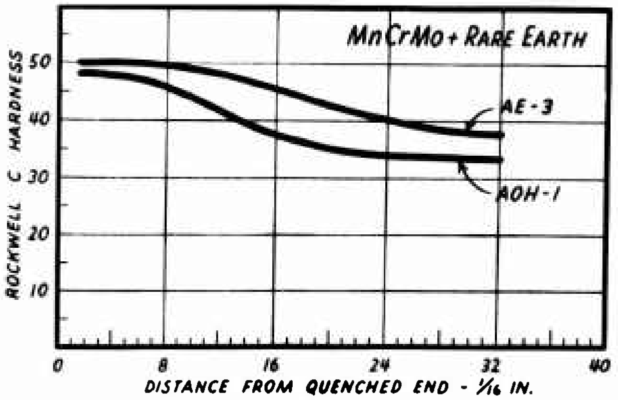


Figure 20—End-quench hardenability curves at position P_1 for production heats of Manganese-Chromium-Molybdenum cast steels containing rare-earth metals (3 lb/ton Lanceramp No. 10)

Base Steel + Rare-Earth Metal

Two acid furnace foundries, one electric and one open-hearth, produced the base steel with an addition to the ladle of 3 pounds per ton of LanCerAmp No. 10. The properties are given in Table 23.

The tensile and yield point values of these steels are comparable to the base steels. The ductility values of the acid electric steel with rare earth were slightly below the values given for the base steels. The hardenability value of the acid open-hearth steel was low because of insufficient quantities of chromium and molybdenum. The hardenability curves of these steels are illustrated in Figure 20.

The impact values for the control heats showed a higher level of values than for the two acid furnace steels containing rare earths in both 1- and 4-inch section sizes at both testing temperatures. The reason for this is not too clear. The inclusion types were not changed entirely away from Type III by the rare-earth additions. The acid electric steel showed the presence of some Type II inclusions. Type I inclusions were present in both steels but apparently insufficient rare-earth metal was added or the percent recovery of rare-earth elements in the steel was too low to secure inclusions of only Type I.

The sulfur content of the acid open-hearth steel was high (.043 percent) and in order to develop the proper (Ce + La)/S ratio of 1.0 a quantity of about 7-3/4 pounds per ton should have been used. If the sulfur content of the AE-1 of Table 22 is compared with the heat AE-3 of Table 23, it will be seen there was no sulfur reduction in these steels.

Base Steel + Rare-Earth Oxide

One acid electric heat was produced using 6 pounds per ton of Remox-C, a rare-earth oxide. The smoke and fumes developed from this addition to the ladle were sufficient to fill the shop, resulting in vision difficulties.

The properties obtained for this steel are given in Table 24. A comparison of the AE-1 values of Table 22 with those of AE-4 of Table 24 would indicate that impact, tensile, and yield strength values are very similar. The ductility values of the AE-4 steel are slightly inferior. The presence of considerable oxides associated with the Type III inclusions may be the reason for the lower ductility properties.

It seems evident that the addition of rare-earth oxide in no way improved the steel properties. The hardenability curve developed by this steel was practically identical to that of AE-1 of the base steel and, therefore, was not plotted.

Base Steel + Rare-Earth Metals + Boron

The base steel (Mn-Cr-Mo) was produced by five foundries, all of which added rare-earth metals (LanCerAmp No. 10) to the ladle followed by boron. The properties of these steels are listed in Table 25. The tensile and yield point values fell within the band established by the other steels (Figure 21). The ductility values varied depending on the inclusion type found in the steel.

The hardenability curves all fell within a narrow band as shown in Figure 22 and some of them were similar to those of the base steel as illustrated in Figure 19. The exceptions were the basic open-hearth steel and the acid open-hearth steel No. 2.

Excellent impact properties for the one-inch section were obtained by the basic open-hearth and the basic electric steels. However, some values were exceptionally low as can be seen from Table 25. The impact properties of the 4-inch section were also very low.

Inclusion Types and Microstructures

The microstructure of the manganese-chromium-molybdenum cast steel, water-quenched and tempered to 260 BHN in the 1-inch section is tempered martensite as shown in Figure 23. The microstructure of the 4-inch section heat treated at the same temperatures as the 1-inch section is also illustrated in Figure 23 and consists of tempered bainite and tempered martensite. Both of the control steels (AE-1 and AE-2) had the same microstructure.

The Mn-Cr-Mo + Rare Earth + Boron steels had a structure that was identical with those of the base steels as can be observed by examining the microphotographs of Figure 24. All the steels containing

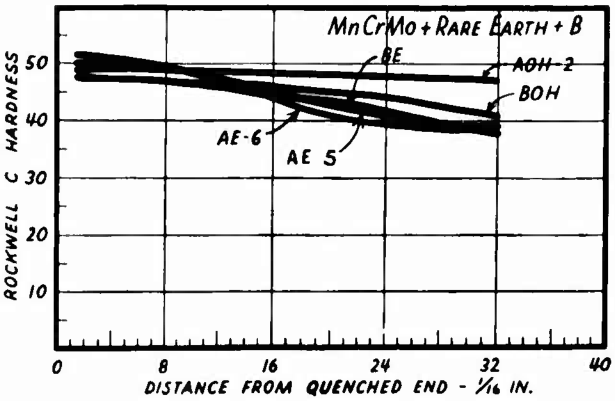
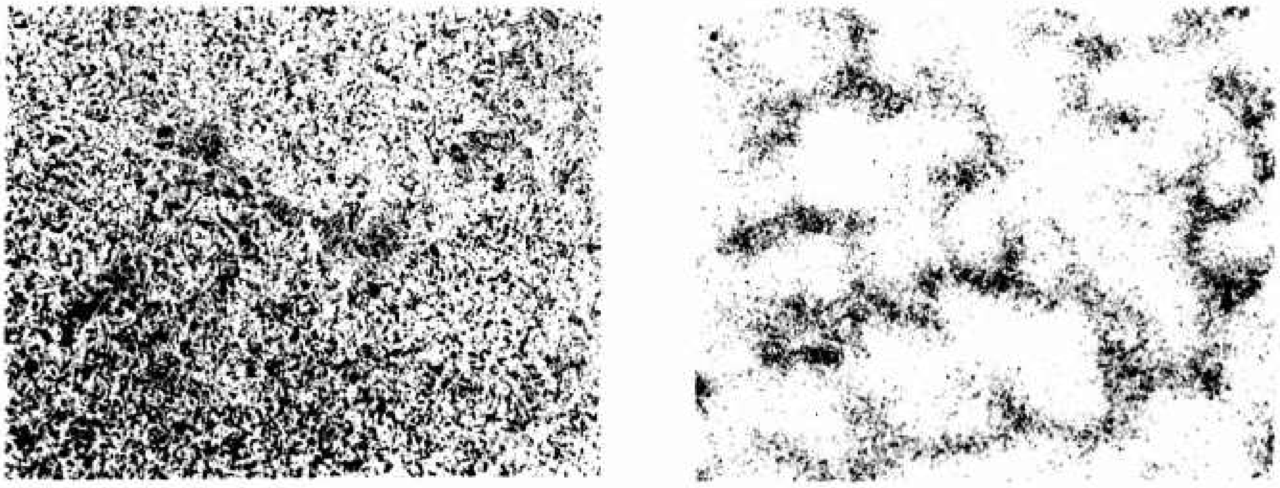


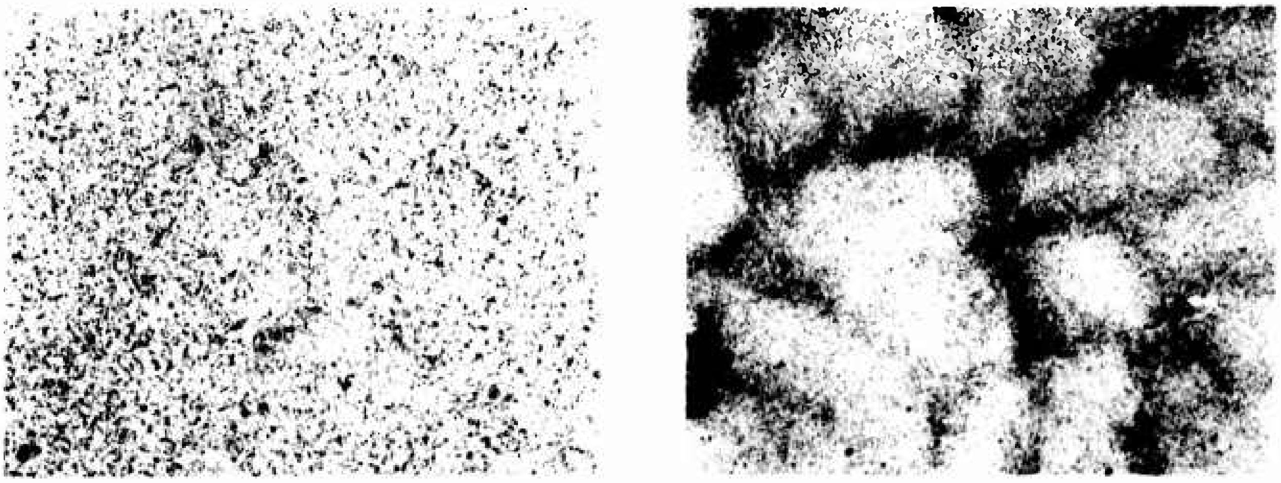
Figure 22—End-quench hardenability curves at position P_1 for production heats of Manganese-Chromium-Molybdenum cast steels containing rare-earth metals plus Boron



Tempered martensite
1-inch section

Tempered bainite and
tempered martensite
4-inch section

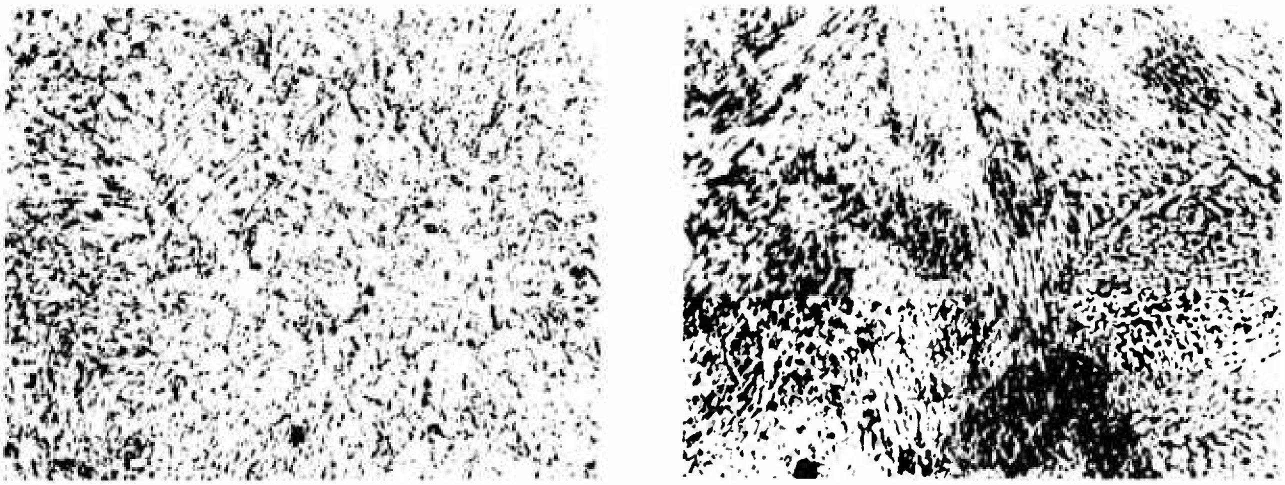
Figure 23—Microstructure of the Mn-Cr-Mo base control steels. Etched with picral, 100X



Tempered martensite
1-inch section

Tempered bainite and
tempered martensite
4-inch section

Figure 24—Microstructure of the Mn-Cr-Mo + Rare Earths + B cast steels. Etched with picral, 100X



Tempered martensite
1-inch Section

Tempered martensite and tempered bainite
4-inch Section

Figure 25—Microstructures of the Mn-Cr-Mo + Rare Earths + B cast steels. Etched with picral, 500X

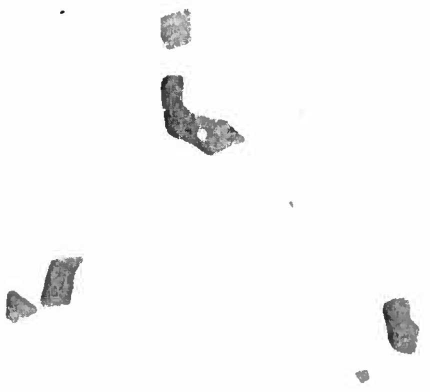
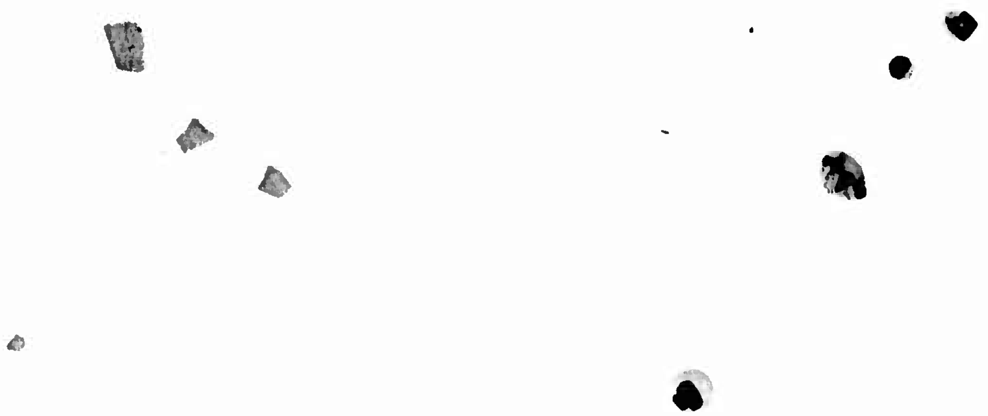


Figure 26—Type III inclusions, typical of the base steels AE-1, AE-2, AE-4. Unetched, 500X

Figure 27—Oxides found in AE-4 steel treated with rare-earth oxides. Unetched, 500X



Typical inclusions - Type III

Type I found in scattered fields

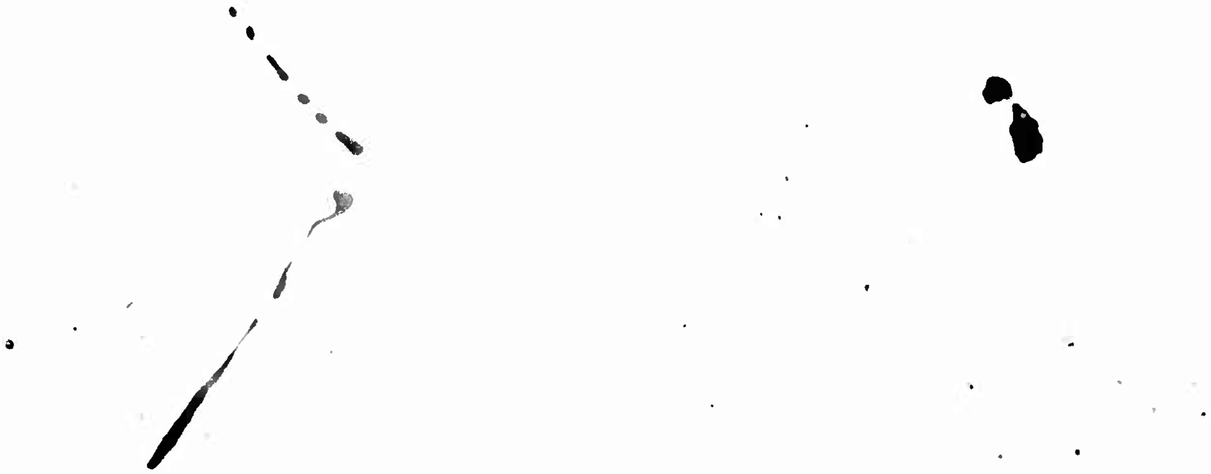
Figure 28—Inclusions in AOH-1 steel treated with rare-earth metals. Unetched, 500X

rare earths, with or without boron, had microstructures the same as illustrated in Figures 23 and 24. The appearance of the microstructure at a higher magnification is shown in Figure 25. These photomicrographs are typical of all the production steels.

The types of inclusions that exist in the 1-inch and 4-inch sections of the production steels are listed in Table 26 and illustrated in Figures 26 to 33 inclusive. The effect of the inclusion types on the reduction of area and percent elongation properties, as well as the low temperature impact properties is illustrated in Figures 21 and 34. Impact values below the minimum requirements were the result of tests on steels containing Type II or Type IV inclusions.

It is rather difficult, from the small amount of data presented, to correlate the (Ce + La)/S ratio with the inclusion type. Perhaps this is because the percent recovery of the Ce + La is estimated at 15 percent from the laboratory studies, whereas in all probability the recovery may vary considerably.

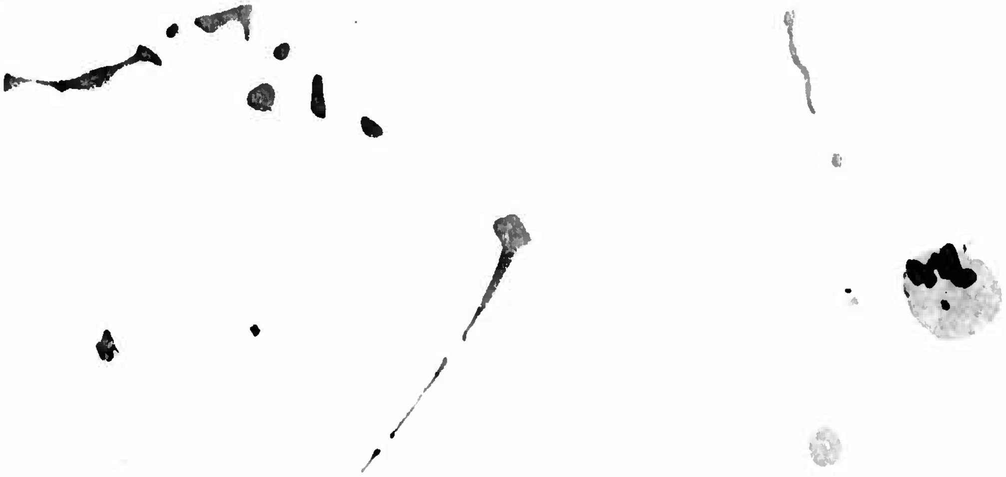
In some cases the inclusion types present in the 4-inch sections are different from those in the



Type II, typical of the 4-inch sections

Type I (duplex) found to the extent of about 1/3 in the 4-inch sections of AE-3 and AE-5. This type predominated in the 1-inch sections of both heats. Type III inclusions were present to the extent of about 1/3 in the 1-inch sections. There was very little Type II inclusions.

Figure 29—Inclusions in AE-3 steel treated with rare-earth metals and in AE-5 steel treated with rare-earth metals + Boron. Unetched 500X



Typical Type II inclusions

Type I inclusions found occasionally

Figure 30—Inclusions in AOH-2 steel treated with rare-earth metals + Boron in both 1-inch and 4-inch sections. Unetched, 500X

TABLE 26

INCLUSION TYPES IN THE PRODUCTION OF Mn-Cr-Mo CAST STEELS†

Type Steel	Furnace Practice	Ladle Al added lb/ton	Deoxidizer other lb/ton	Rare Earth Metals (a) lb/ton	(c) $\frac{Ce+La}{S}$	(f) $\frac{Ce+La}{S}$	Inclusion Type 1-inch Section	Inclusion Type 4-inch Section
Base	AE-1	2	CaSi 2.7‡ FeMn 25‡	0	—	—	III	III
	AE-2	2.5	CaSi 2.5	0	—	—	III	III
Base + Rare Earth	AE-3	2	CaSi 2.7 FeMn 26	3	0.73	—	I + III + Some II	II + I
	AOH-1	2	CaMnSi 11	3	0.52	0.53	III + I	III + I
Base + Rare Earth Oxide	AE-4	2	CaSi 2.7 FeMn 26	6(b)	—	—	III + oxides	III + oxides
Base + Rare Earth + Boron	AE-5	2	CaSi 2.7 FeMn 25	3	0.70	—	I + III + Some II	II + Some I
	AE-6	2	CaMnSi 11	3	0.60	0.42	II	III + IV
	AE-6	2	CaMnSi 11	7	3.00(d)	—	IV	—
	AOH-2	2.2	CaMnSi 11	2.8	0.62	—	II	II
	BE	2	CaMnSi 11	2	1.24	—	I	I
	BOH	2	CaMnSi 11	3	2.20(e)	4.70	III + I + IV	III + I + IV

‡ Approximately equivalent to 4.5 lb/ton of CaMnSi.

† Microscopic specimens taken from Charpy impact test blanks.
CaMnSi = 18% Ca, 16% Mn, 56% Si.
CaSi = 32% Ca, 64% Si.

(a) LanCerAmp No. 10. (b) Remox-C. Rare-Earth Oxide.

(c) The Ce + La content of LanCerAmp is 74 percent. Recovery in molten steel is assumed at 20 percent.

(d) 4 lbs/ton of the total 7 lbs/ton misch metal added to a small, slag free shank ladle, skimmed and immediately poured into 1 inch keel blocks. A reduction of .037 to .017 percent sulfur occurred. See Table 3 page 9 for other instances of desulfurization in acid steels.

(e) Table 29 indicates the Ce + La recovery to be 41 percent or a ratio of 4.50 for a sulfur content of 0.010 percent.

(f) Actually computed from chemical analysis of Ce, La, and S.

Type II inclusions found in 1-inch sections

Type IV inclusions occasionally found in the 4-inch section with the typical Type III inclusions

Figure 31—Inclusions in AE-6 steel treated with 3 lbs/ton rare-earth metals + Boron. Unetched, 500X

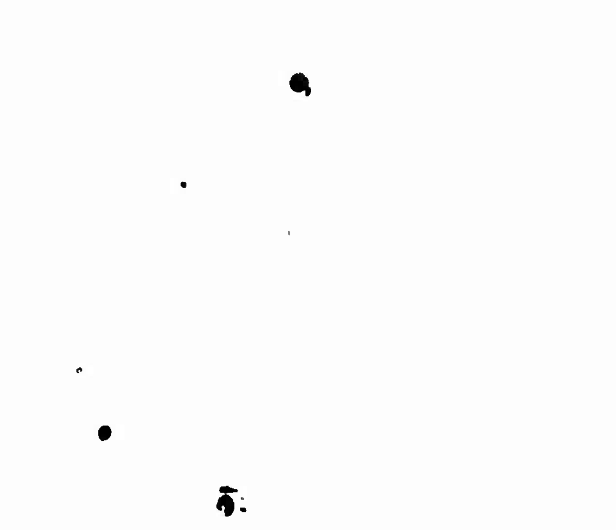


Figure 32—Type I inclusions found in BE steel treated with rare-earth metals + Boron. Unetched, 500X

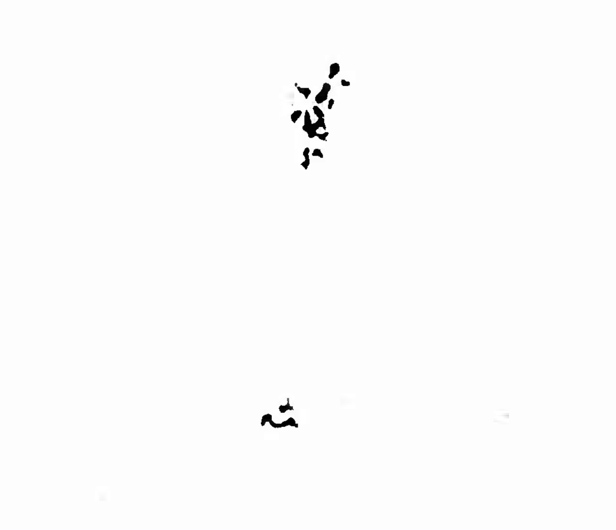


Figure 33—Type IV inclusions found in AE-6 steel treated with 7 lbs/ton of rare-earth metals + Boron and in the 4-inch section of BOH steel treated with 3 lbs/ton of rare-earth metals + Boron. Unetched, 500X

corresponding 1-inch sections. This condition is puzzling because both sections were poured with the same steel directly following each other. The one outstanding example is the AE-6 steel which contained Type II inclusions in the 1-inch section and Types III + IV in the 4-inch section. Also, this study indicates it is possible to have Types III, I, and IV inclusions in the same steel.

The BOH steel with a (Ce + La) S ratio of 2.2 surely should contain only Type IV inclusions according to the laboratory studies, yet Types I, III, and IV were present. Experience with castings of varying sections indicates that both Types I and IV can be found in the same casting.

The results of the production heats certainly indicate that deoxidation methods are very critical from the standpoint of the type of inclusions formed. Evidently the sulfur content of the steel is an important variable.

Impact Properties

All of the commercial steels produced with or without rare-earths were tested at +70 and —40 degrees F for Charpy V-notch impact properties. Specimens were taken from 1- and 4-inch sections. The sulfur content of the acid-produced steels fell in the range of .031 to .043 percent. Two of the acid steels showed Type II inclusions in the impact specimen. Naturally, these values were low, averaging 13 foot-pounds at —40 degrees F and, therefore, they were considerably below the minimum requirements specified in Army Ordnance specifications (see Figure 34). The remainder of the acid practice steels averaged 37 foot pounds at —40 degrees F. Values of about 37 foot-pounds were obtained regardless of whether or not additions were made of rare-earth metals. It is, therefore, indicated that the additions of rare-earth metals to commercial cast steels produced by the acid furnace practice did not improve the low temperature impact properties of these steels. In fact, the rare-earth metals may be responsible for poor impact results because of their active participation in the deoxidizing reaction. The AE-6, P_{11} steel is an exception because of desulfurization.

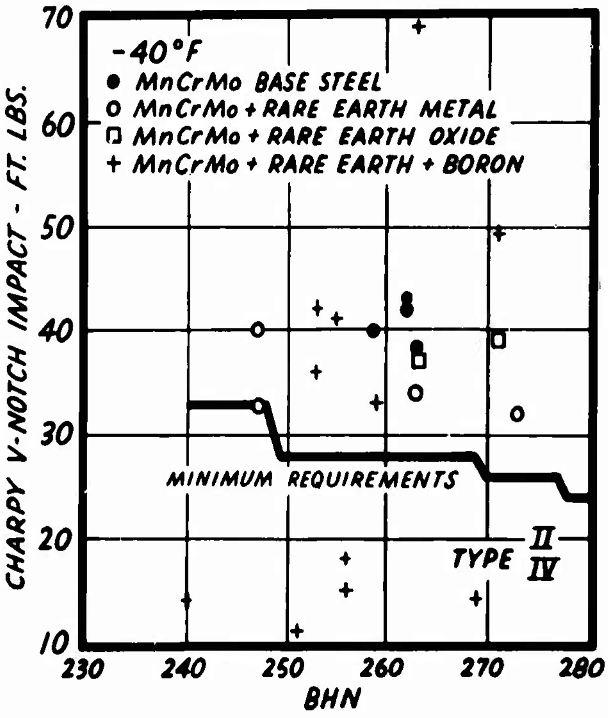


Figure 34—Charpy V-notch impact values vs. BHN for production Mn-Cr-Mo steels at -40 degrees F for 1-inch sections

The sulfur content of the basic practice steels was .010 to .012 percent and impact values of 57 to 70 foot-pounds were secured at +70 degrees F in the 1-inch section. The basic electric steel values averaged only 42 foot-pounds or 5 foot-pounds above the acid steel average. The lower sulfur content would be responsible for this increase without further consideration being given to the fact that this steel contained predominantly Type I inclusions (see Figure 12). Impact values higher than those obtained certainly were expected. Therefore, it could be tentatively concluded that the rare-earth metal additions did not improve the impact properties of the basic electric production steel.

This condition is somewhat reversed when the basic open-hearth steel is reviewed. Charpy impact values of 49 and 69 foot-pounds definitely reflect improvement through the use of rare-earth metals. In this case inclusions Type III, I, and IV were present in the impact test bar. Higher values could have been expected if the inclusions had been predominantly Type I; however, too much rare-earth was added for the sulfur level.

An addition of approximately 3 pounds per ton of rare-earth metals will reduce the sulfur content of basic open-hearth steel by about .004 percent at a sulfur level of .015 percent at the time of tapping.

An average Charpy impact value of 5 foot-pounds at —40 degrees F was obtained for the test bars taken from 1-inch below the surface in the 4-inch sections. This is a very poor value indeed. The only exception to this was the 28 foot-pound value secured for the basic open-hearth steel. This value is not outstanding for it does not meet the minimum impact resistance value specified by Army Ordnance for a hardness of 24 Rockwell-C.

Hardness Survey in 4-inch Sections

A hardness survey at various depths below the surface of the 4-inch section was made on all the production steels as illustrated in Figure 18. The results of the survey are given in Table 27 and the values plotted in Figure 35. The steels were hardness tested in the water-quenched and tempered condition.

Only two steels showed nearly uniform hardness throughout the 4-inch section. However, the average drop in hardness from the surface to the section center was about 26 Brinell hardness numbers. The boron treated cast steels did not consistently show as small a drop as might be expected.

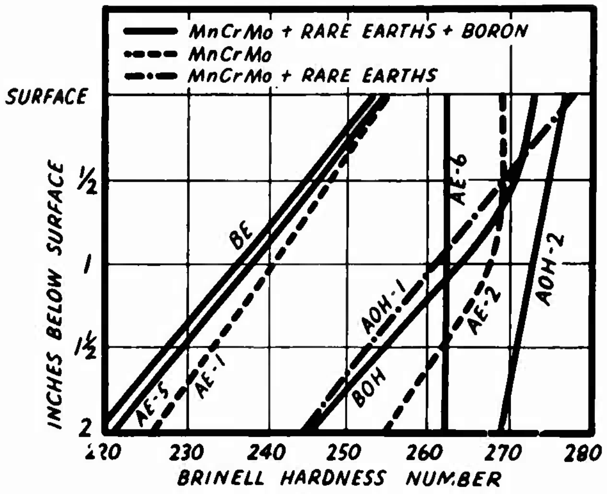


Figure 35—Brinell hardness survey in the 4-inch sections of production Mn-Cr-Mo cast steels after water quench and temper heat treatment. AE-6, AOH-2

TABLE 27

BRINELL HARDNESS SURVEY ON 4-INCH SECTION AT P_1 (Surface to Center)

	Location of Test - Distance from Surface (inches)				
	Surface	½	1	1½	2 (Center)
	MnCrMo (Control Heats)				
AE 1	255	248	241	235	223
AE 2	269	269	269	262	255
	MnCrMo + Rare Earth				
AE-3	255	241	235	232	229
AOH	277	270	262	248	248
	MnCrMo + Rare Earth Oxides				
AE-4	255	248	241	235	229
	MnCrMo + Rare Earth + Boron				
AE-5	255	248	235	229	229
AE-6	262	262	262	262	262
AOH-2	277	276	269	269	269
BE	255	241	238	228	223
BOH	269	273	266	253	245

Rare-Earth Oxides and Fluorides

The one production heat of Mn-Cr-Mo cast steel treated with Remox-C, a rare-earth oxide, did not exhibit any differences in mechanical properties, inclusion types, microstructure, or hardenability from that of the control heat without the rare-earth additions.

A member of the Technical Research Committee made some additional tests on acid electric production heats. The steel studied was of the following average composition:

Carbon	0.28	percent
Manganese	1.00	percent
Chromium	0.50	percent
Molybdenum	0.10	percent

Silicon	0.60 percent
Sulfur	0.045 percent
Phosphorus	0.040 percent

A heat treatment of normalizing at 1700 degrees F, water quenching from 1600 degrees F, followed by tempering between 1150 and 1250 degrees F with water quenching from the tempering temperature was employed. Tensile strength values were approximately 110,000 to 120,000 psi.

The Molybdenum Corporation of America T-Compound consisting of rare-earth oxide plus reductant compounds was investigated as well as a cerium fluoride from Metallurgical Enterprises. Check studies were also made on the same steel without rare-earth additions and with rare-earth alloys in the form of Electro Metallurgical Company's CeMgFeSi alloy, which contains approximately 2 percent Ce and 8 percent Mg. Ductility and low temperature Charpy V-notch impact properties obtained employing these materials to the ladle, are listed in Table 28.

Observations that can be made from studying Table 28 are that adding T-compound, rare-earth fluorides or the CeMgFeSi alloy, in the quantities shown, had no significant effect on the ductility or low temperature impact properties. The steels receiving a secondary deoxidation treatment by additions in the monorail ladle were better than those not given the secondary deoxidation treatment. The aluminum analyses of the steels receiving the secondary deoxidation averaged 0.07 percent whereas without the additional deoxidation treatment, the steels average 0.015 percent.

The fluoride additions in the amount and manner made were not effective; in fact, they actually seemed to be detrimental.

TABLE 28

THE ADDITION OF RARE-EARTH OXIDES AND FLUORIDES TO Cr-Mo ACID ELECTRIC PRODUCTION STEELS†

Rare-Earth Addition	Amount lb/ton	Place	BHN	Red. of Area %	Charpy V-notch +70°F ft-lbs	Charpy V-notch —40°F ft-lbs	Sulfur Content
Regular Secondary Deoxidation (0.028%Ca as CaMnSi + 0.085%Al) Added to 300 lb. Monorail ladle							
0	0	—	241	55.3	46	24	0.034
T-Compound	2.4	Tapping ladle	255	46.1	42	22	0.044
CeMgFeSi alloy	3.0	Tapping ladle	255	52.0	45	29	0.040
No Secondary Deoxidation to 300 lbs. Monorail Ladle							
0	0	—	248	56.2	53	22	0.035
T-Compound	2.4	Tapping ladle	255	52.8	48	19	—
CeMgFeSi alloy	3.0	Tapping ladle	255	60.7	53	20	—
Fluoride	10.0	300 lb. ladle	248	37.3	24	11	0.032
Fluoride	15.0	300 lb. ladle	241	55.1	46	16	0.032
Fluoride	20.0	300 lb. ladle	241	50.0	46	16	0.030
Secondary Deoxidation (0.10%Ca as CaSi + 0.06% Al) Added to 300 lb. Monorail Ladle							
T-Compound	2.4	Tapping ladle	255	51.6	57	25	—
CeMgFeSi alloy	3.0	Tapping ladle	255	50.0	47	25	—
Fluoride	10.0	300 lb. ladle	248	25.0	48	21	0.034
Fluoride	15.0	300 lb. ladle	241	52.3	43	18	0.035
Fluoride	20.0	300 lb. ladle	248	59.4	53	27	0.032

† C 0.28, Mn 1.00, Cr 0.50, Mo 0.10, Si 0.60, S 0.045, P 0.040 percent

Order and quantity of additions at tapping:

1. CaMnSi 3 pounds per ton.
2. High Carbon FeTi 2 pounds per ton.
3. T-Compound or CeMgFeSi as indicated above.

SECTION II

DEFECTIVE CASTINGS FROM THE BASIC OPEN-HEARTH PRODUCTION HEAT

The castings from the basic open-hearth production heat treated with rare-earth metals had to be scrapped because of porosity.

The MnCrMo heat of steel was made in a 25-ton basic open-hearth furnace to the following analyses: Carbon 0.27 percent, manganese 1.30 percent, silicon 0.38 percent, chromium 0.49 percent, molybdenum 0.41 percent, nickel 0.08 percent and phosphorus 0.014 percent. Plant records indicated that the heat contained 0.018 percent sulfur at meltdown and 0.010 percent sulfur in the ladle. The heat received additions of 10 pounds of Ca-Mn-Si, 2 pounds of aluminum, and 3 pounds of misch metal per ton of steel. The misch metal was added as LanCerAmp No. 10 and boron was added as Borosil. The risers showed normal shrinkage and no bleeding.

The foundry indicated that they had found on other occasions, similar porosity type defects in certain castings consisting of heavy sections when misch metal additions were incorrectly made. The porosity is more likely to occur in locations where entrained air might be trapped. They reported, however, that it sometimes occurs in other areas.

Figure 36 shows the type of porosity found in the castings examined. The voids occurred immediately under the top (cope) surface of the castings in relatively heavy sections. Usually the upper surface of the holes was 1/32 to 1/8 inch below the surface of the castings. The voids varied in size up to 3/4 inch in length or depth, but most of them were comparatively small. Some of the cavities were shiny and others were lined with a yellow-green substance. According to the foundry metallurgists, hydrogen sulfide is liberated if the cavities are treated with hydrochloric acid. This confirmed the opinion that the material in the holes was a sulfide.

Several pieces from a defective casting were sectioned for metallographic examinations. The types and quantities of sulfide inclusions found at different locations were determined. The results obtained in the inclusion survey at 50X from the

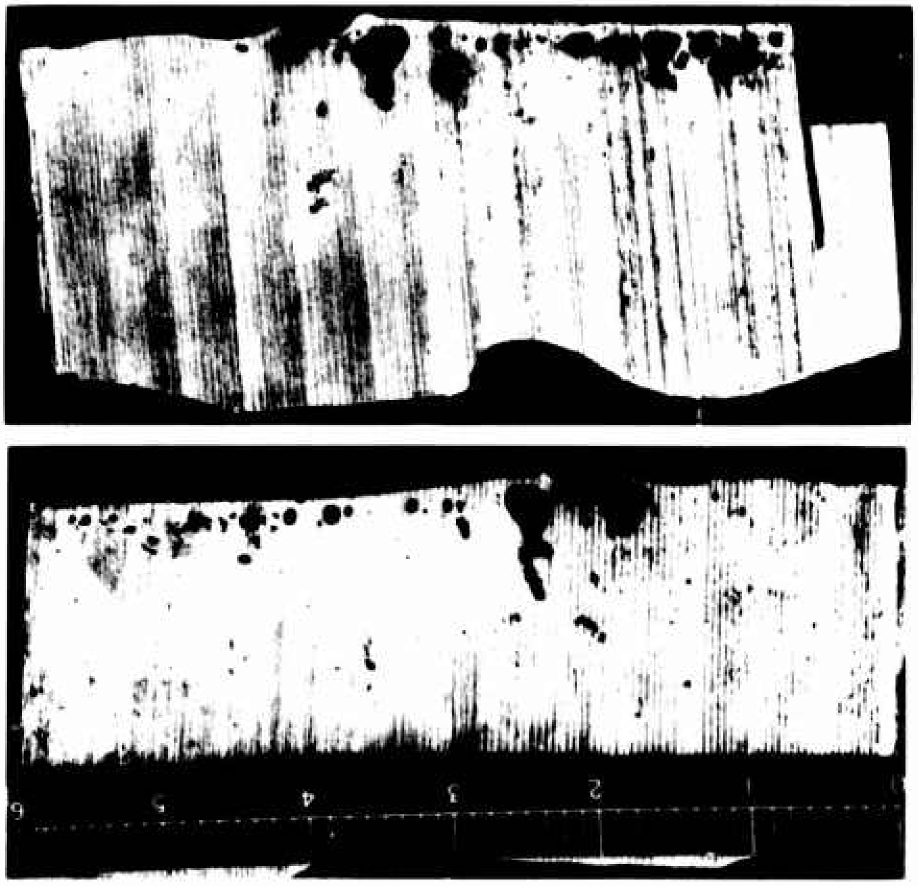


Figure 36 Sections from defective production castings showing porosity near the cope surface

(a)

(b) *0.15 in. below surface*

0.15 in. below surface

(c)

(d) *0.30 in. below surface*

Figure 37—Change in quantity of sulfide inclusions with distance below the top (cope) surface of the production castings (50X)

Cope skin, Fig. 37a 0.00 to 0.10 in. below cope surface

Right end of Figure 37b 0.11 to 0.20 in. below cope surface

Figure 38—Size and volume of inclusions found at two different distances below the cope surface of the production casting (500X)

cope surface to the drag surface of the casting are illustrated by Figures 37 and 38. The section shown is one which avoided large cavities but traversed the region where they were normally found. The surface examined was that shown in Figure 36.

Figure 37 shows a progressive change in the quantity of inclusions with depth below the top (cope) surface of the casting. The extreme skin of the casting was comparatively free of inclusions. The heaviest concentration of nonmetallics was found in the region 0.11 to 0.20 inch below the cope surface. The quantity of inclusions then decreased and areas near the center of the section and near the drag surface of the casting were quite clean (better than 37d).

Figure 38, at higher magnification, shows part of the fields shown in Figures 37a and 37b. The few sulfides present near the cope surface are round and extremely small. The inclusions found at distances between 0.10 and 0.20 inch below the cope surface, in this section, were both large and numerous. They are typical of those found in laboratory experiments when the misch metal additions were too large. Inclusions of this kind have been classified as Type IV in Section I of this report.

Figure 39—Type IV sulfide inclusions found in isolated patches near the section center of the production casting (500X)

Figure 39 shows the type of sulfide inclusions found near the center of the casting. These are Type IV inclusions typical of areas comparatively low in sulfur. Since they are small, rounded, and well dispersed, they do not have a harmful effect on mechanical properties. Inclusions of this kind were also characteristic of Charpy specimens taken from keel blocks poured from the same heat. The Charpy specimens exhibited excellent toughness in tests at +70 and —40 degrees F.

The extent of the sulfur segregation in the section was determined by drilling small holes in regions near, but removed from, visible porosity. The results of the chemical analysis are given in Table 29

TABLE 29

SULFUR SEGREGATION IN PRODUCTION CASTING

	Sample Location	
	Near Cope Surface percent	Near Drag Surface percent
Sulfur	0.021	0.005
Aluminum	0.08	—
Calcium	0.01	—
Lanthanum	0.015	—
Cerium	0.03	—

and they show that the sulfur content near the top surface was four times that near the drag side of the casting. The (Ce + La)/S ratio was 2.14 near the cope surface where porosity occurred.

Previous laboratory studies showed that desulfurization occurs and undesirable Type IV sulfides form in steels treated with excessive amounts of misch metal. Both effects seem to depend on the ratio of the misch metal and sulfur contents. High ratios are undesirable and the laboratory studies indicated that Type IV sulfides are characteristic of steels with (Ce + La)/S ratios exceeding 1.6 Therefore, the results of this commercial heat confirm the conclusions drawn from the steels made in the laboratory.

The excessive quantity of nonmetallics and the porosity found in the scrapped casting seem to have resulted from the addition of too much misch metal for the low sulfur steel produced. The defects were apparently confined to the upper quarter of heavy sections because of the solidification characteristics of steel cast in sand molds. At least a reasonable theory explaining the origin and location of the defects can be built on these premises.

It is known that steel solidifying in sand molds first forms a thin skin of solid metal. Then the rest of the metal loses its superheat gradually with the formation of only small temperature gradients. The bulk of the steel remains liquid for some time and then solidification proceeds progressively toward the center of the section.

Previous laboratory studies indicate that desulfurization occurs when sulfides are precipitated and float out of liquid steel. The solubility of sulfur in steel decreases with temperature and with increasing amounts of misch metal in the steel. Because of rapid solidification, no porosity or Type IV misch-metal sulfides formed in the skin of the casting. Where the steel remained liquid long enough, as in heavy sections, misch-metal sulfides formed and floated upward in the melt. They were trapped under the solidified skin near the cope surface. This accounts for the higher sulfur content and larger inclusion volume near the top of the casting.

The gas which caused the porosity probably precipitated and rose as bubbles. Porosity of the same kind could occur from entrained air, incomplete deoxidation, or hydrogen. In the present case, however, it appears that the precipitated misch-metal sulfides acted as nuclei promoting bubble formation. Putting salt in beer acts by this mechanism to increase bubble formation. Thus, it appears that the formation of concentrated areas of misch-metal sulfides can cause porosity in steels which would otherwise appear sound.

If this theory is approximately correct, several expedients should reduce the likelihood of misch-metal additions causing porosity and dirt in steel castings.

1. Using pads on the top of sections prone to such defects. This practice allows the misch-metal sulfides to float into the pad and cause porosity in regions that can be removed from the casting. This is not an efficient method of production, however.
2. Proportioning the size of the misch-metal addition to the sulfur content of the steel. Steels with lower sulfur contents should receive smaller additions of misch metal.
3. So far as porosity is concerned, the hydrogen content of the melt should be kept low. More trouble would be expected in basic, particularly basic open-hearth, than acid steels and less trouble in heats made with a vigorous boil.

SUMMARY OF THE CONCLUSIONS, PART II

Part II of the report describes the preparation of several Mn-Cr-Mo cast steels by the major steelmaking practices employed in steel foundries. These steels were treated with rare-earth metals and poured into castings of one- and four-inch sections. The various steels were tested to determine their mechanical properties, microstructure, and hardenability.

The laboratory investigation indicated that about 3 pounds per ton of misch metal should be a reasonable quantity of rare-earth metals to add to the production heats. The misch metal selected was Lan-CerAmp No. 10. A base, or control, heat of Mn-Cr-Mo cast steel was made without rare-earth metals by two acid electric foundries. Two heats by acid furnace melting practice were made with the addition of 3 pounds per ton of rare-earth metal. Five heats were made of the Mn-Cr-Mo steel with both boron and rare-earth metals added. Another production heat was made employing rare-earth oxide in place of the rare-earth metal.

Sulfur Removal . . . . There were no indications that sulfur was removed from the acid furnace practice steels. A sulfur reduction of about .004 percent resulted in the basic open-hearth cast steel when treated with rare-earth metal.

Inclusion Types . . . . The rare-earth metal additions were responsible for changing the shape and composition of the sulfide inclusions. In all of the production steels practically the same deoxidation practice was employed and similar quantities of rare-earth metals were added. The inclusions in acid electric steels changed from Type III to Types III + I or to Type I or a combination of Types I + III + II. The sulfur contents were similar in the four acid electric steels, it being about 0.033 percent.

The rare-earth metals produced Types III + I and Type II inclusions on the addition of rare-earth metals. The basic open-hearth steel contained Types I, III and IV inclusions and the basic electric contained Type I upon the addition of rare-earth metals. The sulfur content for the basic practice steels was approximately 0.010 percent.

It is apparent that the sulfur content of the steel and the quantity of rare-earth metals added are very important in determining the type of inclusions. Also, it is probable that pouring temperature and oxidation conditions are responsible for variations in the percent recovery of the misch metal.

All of these variables result in control difficulties in deoxidation and the type of inclusions formed. Apparently, only in the case of the basic electric practice was the proper relation of rare-earth addition to sulfur content obtained. The acid steels, because of their high sulfur content, should have received a larger addition of misch metal while the requirements for the basic open-hearth steel were for a smaller quantity of misch metal than it received.

The ideal situation, of course, would be to add sufficient rare-earth metals to the molten steel to produce only Type I inclusions.

Mechanical Properties . . . . The reason that Type I inclusions are desired in steel castings over other inclusion types is that Type I inclusions are associated with optimum mechanical properties. The strength and ductility properties of the quenched and tempered Mn-Cr-Mo production steels treated with rare-earth metals were typical of other cast steels of similar hardness except when Type II inclusions were present. In such cases they were considerably below the average level. It can be said, therefore, that these limited studies indicated no outstanding improvement in the strength and ductility properties of acid steels through the use of rare-earth metals.

Impact Properties . . . . The addition of rare-earth metal to production steels made by the acid practice did not improve the impact properties of these steels. In fact, improper additions of rare-earth metals are responsible for poor impact properties because of their critical effect on the deoxidizing reactions.

The notched bar impact properties of basic steel at —40 degrees F seems to indicate that much of the improvement in Charpy values is the result of desulfurization. It is doubtful if anyone would consider it economically feasible to use 3 pounds per ton of rare-earths for the purpose of desulfurization of basic heats.

However, one cannot overlook the fact that outstanding Charpy values at low temperature were secured for the one basic open-hearth heat. To what extent the rare-earth metals contributed in developing these exceptional values was undetermined by the study since a reference basic open-hearth heat was not employed.

All impact values secured on the 4-inch section were exceptionally poor. The microphotographs of the heavy sections disclosed some traces of ferrite which may be the reason for the poor values that were obtained.

Hardenability . . . . The limited data seemed to indicate no outstanding improvements were obtained in the hardenability of the production cast steels by the addition of misch metal.

Rare-earth Oxides and Fluorides . . . . The addition of rare-earth oxides and fluorides in the amount and manner added to molten steel were not effective in improving the ductility or Charpy impact properties of production steels.

Defective Castings . . . . Large additions of misch metal in relation to the sulfur content are responsible for a concentration of Type IV inclusions in heavy sections and precipitation of gas porosity along the cope surface of the castings.

PART III

SUMMARY, DISCUSSIONS, AND CONCLUSIONS TO THE RESEARCH REPORT

Information on the effect of rare earths on the properties of cast steels is the result of a laboratory investigation and a study of a number of production heats. Most of the steels produced in the research investigation were treated with misch metal; however, some received additions of cerium fluoride or mixtures containing rare-earth oxides. The studies were devised to answer certain questions that were proposed:

1—How do rare earths remove sulfur from cast steel?

2—How do rare earths improve mechanical properties of cast steels?

3—To what extent can rare earths replace critical alloys?

4—What rare-earth addition practices are preferable?

The laboratory studies were detailed to cover all of these points; the production heats were arranged on the basis of the available knowledge derived from the laboratory studies and they were made to check on points 2 and 4. It is the purpose of this summary to consolidate the known information on the above four questions.

How do rare earths remove sulfur from steel?

Molten cast steel treated with misch metal under certain conditions results in the removal of sulfur. Desulfurization is favored by large additions of rare-earth metals, by low tapping temperatures, by strong deoxidation and by a basic environment such as basic slag, basic ladles, and so forth.

Misch metal additions to cast steel produced under an acid environment and acid slags results in the temporary removal of sulfur from the acid steel but reversion of sulfur to the steel occurs rapidly in the absence of a basic slag. Therefore, to all practical purposes, sulfur is not removed from cast steels produced by the acid practice to which additions of rare-earth metals are made, unless the steel is cast immediately following misch metal additions.

Less than 0.007 percent sulfur was removed by the addition to basic steel of three pounds of misch metal per ton of steel. An equivalent addition of rare-earth oxides containing a reducing agent removed a small amount; however, the results of sulfur removal were not consistent. No significant amount of sulfur was removed from cast steel treated with cerium fluoride.

Additions amounting to five pounds of misch metal per ton of steel removed up to 0.028 percent sulfur from the laboratory basic steels. However, such large additions are undesirable as the properties of the steels are lowered through formation of undesirable inclusion types.

The laboratory studies indicate that the desulfurization reaction is essentially complete in three minutes after the addition of the misch metal and high bath temperatures hinder desulfurization.

Desulfurization occurs with the formation of rare-earth sulfides which are precipitated and float out of the liquid steel. They are trapped by basic slag but reversion to sulfur in the steel occurs in acid practice operations.

How do rare earths improve mechanical properties in cast steels?

The presence of rare-earth metals in cast steels changes the shape, color, and composition of the sulfide inclusions in cast steels. The type of inclusion present in these steels has a pronounced effect on the mechanical properties of cast steel. The properties most influenced are notched impact values, the reduction of area, and elongation values.

The changes in the type of inclusions occurred in those steels treated with misch metal but not in those treated with oxides and fluorides. The influence of misch-metal additions on the sulfides was the same regardless of whether the steels were made by the acid or basic practice. It appears that the sulfur level influences the response of a cast steel to a particular amount of rare-earth elements. Consequently, the ratio (Ce + La)/S is a more useful value than just the total amounts of cerium and lanthanum in the steel as determined by analysis.

Aluminum-killed cast steels ordinarily contain angular or Type III sulfides, however when the aluminum is improperly added film or Type II inclusions result. However, globular (Type I) sulfides are typical of aluminum-killed steels containing cerium and lanthanum in amounts approximating the sulfur content, namely, (Ce + La)/S ratios of 1.0 to 1.5 The mechanical property data of the report indicates that the globular inclusions have a less harmful effect on ductility and toughness of cast steels. It is, therefore, very important to know that the presence of the rare-earth elements in cast steel can improve the notched bar impact values and the ductility properties of aluminum-killed cast steel over and above those properties secured in steels not treated with misch metal.

The situation is not as simple as the previous statement seemed to imply because the amount of rare-earth elements retained in the steel is very important. Additions of one pound per ton of steel did not produce globular sulfides nor did they improve the mechanical properties of the steel. Chemical analyses of such laboratory steels indicated that they were characterized by (Ce + La)/S ratios of 0.8 or less. Such quantities of rare-earth elements, therefore, are not beneficial.

Large additions of misch metal appear to harm the properties of cast steels. Many of the cast steels treated with five pounds or more of misch metal per ton of steel were characterized by the presence of many small irregularly-shaped inclusions which occurred in clouds or clusters (Type IV). Such steels exhibited much poorer ductility than would be expected for their sulfur contents. Chemical analyses of such steels indicated that the sum of their cerium and lanthanum contents exceeded 1.6 times their sulfur contents.

A change of inclusion type from III to I in the quenched and tempered low-alloy, laboratory produced, cast steel (0.025%S) by the addition of misch metal, results in an average improvement of the reduction of area value from about 40 percent to approximately 50 percent at 260 BHN, and the Charpy V-notch impact value at —40 degrees F from about 30 to the range 35 to 45 foot-pounds.

There are certain points that must be considered in relation to the impact properties. High sulfur contents in low-alloy cast steels, with or without the presence of rare-earth metals, are responsible for low impact values. Cast steels made by the acid practice had as good impact properties, for their sulfur content and inclusion type, as cast steels made by the basic practice. Impact properties of cast steels containing rare-earth elements are better than those not treated with rare-earth metals provided the sulfur content is similar and provided the rare-earth elements result in Type I inclusions being formed.

These studies also indicated that misch-metal additions are equally effective in all types of low-alloy cast steels. The ductility and low temperature Charpy V-notch impact values are improved at various hardness levels. The reason for this is that the inclusions are altered to Type I sulfides; however, part of the improvement may be, in certain cases, the removal of some sulfur (basic steels). The addition of boron, vanadium, or high nitrogen contents did not seem to influence the response of cast steels to additions of misch metal.

Reasonably wide variations in carbon, manganese, chromium, and molybdenum contents did not interfere with the effects expected from additions of misch metal. However, the situation seems to be different for titanium. This element has a strong affinity for sulfur and produces film (Type II) sulfide inclusions. Additions of two pounds per ton of misch metal did not prevent the occurrence of Type II inclusions in steels containing 0.07 and 0.17 percent titanium. The cast steels containing such amounts of titanium had very poor tensile, ductility and Charpy impact properties regardless of misch metal treatment.

To what extent can rare-earth metals replace critical alloys?

The laboratory studies indicated that rare-earth elements had no direct effect on hardenability. These experiments showed, however, that boron could be recovered from the oxide addition agents which contain boron. Boron introduced in this way did increase hardenability. The laboratory studies also indicated that additions of misch metal do not interfere with the hardening effects of boron and other elements. However, this limited study showed that the majority of production steels showed very little improvement, if any, in hardenability when the boron treated Mn-Cr-Mo steels are compared to the non-boron-treated steels of similar composition. No analyses were made to determine the boron content of the boron treated production steels but procedures for adding boron were followed as specified in Research Report No. 28 on Boron Treated Cast Steels.

Laboratory produced Mn-Cr-Mo cast steels treated with rare-earth metals were heat treated to simulate heavy 4- and 6-inch sections. The impact and ductility properties of these sections were inferior to those of the 1-inch section. In fact, the Charpy V-notch values at —40 degrees F for the 4-inch section were about 1/2 of that recorded for the 1-inch section. Values for the 6-inch section were even less.

Charpy impact specimens taken from a 4-inch section of the production Mn-Cr-Mo cast steels, one inch from the surface showed very low values, in the neighborhood of only 6 foot-pounds even though a fairly good microstructure of tempered martensite and tempered bainite was observed.

One thing is certain: critical alloys can not be replaced by the use of rare-earth metals.

What rare-earth metal practices are preferable?

The laboratory studies indicated that the best manner of producing production steels treated with boron was to add about 3 pounds of misch metal to the ladle after the usual deoxidizers such as aluminum, calcium, manganese, silicon, and so forth, were added. If boron in the form of Carbortam was to be added it was to be added to the ladle at the same time as the misch-metal additions. LanCerAmp No. 10 was selected as the misch-metal addition because it was packaged in a metal container and it was hoped that by its use the percent recovery of the rare-earth elements would be similar to that obtained in the laboratory studies.

All the production steels showed considerable agitation upon the addition of LanCerAmp No. 10 to the ladle. This agitation was extensive and persisted even after the ladle was on the pouring floor. In fact, pouring was delayed in certain instances until the agitation subsided. It is very possible that the agitation was responsible for excessive loss of boron. This point needs further checking. Perhaps it would be better to add the boron alloy as late as possible after the addition of LanCerAmp No. 10 or to use another misch metal that did not result in such pronounced agitation since LanCerAmp No. 10 contains a volatile material.

The production heats indicated that the formation of Type I inclusions was more difficult than assumed from the laboratory studies. A realization of the importance of the sulfur level should have been recognized from the laboratory studies prior to the preparation of the production heats. Only in one case, the basic electric heat which was the last production heat made, was careful attention given to the probable sulfur content and the amount of misch metal to add. Only this steel contained Type I inclusions throughout.

It will be observed from a study of the inclusion types in the production steels that the percent recovery of Ce + La in the steel varied over rather wide limits. An analysis for cerium and lanthanum of the basic open-hearth steel indicated a 40 percent recovery of Ce + La. However, Table 26 is based on a 20 percent recovery and it is believed that these values should be treated as only rough guides. The difficulties of analysis of rare-earth metals, together with the uncertainty regarding the possible Ce + La recovery in the steel, make the (Ce + La)/S ratio of little practical value.

Instead, it is necessary that the cast steel be carefully and thoroughly studied as to the types of inclusions present. If Types II and III inclusions are pronounced with Type I inclusions also present, it is a certainty that there was insufficient rare-earth metals present in the steel. The reason for this may be the high sulfur content or a low cerium and lanthanum recovery, or both.

If Type I and Type IV inclusions are present in the steel, or Type IV alone is present, then it can be stated that too much misch metal was added.

At least one thing is certain, the control to produce Type I inclusions is within narrow limits and care must be exercised by each foundry in establishing it for their own operations.

The reason that careful planning and tight control is necessary can be illustrated by recalling that defective castings resulting from porosity were produced on the basic open-hearth heat. Too much misch metal (3 lb/ton) was added for the low sulfur content (.012%) with the result of the formation of Type IV inclusions and gas precipitation. An amount of about one-half of the original addition or 1-1/2 pounds per ton would have been sufficient to produce Type I inclusions in this instance and secure castings without the porosity defects. However, 1-1/2 pounds per ton of misch metal would produce nothing but Type II and low ductility cast steels if added to an acid electric heat of .035 percent sulfur. In fact, the production steel studies indicate that an addition of 4 or 5 pounds per ton of misch metal is necessary to produce the desired Type I inclusions.

A considerable amount of basic information on the effect of rare-earth metals is made available in this report. However, a definite formula or cook-book recipe is not presented for the individual foundry to follow. It is unfortunate that each foundry staff must use this report as a background for experimental studies in its foundry.

There is an additional observation that may be made concerning the effect of rare-earth metals on cast steels and this is in relation to the impact properties at low temperatures. Why is it that such high Charpy V-notch values can be secured from basic open-hearth cast steel treated with misch metal? Apparently the low sulfur content insures good values and the presence of only Type I inclusions adds to the improvement of the values. However, both of these conditions were met in the case of the basic electric production steel but those extra high impact properties were not attained (See Table 25). There is a possibility that the low nitrogen content of the steel may be responsible for achieving the high values that are desired. If the nitrogen content of the finished steel is below .008 percent, high impact values will result in the securing of Type I inclusions by the use of misch metal; but if the nitrogen is over about .008 percent then a nitrogen fixer such as titanium is necessary. This is especially true upon the addition of boron to the steel in order to permit the boron to be effective. Nevertheless, titanium apparently has a very pronounced adverse effect on the low temperature notched bar impact properties so it should not be used, or used only sparsely, in cast steels when high Charpy values are desired. This effect is probably due to the formation of film sulfides by titanium.

It seems, that steps should be taken during steelmaking to reduce and maintain the nitrogen content at a low figure so that titanium-bearing alloys, such as Carbortam, are not necessary to fix the nitrogen content as titanium nitrides. If boron is then required it can be added as Borosil and there will be no titanium present to adversely affect the impact properties.

Low nitrogen values, under .008 percent, may be difficult to secure in basic electric practice unless the single oxidizing slag is used. In this case, additions of ferrotitanium may be necessary; however, they should be limited to only 1 or 2 pounds per ton.

The information in these studies should be a good basis for individual foundry study and activity on the production of cast steels containing rare-earth metals.

BIBLIOGRAPHY

1. Spring, L.: "Tests with Cerium in Brass and Steel," Trans. American Foundrymen's Association, Vol. XXX, pp. 626-634 (1922)
2. Gillett, H. W., and Mack, E. L.: "Molybdenum, Cerium, and Related Alloy Steels," The Chemical Catalog Company, Inc., New York (1925)
3. Berry, C. D., and Dorvell, A. A.: "Effect of Cerium on Ductility and Impact Strength of Steel," American Foundryman, Vol. 20, pp. 45-46 (December 1951)
4. Knapp, W. E., and Bolkcom, W. T.': "Rare Earths Improve Properties of Many Ferrous Metals," The Iron Age, Vol. 169, No. 17, pp. 129-134 (April 24, 1952) Vol. 169, No. 18, pp. 140-143 (May 1, 1952)
5. Lillieqvist, G. A., and Mickelson, C. G.: "Properties of Cast Steels Improved by Rare-Earth Element Additions," Journal of Metals, pp. 1024-1031 (October 1952)
6. Steel Founders' Society of America Research Report No. 29, "The Deoxidation and Desulfurization of Cast Steels with Rare-Earth Metals" May 1953
7. Lorig, C. H., et al., "The Improvement of Low Alloy Armor Steels, Part IX," NDRC Research Project MRC-14, OEM-450, April 1944

APPENDIX

TABLE A-1. CHEMICAL COMPOSITION OF EXPERIMENTAL STEELS

	Composition, percent									
Heat	C	Mn	Si	Mo	Cr	Ni	S	B	N	V	Ti
Steels Made to Determine Effect of Holding Time on Temperature and Desulfurization											
9277	(0.23)	(1.25)	(0.40)	(0.10)	(0.07)	(0.07)	0.033		(0.005)		
9794	(0.23)	(1.25)	(0.40)	(0.10)	(0.07)	(0.07)	0.023		(0.005)		
9805	(0.23)	(1.25)	(0.40)	(0.10)	(0.07)	(0.07)	0.030		(0.005)		
9806	(0.23)	(1.25)	(0.40)	(0.10)	(0.07)	(0.07)	0.032		(0.005)		
9889	(0.23)	(1.25)	(0.40)	(0.10)	(0.07)	(0.07)	0.035		(0.005)		
9890	(0.23)	(1.25)	(0.40)	(0.10)	(0.07)	(0.07)	0.034		(0.005)		
Steels Made to Determine Effect of Melting Procedure on Desulfurization and Mechanical Properties											
9795	(0.023)	1.25	0.38	(0.10)	(0.07)	(0.07)	0.015		0.004		
9796	0.21	(1.25)	(0.40)	0.10	(0.07)	(0.07)	0.054		0.004		
9797	(0.23)	(1.25)	0.40	0.10	(0.07)	(0.07)	0.038		0.005		
9798	0.21	(1.25)	(0.40)	0.10	(0.07)	(0.07)	0.044		0.005		
9799	(0.23)	(1.25)	0.39	0.10	(0.07)	(0.07)	0.020		0.004		
9800	(0.23)	0.74	0.42		(0.07)	(0.07)	0.021		0.004		
9807	0.23	(1.25)	(0.40)	(0.10)	(0.07)	(0.07)	0.036		0.006		
9880	0.21	(1.25)	(0.40)	(0.10)	(0.07)	(0.07)	0.034		0.006		
9881	0.26	0.76	0.47	(0.10)	(0.07)	(0.07)	0.035		0.006		
Steels Made to Determine Effect of Rare-Earth-Metal Treatments on Hardenability and on Mechanical Properties											
141	0.24	1.16	0.42	0.45	0.55	0.28	0.038		(0.005)		
9801	0.21	(1.25)	(0.40)	(0.40)	(0.50)	(0.25)	0.041		0.006		
9802	(0.23)	(1.25)	(0.40)	(0.40)	0.49	(0.25)	0.031		0.005		
9803	0.21	1.14	0.39	0.35	(0.50)	(0.25)	0.029		0.005		
9804	(0.23)	(1.25)	0.40	0.40	(0.50)	(0.25)	0.027		0.004		
9808	(0.23)	(1.25)	0.40	(0.20)	(0.50)	0.04	0.031		0.006		
9809	(0.23)	(1.25)	(0.40)	(0.20)	0.50	(0.25)	0.026	0.006	0.004		
9810	(0.23)	1.15	(0.40)	(0.40)	(0.50)	(0.25)	0.028	0.005	0.002		
9811	(0.23)	(1.50)	(0.40)	(0.40)	(0.50)	0.25	0.035		0.005		
9812	(0.23)	1.42	(0.40)	(0.40)	(0.50)	(0.25)	0.022		0.006		
9813	0.21	1.57	(0.40)	(0.40)	(0.50)	(0.25)	0.028	0.006	0.003		
9875	(0.23)	(1.50)	0.41	(0.20)	(0.50)	(0.25)	0.031	0.006	0.002		
9876	(0.23)	(1.50)	(0.40)	(0.40)	1.04	(0.25)	0.026		(0.005)		
9877	(0.23)	1.46	(0.40)	(0.40)	(1.00)	(0.25)	0.022	0.006	0.004		
9878	0.24	(1.50)	(0.40)	(0.20)	(1.00)	(0.25)	0.028	0.0055	0.005		
9888	0.23	(1.25)	(0.40)	0.20	(0.50)	(0.25)	0.026		0.006		
Steels Made to Determine Effect of Different Rare-Earth Addition Agents for Steel											
9894	(0.23)	(1.25)	(0.40)	(0.40)	(0.50)	(0.25)	0.024		(0.005)		
9895	(0.23)	(1.25)	(0.40)	(0.40)	(0.50)	(0.25)	0.023	0.003	(0.005)		
9896	0.21	1.17	0.31	(0.39)	(0.50)	(0.25)	0.029	0.0015	(0.005)		
9897	(0.23)	(1.25)	(0.40)	(0.40)	(0.50)	(0.25)	0.028		(0.005)		
143	(0.23)	(1.25)	(0.40)	(0.40)	(0.50)	(0.25)	0.037		(0.005)		
144	(0.23)	(1.25)	(0.40)	(0.40)	(0.50)	(0.25)	0.035		(0.005)		
Steels Made to Study Possible Interference by C, N, V, Ti, and B											
9879	(0.23)	1.40	(0.40)	(0.50)	(0.50)	(0.50)	0.029		(0.005)	0.11	
9882	0.24	(1.25)	(0.40)	0.49	(0.50)	(0.50)	0.026		0.017		
9883	(0.23)	(1.25)	(0.40)	0.51	0.51	(0.50)	0.023		0.017		
9884	0.22	(1.25)	(0.40)	0.46	(0.50)	0.51	0.028		0.001		0.09
9885	(0.23)	(1.25)	0.46	0.49	0.49	(0.50)	0.026		(0.005)		0.08
9836	0.40	(1.25)	(0.40)	(0.50)	(0.50)	(0.50)	0.027		0.006		
9887	0.44	1.25	(0.40)	(0.50)	(0.50)	(0.50)	0.030		(0.005)		
9891	(0.23)	(1.25)	(0.40)	(0.50)	(0.50)	(0.50)	0.025	0.005	(0.005)		
9892	(0.23)	(1.25)	(0.40)	(0.50)	(0.50)	(0.50)	0.029	0.005	(0.005)		
9893	0.22	1.33	(0.40)	(0.50)	(0.50)	(0.50)	0.026	0.0055	(0.005)	0.02	0.17
9898	(0.23)	(1.25)	(0.40)	(0.50)	(0.50)	(0.50)	0.026	0.003	(0.005)		
9899	(0.23)	(1.25)	(0.40)	(0.50)	(0.50)	(0.50)	0.022	0.0045	0.016		
142	(0.23)	(1.25)	(0.40)	(0.50)	(0.50)	(0.50)	0.035		(0.005)		

Note: Parentheses enclose intended compositions of element in the steels which were not analysed.
All heats were deoxidized with aluminum except Heat 9807. Some analyses for Al, Ce and La are given in the text.
Sulfur analysis was three minutes after rare earth-metal addition.

TABLE A-2. DATA ON POURING TEMPERATURES, DESULFURIZATION, AND INCLUSION CHARACTERISTICS OF EXPERIMENTAL STEELS

Heat	Furnace Lining	Special Element	Pouring Temperature, °F	Rare-Earth Addition,[4] lb/ton	Sulfur, %		Sulfide-Inclusion Type[1]	
					Melt	Final[2]	After Deoxidation[3]	After Rare-Earth Addition
Steels Made to Determine Effect of Holding Time and Temperature on Desulfurization								
9277	Basic		3050	5	0.043	0.033	....	....
9794	Basic		2840	5	0.042	0.023	III	IV
9805	Silica		2860	5	0.04[illegible]	[illegible]	III	IV
9806	Silica		2850	5	[illegible]	[illegible]32	....	I
9889	Silica		2870	0	0.03[illegible]	[illegible]5	III	III
9890	Basic		2860	5	0.039	0.[illegible]4	III	I
Steels Made to Determine Effect of Melting Procedure on Desulfurization and Mechanical Properties								
9795	Basic		2870	5	0.043	0.015	III	I
9796	Basic		2840	5	0.059	0.054	III	I, II
9797	Basic		3040	5	0.044	0.038	III	I
9798	Basic		2850	0	0.044	0.044	. .	II
9799	Basic		2840	0	0.020	0.020	....	III
9800	Basic		2850	5	0.042	0.021	III	I
9807	Basic		2880	5	0.042	0.036	I	I
9880	Silica		2870	5	0.037	0.034	III	I
9881	Silica		2870	5	0.039	0.035	III	I
Steels Made to Determine Effect of Rare-Earth-Metal Treatment on Hardenability and Mechanical Properties								
141	Basic		2860	0	0.038	0.038	....	III
9801	Basic		2870	0	0.041	0.041	.	II
9802	Basic		2850	1	0.032	0.031	III	II
9803	Basic		2870	2	0.033	0.029	III	I
9804	Basic		2860	3	0.033	0.027	III	I
9808	Basic		2850	3	0.033	0.031	III	I
9809	Basic	0.006B	2850	3	0.032	0.026	III	I
9810	Basic	0.005B	2880	3	0.033	0.028	III	I
9811	Basic		2880	0	0.035	0.035	....	III
9812	Basic		2870	3	0.029	0.022	III	I
9813	Basic	0.006B	2860	3	0.034	0.028	III	I
9875	Basic	0.006B	2870	3	0.035	0.031	III	I
9876	Basic		2870	3	0.034	0.026	III	I
9877	Basic	0.006B	2860	3	0.033	0.022	III	I
9878	Basic	0.0055B	2860	3	0.034	0.028	III	I
9888	Basic		2860	3	0.028	0.026	III	I
Steels Made to Determine Effect of Different Rare-Earth Non-Metallic Addition Agents for Steel								
9894	Basic		2850	3	0.028	0.024	III	I
9895	Basic	0.003B	2860	3	0.029	0.023	III	III
9896	Basic	0.0015B	2860	3	0.029	0.029	III	III
9897	Basic		2870	3	0.028	0.028	III	III
143	Silica		2870	3	0.039	0.037	I(5)	III
144	Silica		2850	3	0.036	0.035	III	III
Steels Made to Study Possible Interference by C, N, V, Ti or B on Rare-Earth-Metal Effects								
9879	Basic	0.11V	2880	2	0.032	0.029	III	I
9882	Basic	0.017N	2860	0	0.026	0.026	....	III
9883	Basic	0.017N	2860	2	0.028	0.023	III	I
9884	Basic	0.09Ti	2880	0	0.028	0.028		III, II
9885	Basic	0.08Ti	2870	2	0.030	0.026	III, II	I, II
9886	Basic	0.40C	2870	2	0.029	0.027	III	I
9887	Basic	0.44C	2880	0	0.030	0.030	III	III
9891	Basic	0.005B	2870	2	0.028	0.025	III	I, II
9892	Basic	0.005B	2860	2	0.030	0.029	III	I
9893	Basic	0.0055B, 0.017Ti	2870	2	0.028	0.026	III	I, II
9898	Basic	0.003B	2850	0	0.026	0.026	III	III
9899	Basic	0.0045B, 0.016N	2870	2	0.026	0.022	III	I
142	Basic		2880	2	0.039	0.035	III	I, II

---

(1) Metallographic specimens were taken from steel cast three minutes after the final addition except for group A. In this group the inclusion type refers to samples cast after holding 1/2 minute.

(2) Sulfur contents are for 3-minute holding times.

(3) All heats except 9807 were provided with two pounds of aluminum per ton.

(4) Misch metal produced by American Metallurgical Products Company, except for Group D.

(5) Aluminum added after rare-earth addition.