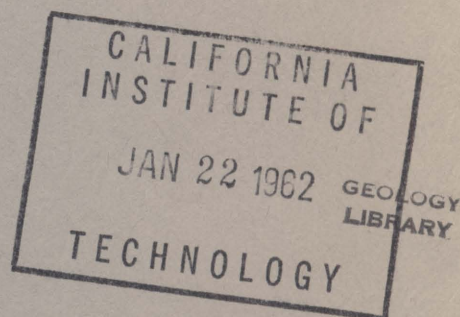RI bureau of mines
report of investigations 5895

PRODUCING AND LADLE-TREATING
MEDIUM-CARBON ALLOY STEELS
WITH RARE-EARTH METALS AND OXIDES

By R. J. Leary, E. J. Ostrowski, and N. Derick

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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by

R. J. Leary,[2] E. J. Ostrowski,[3] and N. Derick[4]

SUMMARY

Significant improvements in surface conditions or mechanical properties of steels have been attributed by several investigators to ladle additions of small quantities of rare-earth metals or their oxides. To investigate systematically these effects in wrought and in cast plain carbon and alloy mechanical steels containing approximately 0.35 percent carbon, heats of four representative compositions were melted by the Bureau of Mines in a 4-ton open-hearth furnace. Each heat was cast into three sets of ingots to exemplify respectively, treatments with (1) rare-earth metals, (2) rare-earth metal oxides, and (3) an untreated set as a control.

The development of melting, casting and rolling practices is described and discussed. Lance injection of oxygen shortly after melt raised the temperature of the metal immediately as much as 500° F., principally because mechanical agitation exposed the high-carbon metal to the flame and furnace roof. An exceptional degree of superheat in the metal at the termination of the refining period was attributed to oxygen injection during the refining period. Bath temperatures higher than industrial practice were permitted by the all-basic furnace lining. Rates of carbon elimination as high as 0.036 percent carbon per minute were achieved by oxygen injections.

Control of chemical composition was at least comparable to industrial experience, and recovery of alloying elements was higher.

Recoveries of rare earths from rare-earth metals averaged 28 percent and were remarkably consistent. (This level of recovery is considered relatively high in view of the high free energy of rare-earth oxide formation.) Only a small fraction of the rare-earth oxide material was retained in the ingot

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product. The reason for a cerium to lanthanum (Ce:La) ratio of 3:1 in the ingot product against ratios of 1.5:1 in the rare-earth metal mixture and 2:1 in the oxide material is not known.

Surface quality of 4-inch-square billets rolled from the ingots produced was judged to be representative of the base steel compositions. Billets from ingots treated with rare-earth metals had significantly fewer light seams but did contain myriad shallow, longitudinal discontinuities ranging from three sixteenths to one-half of an inch in length. These were not true seams. Although the surface of the billets was completely removed by grinding, this condition was again observed in the bars produced from these billets.

Cross-sectional macroetch specimens from the billet product representing respectively the top and bottom of the product from each ingot were comparable in appearance to industrial experience with these grades. No difference was found between untreated specimens and those representing the rare-earth oxide treatment. However, steels that had been treated with rare-earth metals disclosed a characteristic pattern of irregularly-shaped voids adjacent to the periphery of the cross section. The investigators believed that these voids were related directly to the characteristic surface defects observed in the billets.

INTRODUCTION

The Watertown Arsenal entered into a cooperative agreement with the Bureau of Mines to investigate systematically the comparative effects upon the mechanical properties of carbon and alloy steels resulting from additions of rare-earth metals and rare-earth oxides to the ladle before teeming. Under the agreement the steels would be prepared in a 4-ton open-hearth furnace at the Pittsburgh Metallurgy Research Laboratory, and the Bureau of Mines would arrange for and supervise the rolling and finishing of wrought bar products from the resulting ingots. The furnace is a tilting, one-way fired, recuperative, and basic-lined type, and holds 4 tons of molten steel. By using a similar size furnace, Work and his coworkers[5][6] demonstrated that steels conforming to commercial chemical composition and soundness could be produced.

Published work had suggested the possibility of improving the hot workability of wrought alloy steels by treatments with rare-earth[7] metals and had indicated quite definitely that under certain conditions a rare-earth metal

[5]Work, H. K., and Banta, H. M., An Experimental Open-Hearth Furnace: Open Hearth Proc., AIME, vol. 22, 1939, pp. 161-174.
[6]Work, H. K., and Webb, W. R., Operation of an Experimental Open-Hearth Furnace: Open-Hearth Proc., AIME, vol. 28, 1945, pp. 20-35. (This article was reprinted in Blast Furnace and Steel Plant, vol. 33, 1945, pp. 959, 1116.)
[7]Henke, R. H., and Lula, R. A., Rare-Earths Counteract Hot-Rolling Defects in Stainless Steel: Jour. Metals, vol. 6, 1954, pp. 883-888.

treatment would enhance the mechanical properties of cast carbon and alloy steels.[8][9] With regard to wrought alloy steels, however, the data reported appeared too limited in scope to form any quantitative conclusions regarding the possible benefits to mechanical properties from rare-earth metal treatments. The Arsenal realized that a number of the compositions widely used for ordnance purposes were basically similar to the wrought steels that had been investigated, and that, in consequence, any significant improvement in mechanical properties from treatments with rare-earth metals or rare-earth metal oxides would allow either the production of stronger ordnance steels from the same base alloy compositions, or, as an alternative, the production of steels of equal strength from compositions containing smaller amounts of critical alloying elements.

This report is confined to a description and discussion of the operations involving the melting, refining, treating and casting of ingots by the Bureau of Mines and the subsequent rolling operations by a contractor, the Universal-Cyclops Steel Corp.

<div align="center">ACKNOWLEDGMENT</div>

The Bureau of Mines is grateful to E. J. Reagan, H. Freeman, and D. W. Clayton of Universal-Cyclops Steel Corp., for undertaking and executing a difficult rolling and finishing operation.

<div align="center">EXPERIMENTAL PLAN</div>

The Watertown Arsenal desired to determine the effects upon mechanical properties of wrought and cast steels, resulting from ladle additions of rare-earth metals and rare-earth oxides respectively.

This required (1) that for each ladle addition a pair of ingots must be produced to provide, respectively, the wrought and the as-cast product and (2) that three such pairs be produced for each type of steel to represent the two forms of treatment together with an untreated pair to exemplify the base composition. The Arsenal further desired to investigate in this manner four base compositions of medium-carbon steels, one plain carbon and three alloys.

The four base compositions are listed in table 1. Table 2 lists the shapes, sizes and weights of wrought product desired from each ingot rolled. The ingots for examination in the as-cast condition were to weigh approximately 500 pounds each.

[8]Lillieqvist, G. A., and Mickelson, G. C., Properties of Cast Steels Improved with Rare-Earth Element Additions: Jour. Metals, Vol. 4, 1952, pp. 1024-1031.

[9]Briggs, Charles W., The Effect of Rare-Earth Metals in Cast Steels, Part III. Summary, Discussions and Conclusions: Steel Founders' Soc. Am., Cleveland, Ohio, 1954, pp. 54-57.

TABLE 1. - Nominal compositions desired and the composition ranges adopted

Type of steel	Type of specification	Chemical composition, weight-percent							
		C	Mn	P	S	Si	Ni	Cr	Mo
Plain carbon......	Nominal......	0.35	0.75	0.025 (maximum)	0.025 (maximum)	0.25	-	-	-
	Full range...	.32/.38	.60/.90	.025 (maximum)	.025 (maximum)	.15/.30			
Alloy, molybdenum.	Nominal......	.35	.80	.025 (maximum)	.025 (maximum)	.25	-	-	0.25
	Full range...	.33/.38	.70/.90	.025 (maximum)	.025 (maximum)	.20/.35	0.25 (maximum)	0.20 (maximum)	.20/.30
Alloy, low nickel-chromium-molybdenum	Nominal......	.35	.90	.025 (maximum)	.025 (maximum)	.25	.55	.50	.20
	Full range...	.33/.38	.75/1.00	.025 (maximum)	.025 (maximum)	.20/.35	.40/.70	.40/.60	.15/.25
Alloy, high nickel-chromium-molybdenum	Nominal......	.35	.95	.025 (maximum)	.025 (maximum)	.35	1.00	.70	.35
	Full range...	.33/.38	.85/1.10	.025 (maximum)	.025 (maximum)	.30/.45	.90/1.10	.60/.80	.30/.40

TABLE 2. - <u>Bar product requirements from each ingot rolled</u>

Size	Section	Total lineal footage required, feet	Bar weight per lineal foot, pounds	Minimum bar weight required, pounds	Estimated weight of billets required, pounds
5/8 inch....	Square....	100	1.32	132	[1]200
7/8 inch....	Round.....	30	2.05	62	[1]100
1-1/4 inches	..Do......	100	4.18	418	470
3 inches....	..Do......	12	24.0	288	320
Weight from each ingot..				900	1,090

[1]Minimum piece weight of billet that could be rolled was 100 pounds.

Although the three ingot pairs of one steel type might have been produced from as many heats, a plan for casting all three pairs from one heat was drawn up to avoid complicating the comparisons between treatments with the variation in mechanical properties between heats that has been described by Wells and Mehl.[10] This plan required, however, three separate ladles for the respective ladle treatments. By using a different ladle to treat each batch from the same heat there would be no risk of contamination from reaction products that might have remained from the preceding treatment.

Accordingly, four heats were planned, one of each of the chemical compositions listed in table 1; each heat lot was to be teemed into three ladles for as many ladle treatments, and from each of these ladles two sizes of ingots were to be cast.

EQUIPMENT AND PROCEDURE

Melting and Casting

Open-Hearth Furnace

The furnace arrangement is sketched in figure 1. It was patterned after the Jones & Laughlin Steel Corp. experimental furnace described by Work and Banta,[11] but the Bureau of Mines furnace is enclosed in a steel frame mounted on rollers and rockers for tilting in either direction to permit easy removal of metal and slag. This furnace was continuously fired from one end using natural gas that was combusted with preheated air delivered from the recuperator through the overhead duct. High-purity oxygen was available at the furnace for introduction into the air stream, the fuel stream, or both. Waste gases from the furnace chamber flowed through a slag pocket and then upward past three banks of silicon carbide recuperator tubes to the stack. This three-pass recuperator heated the combustion air to approximately 1,700° F. at the outlet from the last pass. Heat losses in

[10]Wells, Cyril, and Mehl, R. F., Transverse Mechanical Properties in Heat Treated Wrought Steel Products: Trans. Am. Soc. Metals, vol. 41, 1949, pp. 731-739.
[11]Work cited in footnote 5.
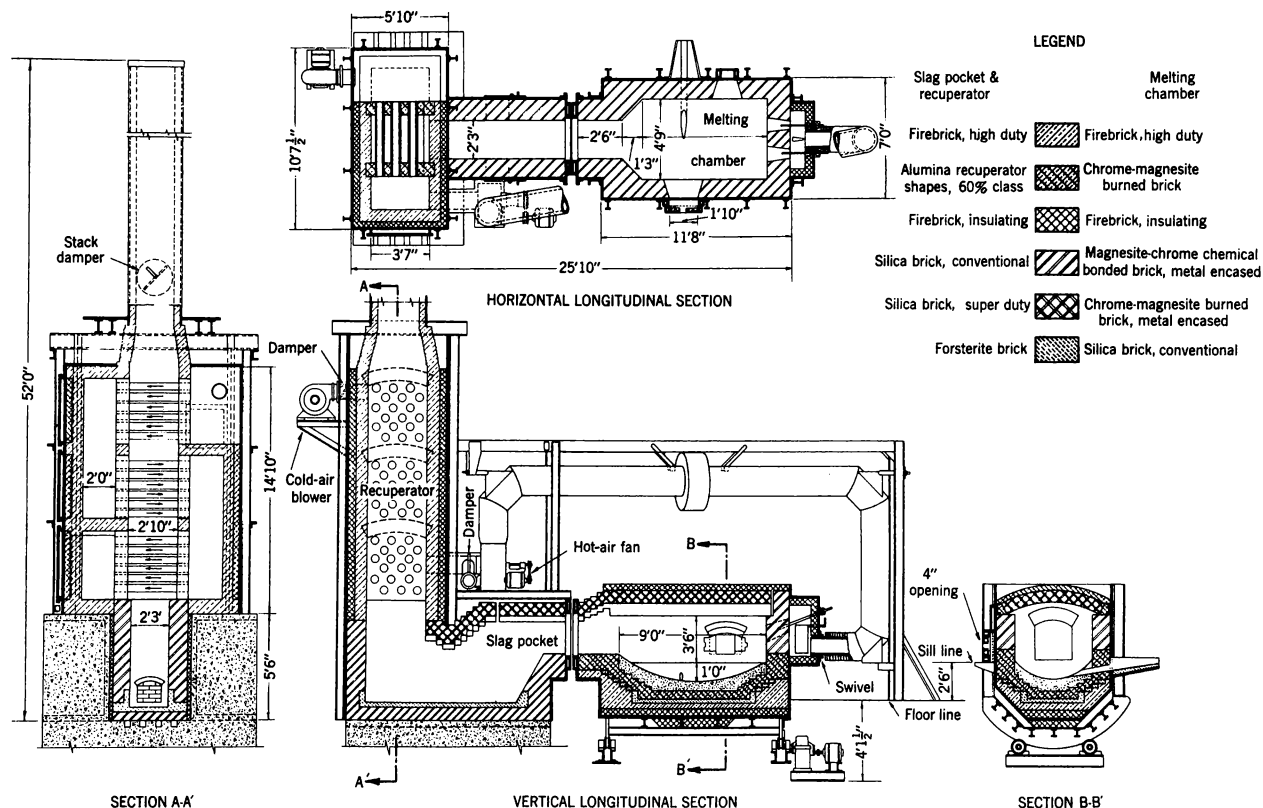
FIGURE 1. - Cross Section of 4-Ton Experimental Open-Hearth Furnace.

the overhead hot-air duct to the furnace reduced this temperature to approximately 1,400° F. at the entry to the wind box adjacent to the burner ports. Preheated air flow and furnace pressure were controlled manually by dampers at the intake of the cold air fan, at the exit from the hot air fan, and in the stack. Distribution of air to the twin burner ports was adjusted by a deflector in the wind box.

Normally, a flow of approximately 800 std. c.f.m. of preheated air was maintained, and the flow of fuel was adjusted for complete combustion by reference to the preheat temperature of the air; that is, in this system where the pressure head was small, the gravimetric flow of air, hence, the fuel flow requirement, was inversely proportional to the preheat temperature of the air. When oxygen was used to assist combustion, a stoichiometric adjustment was made to the rate of fuel flow.

Lining

This furnace has an all-basic lining as shown in figure 1. A distinctive feature was the use of metal-encased, burned, magnesite-chrome brick in a sprung-arch roof.

Charging

Solid materials were charged through the front door, although a small door in the backwall near the firing end could also be used. This small door was intended primarily for inspecting burner alignment and for charging molten metal. The backwall was made up with a taphole to provide a capacity of approximately 8,400 pounds, but the furnace capacity was limited to 6,000 pounds with the tapping notch that was usually employed in process experiments.

Instrumentation

Continuous records were charted of fuel flow, air flow, preheat air temperature at the hot air fan and at the furnace wind box, roof temperature, furnace pressure, and carbon dioxide in waste gases. Intermittent measurements of bath temperature were obtained with a specially designed immersion thermocouple unit connected to a recording potentiometer. Flows of oxygen and other gases that might be injected were indicated by rotameters, and associated pressure and temperature gauges.

Auxiliary Equipment

Crane

The furnace area was serviced by a 10-ton electric overhead traveling crane.

Ladles

Two sizes of ladles were used; a large primary ladle holding approximately 7,000 pounds of steel from the tap, and three smaller secondary ladles, each holding a maximum of 2,800 pounds for the rare-earth treatments and final teeming. All ladles were equipped with suitable stoppers and nozzles for teeming metal through the bottom of the ladle. Each of the small ladles was fitted with two nozzles and stoppers to allow simultaneous teeming of both the large and the small ingots. To provide a uniform, known weight of metal for treatment in the small ladles, the relations between metal depth and metal weight were established, and each ladle was marked for filling to a precise height.

Ingot Molds

In order to produce the weights of bars and as-cast ingots required, the following conditions were established: The ingots should be big end up, hot topped, and approximately square in cross section;[12] the relative volume of the hot-top should be a minimum of 13 percent of the total ingot weight;[13]

[12]Forsyth, H. J., and Ekholm, L. G., Molds and Pouring Practice: ch. 10 in Basic Open-Hearth Steelmaking: AIME, New York, N.Y., rev. ed., 1951, p. 404.

[13]Work cited in footnote 12, pp. 411-412. The hot-top volume of 15 percent described in this reference was relative to the volume of the ingot body; it would be 13 percent of the total volume cast, that is, ingot body and hot top.
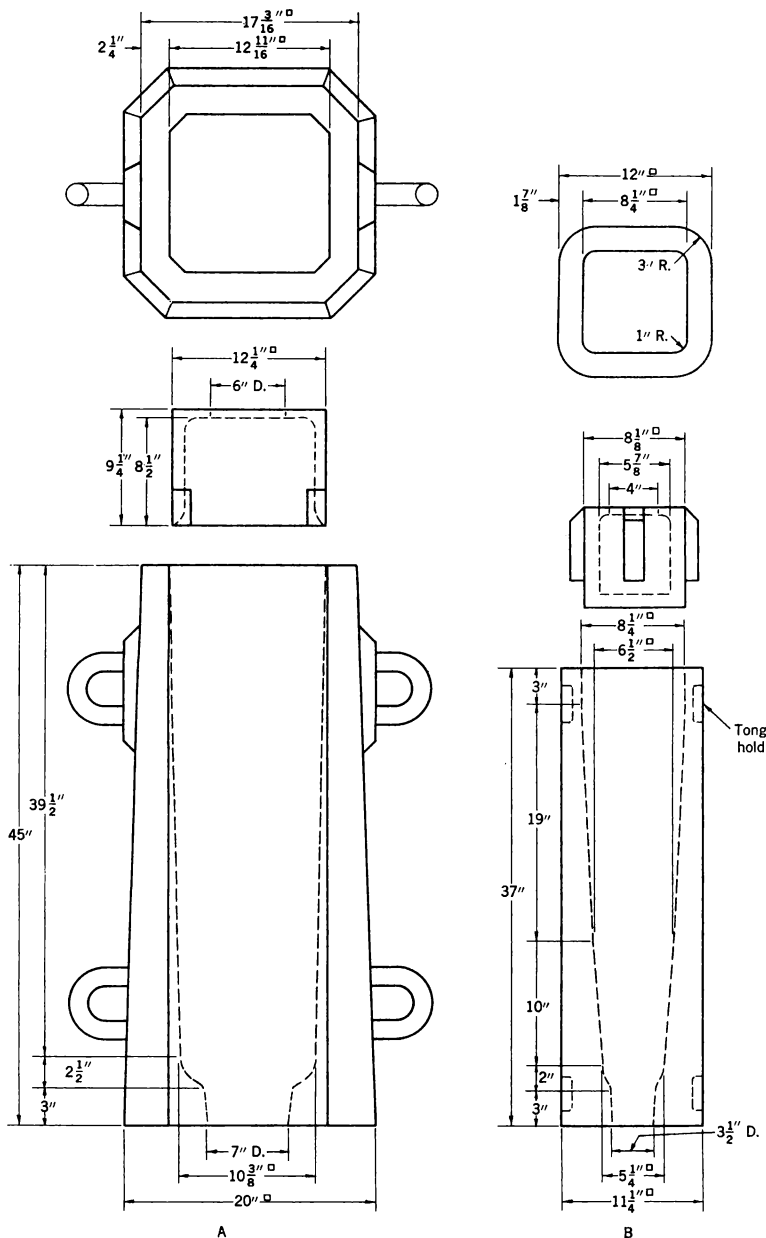
FIGURE 2. - Ingot Molds and Hot Tops: A. 12-11/16 In.
Square by 30-1/2 In. Big-End-Up Mold; B.
8-1/4 In. Square by 32 In. Big-End-Up Mold.

the taper of the ingot body should be between one-fourth and one-half inch per foot of ingot body length;[14] and the ratio of ingot body height-to-width would not be critical, as solidification would be essentially transverse in the size range of ingots to be cast.[15]

From the authors' industrial experience and also from discussion with representatives of Universal Cyclops Steel Corp., (the contractor who was to perform the rolling and finishing operations) it seemed that the minimum weight of billets to be produced from each ingot should aggregate approximately 1,170 pounds. For several years the contractor used a mold which conformed to the specifications in the preceding paragraph and, produced an ingot of the weight required. This mold and the mating hot top are sketched in figure 2 (A). A hot-topped ingot poured 40 inches high in this mold to the hot-top junction would weigh 1,525 pounds; the hot-top volume would be 13.6 percent, and on the basis of 5 percent bottom crop and 3 percent scaling losses, the total loss in crops and scale would be 21.6 percent. This would leave a billet yield of 78.4 percent and give 1,197 pounds of billet product, an amount sufficient to assure the production of the minimum bar weights required.

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[14] Work cited in footnote 12, p. 407.
[15] Marburg, Edgar, Accelerated Solidification in Ingots: Its Influence on Ingot Soundness: Trans. AIME, vol. 197, 1953, pp. 166, 168-169.

The ingots to be examined as-cast also were produced in big-end-up molds and were hot topped. Sketches of this mold and hot top appear in figure 2 (B). Ingots poured 33 inches high to the hot-top junction in this mold were estimated to weigh 475 pounds.

Chemical Analyses

Samples of metals or slags representative of the experimental operations were analyzed by the Bureau except spectrographic determinations of cerium and lanthanum, which were performed by a commercial laboratory. Many of these analyses were made during the melting operations, including determinations of carbon, sulfur, manganese, nickel, chromium, and molybdenum in the metals and iron in the slag. The timing of these samples and the elements requested for determination are discussed in the following paragraphs.

Steel Compositions Melted

Composition limits had to be established for each steel type with reference to the respective nominal levels (table 1) to provide a basis for determining the suitability of the steel compositions actually produced. Limits corresponding to commercial practice were constructed by applying standard ranges for the respective elements as they appeared in the current lists of American Iron and Steel Institute (AISI) standard grades[16] [17] that corresponded most nearly to the respective nominal compositions. These limits are listed in table 1. Where nickel, chromium or molybdenum were not specified, limits upon residual concentration of these elements were established at the AISI limits.[18] It was expected, however, that residual concentrations of these elements would be too low to be of any concern because low-alloy scrap was to be used for these heats. Maximum limits for phosphorus and sulfur were established at the 0.025 percent level desired by the Arsenal although these limits were much lower than the standard AISI limits of 0.040 percent.

Charging and Melting

Planning the Charge

The three distinct objectives that had to be reconciled in devising the charging and meltdown practice, were as follows:

1. Charge a sufficient quantity of ferrous materials to obtain finally the full amount of ingots required from a heat.

2. Proportion the charge ingredients to minimize the residual concentrations of phosphorus, sulfur, and alloying elements (copper, nickel, cobalt, molybdenum).

[16]American Iron and Steel Institute, Sec. 8 in Steel Products Manual. Hot Rolled Carbon Steel Bars: New York, N. Y., 1952, p. 43.
[17]_____. Sec. 10 in Steel Products Manual. Hot Rolled Alloy Steels: New York, N.Y., 1949, pp. 32-34.
[18]Work cited in footnote 17, p. 35.

3. Melt-in with sufficient carbon to refine the heats and have the molten steel at a very high temperature level at tap for successful teeming.

The first objective required careful analysis of the expected losses in yield incidental to the successive steps in melting, refining, tapping, and teeming because the total ingot weight required was close to the capacity of the furnace. Referring again to the experimental plan, three large and three small ingots were required from each heat. The description of ingot molds given above showed that each large ingot should weigh approximately 1,525 pounds and each small one 475 pounds, a total of 2,000 pounds per treatment. Thus, the three treatment pairs aggregated 6,000 pounds. After allowing for tapping and teeming losses, it was determined that approximately 7,200 pounds of iron (Fe) would be required in the molten bath at the time when refining began. In view of the furnace capacity, this amount of iron had to be obtained from a high-grade charge to minimize the total weight of charged materials. The charge proportions of pig iron and scrap were of some concern in this regard because the percentage of iron in pig iron as shown in table 3 was somewhat less than in good steel scrap.

The selection and proportioning of charge materials was recognized as important beyond their influence upon the total weight charged for two additional reasons: (1) The loads of phosphorus and sulfur that were introduced to a heat would depend on these factors, and (2) the proportion of pig iron would control the concentration of carbon at melt. No difficulty was foreseen in achieving low residual concentrations of alloying metallics such as nickel, chromium, and molybdenum; it was simply a matter of selecting a source of low-residual scrap.

Effective control over phosphorus and sulfur involved a basic conflict in the selection of charge materials from those available, principally because of the high-temperature refining practice that was required for successful teeming. As implied previously, this required a high-carbon melt which might be obtained either from, at one extreme, an all-scrap charge supplemented by several percent carbon as coke, or, at the other extreme, an all-pig iron charge. A scrap-coke charge would introduce a very low concentration of phosphorus, perhaps 0.03 percent, but the sulfur load, approximately 0.06 percent, would be unreasonable in attempting to make steels finishing under 0.025 percent in each of these elements. An all-pig iron charge would introduce, by contrast, 0.18 percent phosphorus and only 0.02 percent sulfur, a phosphorus concentration that could be reduced to the specification limit only under near-ideal conditions. Moreover, in these experiments the high-temperature refining practice required would not be conducive to efficient dephosphorization. This practice involved achieving a high metal temperature early in the refining period while the melt was still at a high carbon level, a relatively small ratio of slag weight to metal weight, and a slag composition lean in iron oxide. Each of these factors was recognized as a step away from effective dephosphorization.[19]

[19]Philbrook, W. O., and Washburn, F. M., Slag Control: Ch. 6 in Basic Open-Hearth Steelmaking: AIME, New York, N.Y., rev. ed., 1951, pp. 231-233.

TABLE 3. - Composition of steelmaking materials

Steelmaking material	Chemical composition, weight-percent[1]														
	C	Mn	P	S	Si	Ni	Cr	Mo	Fe	CaO	MgO	SiO$_2$	Al$_2$O$_3$	Al	Ca
Initial charge:															
Pig iron.......................70-pound pigs	4.0	1.1	0.14	0.02	1.8	-	-	-	92.7	-	-	-	-	-	-
Steel scrap, plate..........4- by 4- by 1 inch	.20	.6	.02	.04	.1	-	-	-	-	-	-	-	-	-	-
Steel scrap, punchings........1 inch diameter by 1/2 inch	.15	.6	.02	.04	.1	-	-	-	-	-	-	-	-	-	-
Lime, pebbled................. 1- by 3/8 inch	-	-	-	-	-	-	-	-	-	94.5	1.2	1.5	0.1	-	-
Limestone.......................4- by 2 inches	-	-	-	-	-	-	-	-	.7	52.0	0.3	3.2	1.3	-	-
Alloys:															
Anthracite..............minus 8, plus 20 mesh	83.0	-	-	.7	-	-	-	-	.5	.2	.1	6.5	4.0	-	-
Silicomanganese.................4- by 2 inches	2.33	68.92	(.15)	-	15.85	(.08)	(0.07)	-	(16.75)	-	-	-	-	-	-
Ferromanganese, high carbon...................4- by 1 inch	6.99	72.85	-	-	.39	-	-	-	-	-	-	-	-	-	-
Ferrosilicon, 50 percent grade.............5- by 2 inches	(.04)	(.50)	(.02)	(.01)	48.81	(.15)	(.10)	-	(48.6)	-	-	-	-	-	-
Nickel oxide pellets...........1 inch diameter	-	-	-	.004	-	78.6	-	-	-	-	-	.5	-	-	-
Ferromolybdenum............minus 1-1/2 inches	.10	.03	.058	.076	.86	-	-	72.84	-	-	-	-	-	-	-
Ferrochromium, high carbon...............5 pounds by 1 inch	3.66	(.30)	(.01)	(.07)	1.27	(.33)	68.57	-	23.53	-	-	-	-	-	-
Fluxes and refining agents:															
Alumina ore.....................minus 1/4 inch	-	.50	.17	-	-	-	-	-	8.5	1.5	1.7	20.0	49.1	-	-
Lime, pebbled...................1- by 3/8 inch	Listed above.														
Deoxidizers:															
Calcium-silicon...............minus 3 inches	(.60)	-	-	-	62.70	-	.56	-	1.98	-	-	-	-	-	29.94
Aluminum.......................1-pound stars	-	-	-	-	-	-	-	-	-	-	-	-	-	99.0	-
Rare-earth mixtures:															

Rare-earth mixtures:	
Lanceramp No. 1.................4-ounce balls	La:- (30 minimum); Ce:- (45/50); Nd + Pr:-(15/19); Higher rare-earths: (approximately 5); (minimum 95 percent rare-earth metals: balance Fe, Si, Ca, etc.)
RareMet 5-C....................minus 35-mesh	(50 parts crude rare-earth compounds: 90 percent rare-earth oxides, 3 percent rare-earth fluorides, 7 percent other oxides. Rare-earth elements distributed as 50 percent Ce, 25 percent La, 18 percent Nd, 5 to 6 percent Pr, and 1 to 2 percent higher rare-earths. 12 parts calcium silicon alloy 4 parts sodium nitrate)

[1]Concentrations of constituents quoted by suppliers as "typical" are enclosed in parentheses.

The third objective, namely, to melt-in at a high level of carbon, was adopted to compensate for the large losses in metal temperature that had been experienced during tapping and teeming in the preliminary trials. It was definitely established by those trials that the heats must be refined to a terminal temperature well above 2,900° F. for successful second-ladle teeming. The additional high-temperature heat thus required could be gained most readily by oxidizing sufficient carbon from the metal. Therefore, the amount of carbon charged was increased beyond the usual level to assure a carbon concentration of 2.0 percent or more at melt-in.

Attempts were made in preliminary heats to use a charge of 41 percent pig iron, 58.3 percent scrap, and 0.7 percent coke, the latter estimated to be the amount of coke required to melt-in at the level desired. Control over phosphorus would be no problem with this charge. Unfortunately, this charge was impractical. Carbon contents at melt-in varied widely from heat to heat, and in general, they were too low for successful refining. Further, the coke introduced too much sulfur, as the best available coke contained at least 0.6 percent sulfur, and its carbon to sulfur weight ratio of 120:1 when compared to Bureau of Mines pig iron (600:1 ratio) meant a fivefold increase in sulfur load per unit of coke carbon.

The following charge was finally selected:

Material:	Weight, pounds	Weight-percentage of metallic materials
Limestone.....................	150	-
Pebble lime...................	240	-
Pig iron......................	5,600	70.8
Steel scrap:		
Plates....................	1,600	20.3
Punchings.................	700	8.9
Total...............	8,290	100.0

Compositions of these materials are listed in table 3. The pig iron had been selected from the production of the laboratory's experimental blast furnace for a sulfur content of 0.020 percent or less, and since open-hearth slag, which may contain as much as 2 percent or more P_2O_5, had not been used in the burden of that furnace, the phosphorus content of 0.18 percent was as low as the ordinary run of basic iron produced from Lake Superior ores. The steel scrap was ideal for this work. The 4- by 4- by 1-inch plates and the 1-inch diameter by 1/4-inch punchings were clean structural scrap that packed very well with the pig iron to form a well-mixed charge.

Operations

Heats were scheduled for production during the day shift only, but crews were maintained on the other two shifts to heat and maintain the furnace in preparation for the next day's operations. The furnace was always ready for charging by this arrangement. At the beginning of the day shift, the furnace was already heated at the operating temperature of 3,020° F., was drained dry, and the hearth was in sound condition.

The first step in charging was to spread the limestone over the hearth. The pig iron, steel scrap, and pebbled burnt lime then were charged together into the furnace over the limestone. The initial charging of limestone in the manner described was advantageous in two respects: First, the condition of the hearth was preserved from damage by the heavy pigs as they fell upon it, and second, in the final stages of the meltdown, the violent boiling from the calcination of the limestone served to stir the melt and bring up the last vestiges of solid iron and scrap from the hearth.

In the second heat melted (OH-292), the burnt lime charge was reduced to 160 pounds but the resultant slag was deficient in basicity, therefore, the original amount of 240 pounds was charged in all subsequent heats.

If nickel or molybdenum were specified, the respective alloys (table 3) were charged at this time or shortly thereafter. Nickel oxide pellets were used because a stock was on hand and not for any preference for this material over nickel metal. The amounts charged were estimated to be sufficient to meet the specifications.

As soon as charging was completed the doors were banked and the meltdown period commenced. At this time, also, 22 std. c.f.m. of high-purity oxygen was bled into the stream of preheated combustion air. Compared to an average air flow of 800 std. c.f.m., this degree of oxygen enrichment increased the allowable firing rate by 13 percent while decreasing the total flow of gases by only 4 percent.

In the meltdown period the charge was stirred with a steel bar frequently to distribute the unmelted material evenly and thus hasten the melting. When no solid materials were detected on the hearth while stirring, the heat was declared melted. The time to melt ranged from 2-1/2 to 3 hours.

Refining

Objectives

The refining practice was planned to accomplish the usual objective of open-hearth refining, that is, to transform a bath just melted containing substantial concentrations of phosphorus, sulphur, silicon, and manganese into a melt having sufficient superheat for successful teeming, and a chemical composition suitable for deoxidation and alloying.

The necessity for a metal temperature higher than normal at the end of the refining period, coupled with a much higher rate of heat loss from the furnace walls compared to industrial furnaces, caused temperature attainment to be considered as the primary objective of the refining practice. Once the temperature relationships had been worked out, any needed adjustments to the refining practice for metal composition and cleanliness control could be incorporated without difficulty.

A brief review of the temperature relationships in open-hearth steelmaking as sketched in figure 3 will show that, at the time the charge became
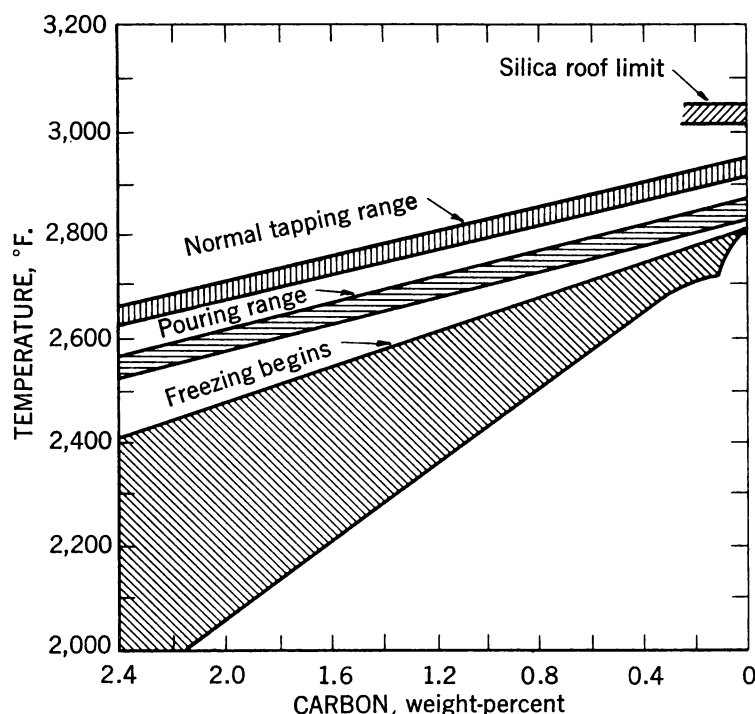
FIGURE 3. - Open-Hearth Steelmaking Temperatures
Related to Carbon Concentration.

completely melted, the temperature of the metal depended essentially upon the carbon concentration, indicated by the liquidus line. In practice, the average temperature would be somewhat higher because of the thermal gradient from the flame through the slag and metal. This thermal gradient through the metal bath would be relatively small owing to the high thermal diffusivity of the metal compared to the slag above and the hearth beneath; stirring produced by carbon oxidation in the metal would diminish it further. For the experimental furnace it was estimated that the gradient would result in an average metal temperature from 15 to 25° F. above the liquidus when the charge had become completely molten.[20]

From this point the refining practice for this work had to superheat the metal approximately 200° F. with respect to the liquidus temperature corresponding to 0.30 percent carbon, the average level of carbon where furnace deoxidation and alloying would take place. This superheat was about 50° F. higher than the requirement in an industrial-sized operation.[21]

Principal sources of superheat were two--the flame and the oxidation of carbon. Sensible heat contributed by oxidation of phosphorus, silicon, and manganese was substantial, but this heat was not considered because it would be evolved during refining in a pattern that would not vary greatly over the range of refining practices that might be considered. The time rate of heat supply from both the flame and the carbon reaction was an important factor as the total heat lost to the furnace walls, roof and hearth in the refining period was essentially time-dependent. In addition, the amount of sensible heat required by the bath to maintain its temperature above the liquidus during carbon oxidation had to be supplied fast enough at least to match the natural rate of carbon drop, that is, oxidation by means of oxygen supplied through the slag from the furnace atmosphere.

[20] Larsen, B. M., Rates of Open-Hearth Reactions: ch. 22 in Basic Open-Hearth Steelmaking. AIME, New York, N.Y., rev. ed. 1951, p. 884.

[21] Flagg, H. V., Lambert, R. A., and Larsen, B. M., Open-Hearth Fuels, Combustion and Instrumentation: ch. 4 in Basic Open-Hearth Steelmaking. AIME, New York, N. Y., rev. ed., 1951, pp. 112-113.

The rate of heat loss to surroundings was necessarily high compared to industrial open-hearths, due to the large area of walls, roof and hearth exposed per unit of metal weight. This was compensated by introducing oxygen into the burners to intensify combustion of the natural gas fuel. The maximum firing rate therefore was increased 13 percent. Beyond that, oxygen enrichment increased the percentage of gross available heat from combustion (referred to a critical process temperature of 3,000° F.) by 15 percent for a total increase of 30 percent in the flux of useful heat.

The rate of actual bath oxidation in this furnace was approximately one point (0.01 percent) of carbon per minute at carbon levels corresponding to the latter stage of the refining period for these heats. This rate was also experienced by Work and Webb.[22] Since the liquidus temperature rose about 1.6° F. per point of carbon removed, at least an equivalent amount of heat had to be absorbed by the bath to prevent freezing. The carbon reaction in the metal forms carbon monoxide and liberates 980 B.t.u. per ton of steel for each point of carbon oxidized.[23] Taking the heat capacity of molten steel as approximately 0.19 B.t.u. per point per degree Fahrenheit,[24] this quantity of heat is equivalent to a rise of 2.6° F. After allowing for the liquidus change, the authors believed that each point of carbon oxidized to carbon monoxide could result in a maximum of 1° F. rise in the superheat. This analysis proved that the need to gain 200° of superheat would require either a very high level of carbon at melt--perhaps more than 2.30 percent-- or an additional source of heat. This theory also showed that refining with ore was precluded since its net heat effect (including heat from the oxidation of carbon monoxide to carbon dioxide above the slag) was endothermic.[25]

Therefore, the only practical alternative, a refining procedure based on direct oxidation, was adopted. As this procedure was planned, the charge should melt-in at more than 2.0 percent carbon to provide plenty of carbon for oxidation; high-purity oxygen should then be injected into the metal through a lance. From past experience a lance of 1/2-inch steel pipe was used with its outer wall covered with a thin coating of air-setting fireclay mortar to prolong its life. When a lance became too short to be usable during a blowing period, it was quickly replaced and the blowing was resumed.

This practice had several advantages from the thermal standpoint. First, the metal would be violently agitated during a blow, exposing it to the high temperatures of the flame and roof, and an initial gain in superheat from this cause would be expected. Second, the rate of carbon drop also would be greatly accelerated and the total quantity of heat lost to the furnace would be minimized; and last, the abundance of oxygen supplied to the metal, coupled

[22]Work, H. K., and Webb, W. R., Operation of an Experimental Open-Hearth Furnace: Open-Hearth Proc., AIME, vol. 28, 1945, p. 29.

[23]Darken, Lawrence S., Thermal Changes in Melting and Refining: Ch. 19 in Basic Open-Hearth Steelmaking. AIME, New York, N.Y., rev. ed., 1951, p. 777.

[24]Chipman, John, Physical Chemistry of Liquid Steel: Ch. 16 in Basic Open-Hearth Steelmaking. AIME, New York, N.Y., rev. ed., 1951, p. 622.

[25]Work cited in footnote 23, p. 781.

with the extremely steep concentration gradients resulting from blowing, should result in a significant degree of oxidation of the carbon monoxide to carbon dioxide close enough to the metal to impart to it some of the heat evolved from that reaction.

Detailed Practice

Immediately after melting, samples of metal and slag were obtained. A pencil-shaped sample of metal was used for estimating carbon rapidly using a magnetic carbon tester located at the furnace. A second metal sample secured as a pin in an evacuated glass tube was sent to the analytical laboratory for carbon and sulfur determinations. Slag samples were taken and analyzed. The metal pencil sample was analyzed for other elements. Elements determined and reported in the refining period included carbon, manganese, sulfur, silicon, nickel, chromium and molybdenum in metal samples and iron in slag samples. At this time, a metal temperature reading was obtained with an immersion-type platinum-platinum, 10-percent rhodium thermocouple connected to a high-speed potentiometric recorder.

Injection of high-purity oxygen was then commenced. Flow rates ranged among the heats from 65 to 79 std. c.f.m., sufficient to oxidize 5.5 to 6.7 points of carbon per minute to carbon monoxide. Flowing pressures at the lance inlet averaged approximately 30 p.s.i.g. At high levels of carbon, the lancing was continued for as long as 10 minutes, but when the carbon had dropped approximately 1 percent or less, the lancing periods were shortened in order to prevent the reactions from getting out of control and, as a practical point, to guard against overheating the roof.

Immediately following each period of lancing, metal and slag samples were secured, and usually a metal temperature reading was taken. Estimation of the carbon concentration by the magnetic method required only a minute or two. Oxygen injection then was resumed.

When the estimated carbon concentration in the metal reached 1.0 percent (as estimated by the magnetic carbon tester) the furnace was tilted and the slag was skimmed from the metal. Then, 30 pounds of 50-percent ferrosilicon was added to the bath followed by a mixture of 180 pounds of burnt lime and 29 pounds of alumina ore. Experiments had shown that the introduction of silicon in this manner facilitated the formation of a fluid slag. Moreover, it conserved heat compared to using sand, as calculations indicated a net gain of 101° F. in bath temperature against a drop of 127° F. when using sand.

Immediately after the materials for the second slag were charged, the furnace door was closed and oxygen injections were resumed as before. From this point, estimates of carbon content from the magnetic test pencils were compared with the values determined chemically by the laboratory to establish a relation between carbon drop and the passage of time for use in estimating the instant the carbon content had reached the desired level for deoxidation of the bath in the furnace. Tapping the heats at such carbon contents that the ladle additions of anthracite would be minimized and, if possible, avoided was considered important for two reasons. First, anthracite additions were

recognized as a potential source of hydrogen which conceivably could react to impair the effectiveness of the rare-earth metal treatments upon mechanical properties, and second, as a matter of practical experience, the recovery of carbon from anthracite added to the ladle was quite variable, and if much had to be used, the chance of meeting the carbon specification would be diminished considerably.

Furnace Deoxidation and Alloying

After the heats had been refined to an estimated level of carbon which was suitable for the steel composition being made, the next step was to halt the oxidizing action upon the remaining carbon by blocking the heat. The desired carbon level at block was calculated by subtracting from 0.35 percent carbon (the concentration specified) the estimated pickup of carbon from the various ferroalloys that were added.

The primary furnace deoxidizer was silicon, introduced as silicomanganese. The two suppliers of rare-earth materials for these experiments both had recommended that at least 0.10 percent silicon should be added in the block. For these heats, silicomanganese could be used for this purpose without exceeding the manganese specifications. The investigators believed that this method was desirable, because by comparison to ferrosilicon alone, more complete deoxidation should result,[26] and the deoxidation products formed should be more fluid, hence more easily cleansed from the metal.[27] In heat 291, 86 pounds of silicomanganese was added. When the heat finished high in manganese, the basic addition for the remaining heats was reduced to 79 pounds. This amount introduced 0.17 percent silicon into the metal bath.

Immediately after the deoxidizing addition (the furnace block) was completed, the alloying additions were shoveled into the furnace. The entire operation, blocking and alloying, took only 2 to 3 minutes. Alloying for silicon was accomplished partly by the silicomanganese addition, and after making allowance for silicon recovered from the ladle deoxidizers (description follows), the balance needed was added as 50 percent ferrosilicon. The bulk of the manganese required for the manganese specification was provided by the silicomanganese, and such additional amounts that were required were met by adding high-carbon ferromanganese. If chromium was specified the entire quantity was added at this time as high-carbon ferrochromium.

A distinctive feature of the furnace deoxidization practice was an addition of pebbled burnt lime to the slag immediately after the alloy additions had been completed. Eighty pounds was spread over the slag. The lime had two beneficial effects. It thickened the very fluid slag and suppressed the diffusion of oxygen through it. Since the metal could be reoxidized only by oxygen supplied from the slag[28] [29] the effect of this practice was to retard reoxidation. Further, the stiffened slag would not run freely through the

[26]Work cited in footnote 24, pp. 673-675.
[27]Belding, H. Ross, and Kulp, R. K., Finishing and Deoxidation Practice: ch. 9 in Basic Open-Hearth Steelmaking. AIME, New York, N.Y., rev. ed., 1951, p. 352.
[28]Work cited in footnote 20, pp. 893-894.
[29]Work cited in footnote 27, p. 348.

tap hole at the tap and, by remaining in the furnace, would not interfere with
the ladle deoxidation and rare-earth treatments that followed.

Ladle Deoxidation and Rare-Earth Treatments

Supplemental deoxidation in the ladle after tapping was recognized as
both a practical necessity for a fully killed steel and a critical factor in
determining the grain-coarsening tendencies of the steel, its cleanliness,
and the effectiveness of the treatment with rare-earth materials.

The question of deoxidizing to a fully killed condition was disposed of
by the necessity for extra-strong deoxidation preparatory to adding the rare-
earth materials. Specifications called for an austenitic grain size of 6 to 8
in specimens cut from the wrought product and tested by the standard ASTM
Grain-Size (McQuaid-Ehn) test.[30] Past experience showed that an aluminum
addition to the ladle of 2 pounds per ton would meet this requirement.[31]

Controlling the cleanliness of the product as indicated by the type,
quantity, and size of indigenous inclusions was another matter. Commercial
steels of equivalent composition usually are not required to meet direct
cleanliness specifications. The question of cleanliness, however, is relevant
to the mechanical properties that often are specified, particularly, trans-
verse impact strength. For this reason the final deoxidation practice, before
the rare-earth materials were added, was evaluated also regarding its effects
upon steel cleanliness. Fortunately, the recommended practice of adding
calcium-silicon alloy before the rare-earth agents was consistent with this
desire for cleanliness because this alloy (and modifications of it) is widely
regarded as the best means for controlling inclusion compositions to minimize
their effects on mechanical properties.

Deoxidizing the metal for the successful rare-earth treatment involved a
consideration of the dissolved hydrogen and nitrogen in it. The input of
hydrogen from the charge was minimized by using dry materials. Its elimina-
tion from the melt was promoted by the vigorous agitation afforded by the
oxygen refining practice. Finally, to reduce to a minimum the chance of con-
tamination during deoxidation, the ferroalloys were dried thoroughly, and only
freshly calcined pebble lime was used. For these reasons the authors believed
that the hydrogen level was less than normal open-hearth experience, low
enough to have no adverse effects on rare-earth treatments. Nitrogen levels
were checked by analysis of specimens secured from several preliminary heats;
these ranged from 0.004 to 0.006 weight-percent nitrogen, a trifle less than
conventional basic open-hearth levels and too low to require any corrective
treatment with titanium. Oxygen, of course, would be minimized by the deoxi-
dation practice described, first, in the furnace, then by the successive
ladle additions of aluminum and calcium-silicon alloy. All of these points

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[30]American Society for Testing Material, Standard Classification of Austenite
    Grain Size in Steel: Standard E19-46, in ASTM Standards pt. 3, Metals
    Test Methods, Philadelphia, Pa., 1958, pp. 488-490.
[31]Work cited in footnote 27, p. 361.

were given careful consideration, as the high affinity of the rare-earth metals for these dissolved gases was well-known.[32]

As stated earlier, it was decided to tap the entire heat into one large ladle, to then teem three batches successively from this ladle into as many small ladles where the respective rare-earth treatments would be undertaken, and to finally teem two ingots, one large and one small, from the steel in each small ladle. To guard against the effects of oxidation that would occur during the fillings of the large and the small ladles respectively, deoxidation additions were planned for each ladle. In addition, the small-ladle deoxidation was arranged for the rare-earth treatments also to be carried out.

Ladle deoxidation was adapted to the two-ladle teeming practice from that established by Briggs.[33] It was based upon adding 0.10 percent calcium (in a deoxidizing alloy) before adding the rare-earth materials. For these heats this practice took the form of 2 pounds of aluminum alloy 2S per ton, and 2 pounds of calcium-silicon alloy per ton in the first ladle, equivalent to 0.10 percent aluminum and 0.03 percent calcium. In the second ladle 4.2 pounds of calcium-silicon per ton was used, equivalent to 0.07 percent calcium, for a total calcium addition of 0.10 percent.

Aluminum fastened to the end of a long heavy steel bar was plunged into the pool of metal in the ladle while tapping. Next, the calcium-silicon alloy was added. In this instance the granular material was contained in a steel can having holes punched in it.[34] A similar device was used to add calcium-silicon alloy to the second ladle. While filling continued, the appropriate rare-earth mixture was then plunged into the pool. The first small ladle in each heat received rare-earth metals as Lanceramp No. 1 alloy; the second small ladle received rare-earth metal oxides as RareMeT 5-C[35] and the third ladle remained untreated.

Both suppliers recommended that two pounds of rare-earth metals per ton or an equivalent weight of rare-earth metal in the oxide form should be

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[32]Yost, Don M., Russell, Horace, Jr., and Garner, Clifford S., The Rare Earth Elements and Their Compounds: John Wiley & Sons, New York, N.Y., 1947, p. 54, and
Knapp, W.E., and Bolkcom, W. T., Rare Earths Improve Properties of Many Ferrous Metals: Iron Age, vol. 169, No. 17, pp. 129-134, and No. 18, 1952, pp. 140-143.

[33]Briggs, Charles W., The Effect of Rare-Earth Metals in Cast Steel. Part II. The Production of Commercial Cast Steel Containing Rare-Earth Additions: Steel Founders' Soc. Am., Cleveland, Ohio, 1954, p. 36.

[34]Pierce, Earl W., Device for Introducing Solid Materials into Molten Metals: U.S. Patent 2,585,404, Feb. 12, 1952.

[35]Both the rare-earth metal and the rare-earth metal oxide materials were proprietary preparations. Lanceramp No. 1 was supplied by American Metallurgical Products Co., Pittsburgh, Pa. RareMeT 5-C was supplied by Molybdenum Corp. of America, Pittsburgh, Pa. These materials were selected for use in this investigation because the bulk of the previous work reported in the literature was concerned with them.

added. Boulger[36] reported that the type of sulfide inclusions formed in castings varied with the ratio of the sum of the lanthanum and cerium concentrations in the treated steel to its sulfur content. From his experience, if this ratio fell below 1.0, Type II inclusions were formed. These would appear as intergranular films or chains and are known to be most harmful to the toughness and ductility of cast steels. If the ratio exceeded 1.6, then characteristic small, irregularly-shaped inclusions formed in clusters or clouds and resulted in poor ductility values. Ratios between 1.0 and 1.6 were associated with Type I globular sulfide inclusions, the type that resulted in optimum ductility values.

Since the initial product would be cast ingots, Boulger's ratio was considered in planning how much of the metal mixture to add. Although some desulphurization by the rare-earth metals was expected, there was no precise information available as to how much desulphurization would occur. A wide range of recoveries from these additions also had been reported. Substantial desulphurization would raise the ratio, as would a high recovery of lanthanum and cerium. At the other extreme a low recovery of these elements would result in a low ratio. Calculations demonstrated that if a single uniform treatment practice were to be adopted for straightforward comparison between steel types, an addition of 2 pounds of rare-earth metals would be the best compromise. Since it was planned to treat 1.1 tons in the second ladle and the Lanceramp material was stated to contain 95 percent rare-earth metals (see table 3), 2.4 pounds of Lanceramp No. 1 was added.

As listed in table 3, the rare-earth oxide material contained 75 percent crude rare-earth compounds that were approximately 93 percent metal oxides. To treat an equal amount of metal with an equivalent amount of rare-earth metals as tetravalent oxides, 4.1 pounds of RareMeT 5-C compound was added.

In the case of the two heats (OH-303 and OH-304) where the third small ladle could not be used, the nontreated set of ingots was simply teemed directly from the large ladle, the larger ingot being teemed first.

Heat was conserved in these operations by preheating the ladles to a red heat.

Cooling the Ingots

Alloy ingots of the types and sizes to be produced are known to be susceptible to flaking and thermal ruptures if allowed to air cool after teeming. The high nickel-chromium-molybdenum type was most critical, because of its great hardenability. The I-T diagram of a similar steel, A4340,[37] indicated that by stripping the ingots from the molds promptly and then immediately burying them in sand, a satisfactory cooling rate could be achieved.

[36]Boulger, F. W., Udy, M. C., Wahll, M. J., and Frazier, R. H., The Effect of Rare Earth Metals in Cast Steels. Part I. Laboratory Studies at Batelle Memorial Institute: Steel Founder's Soc. Am., Cleveland, Ohio 1954, pp. 11-20.

[37]United States Steel Corporation, 1953 Supplement to the Atlas of Isothermal Transformation Diagrams; Pittsburgh, Pa., 1953, p. 308.

To test this arrangement, the product from a heat that was melted for another project was cast into one of the large-size molds, and the ingot produced from this mold was stripped while red hot and buried in sand with a chromel-alumel thermocouple placed in contact with the ingot. The temperature was recorded for 40 hours at which time it reached 350° F., a temperature well below the Ms (martensite) temperatures of the steels to be melted. This experiment suggested that cooling in sand should be entirely sufficient.

The procedure adopted, then, was to hold the ingots undisturbed in the molds for 1 hour, a sufficient time for solidification to be completed, and to then strip them promptly, die stamp an identification on each, and bury all ingots from one heat together in sand. As a further check on identity, the position of each ingot in the cooling bed was recorded. At the end of 5 days in the cooling bed the ingots were removed and air cooled.

Rolling and Finishing Operations

Bar Product Requirements

The quantities of bars required from each ingot rolled are listed in table 2. A contractor was engaged to perform the rolling and finishing operations.

Blooming Mill Practice

All 12 ingots were charged cold into a gas-fired furnace that had been cooled to approximately 1,200° F. to minimize thermal shock to the ingots. The doors were closed immediately and the ingots were left to be heated by radiation for one-half hour. Then firing was begun. The ingots were heated slowly to the desired drawing temperature of 2,200° to 2,250° F. over a period of 10 hours and then were soaked at this temperature level for 2 hours before being drawn for rolling. Each ingot was bloomed from the initial 12-11/16-inch-square section to a 4-inch-square billet in 24 passes. The pass sequence is shown in figure 4. Temperatures were measured by an optical pyrometer. They ranged from 2,070 to 2,115° F. among the ingots in the second pass. Between the second and the last pass the temperature dropped 190 to 240° F.

The product of each ingot was cropped at both ends and was sheared into appropriate lengths for the respective bar rollings as follows: Topmost cut of 375 pounds marked "T" for rolling to 3-inch rounds; next four cuts (or five cuts, depending on the total length of the billet) marked "D", "E", "F", "X", "(Y)" for 1-1/4-inch rounds; next cut of 100 pounds marked "M" for 7/8-inch rounds, and bottom-most cut of 175 pounds marked "B" for 5/8-inch squares.

Each billet cut was stamped on the end nearest the top of the ingot with heat number, ingot number and cut letter.
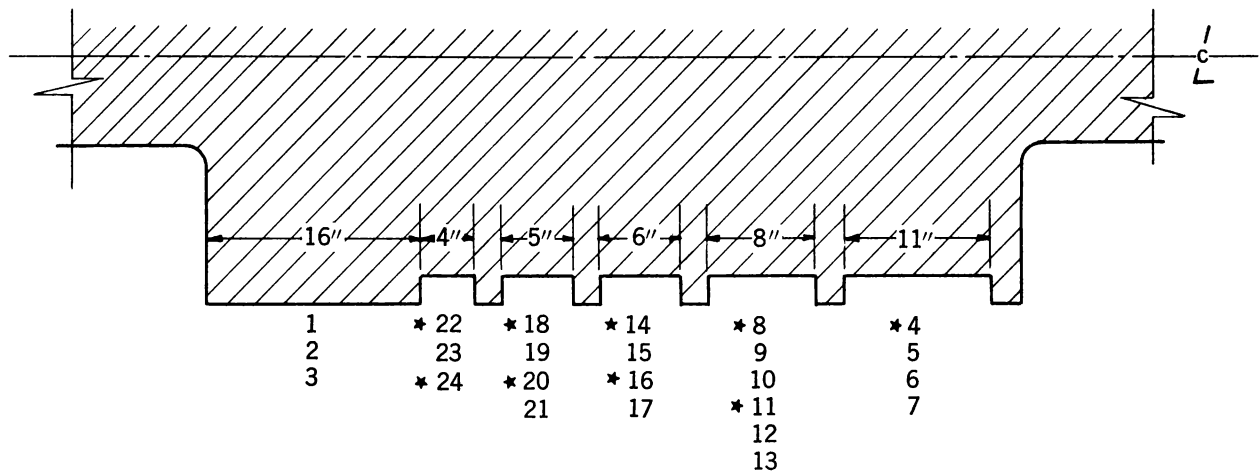
* Bloom turned 90° before entering pass

FIGURE 4. - Sequence of Passes in Blooming Mill.

Immediately after shearing, the billets were charged for controlled cooling into a gas-fired annealing furnace held at 1,190-1,210° F. After charging, the temperature of the furnace ranged from 1,100° F. at the bottom to 1,190° F. at the top. After heating for one hour the temperatures were respectively, 1,160 and 1,240° F.

Billet Testing, Inspection and Preparation

Austenitic grain size was determined in the mill laboratory by the standard ASTM (McQuaid-Ehn) method upon samples cut from the top end of the billet product from each ingot. All of the tests indicated a grain size of 7 to 8.

The soundness of the billet product was rated by examining deep-etched cross-sectional specimens sawed from the top and the bottom of the billet product from each ingot. Each of these specimens was rated by both the mill and Bureau metallurgists and where an unsatisfactory condition was disclosed they jointly determined how much cutting back and retesting was required.

All of the billets were pickled in a dilute solution of inhibited sulfuric acid to remove the mill-formed scale from the surface preparatory to surface inspection and preparation.

Surface quality was rated by a detailed inspection of the topmost, T, and the next to the bottom,M, billets. These cuts were selected because (a) observations during rolling indicated that most of the surface defects would occur in the top-cut part of the billet product, and (b) the M billet cuts seemed to contain the fewest surface defects. The top-cuts alone comprised approximately 30 percent of the billet weight produced from each ingot. Each cut was examined on each side. Each surface defect was measured and was classified as to type and severity.

Billet weights were estimated by measuring the cross section and length, calculating the volume, and then converting the volume into the weight equivalent by a density factor that was calculated from weighting the bottom cuts. This substitute for weighing was adopted because it was not possible to weigh each billet separately in the busy mill yard.

After testing and inspection was completed, the billets were prepared for bar rolling by grinding out all defects visible upon the pickled surface.

Bar Mill Practice

Preparatory to bar rolling, all of the billets were sorted into four sets. Each set consisted of all of the billets produced from the twelve ingots that were to be rolled to one bar size. All billets in a set were heated and rolled in one lot, and if annealing or drawing treatments were specified, the bars from that set were heat-treated in a single furnace load. As the differences in bar sizes necessitated separate rollings in several bar mills and at different times, the four sets could not be handled identically. However, this handling procedure minimized differences in processing conditions among bars of a particular set, that is, a single size.

The 3-inch-diameter round bars were rolled directly from 4-inch square billets.

Both the 1-1/4-inch and 7/8-inch diameter round bars were produced in a 10-inch mill. This was a multiple-stand bar and rod mill with fixed guides in the single-pass finishing stands.

The 5/8-inch-square bars were produced from 2-1/2-inch square billets that had been recogged from the primary 4-inch square billets.

Billets for either recogging or bar rolling were charged cold into a hot furnace (approximately 2,200° F.) except the high Ni-Cr-Mo billets (heat OH-304) which were charged into a furnace cooled to 1,200° F. Specifications required that billets be drawn and rolled when thoroughly heated without holding at the drawing temperature, because it was known that such holding would tend to increase the depth of the decarburized zone beneath the bar surface. This object was not attained completely because rolling operations for the 1-1/4-inch-diameter round bars extended over a 3-hour period although all the billets were ready to roll when rolling commenced (the entire set had been heated together in one furnace).

The end-for-end identification of each billet was maintained in the bar product by charging the billets into the heating furnace in such a way that the leading end of the bar produced corresponded to the topmost end of the billet. Stamping the front end of each bar on the run-out table thus amounted to stamping the topmost end.

Bar mill stamping was simplified and the risk of losing the identity of a piece from illegible stamping on the sides of the small round bars was minimized by using a code for bar identification. This code consisted of an

ingot serial number to identify the steel types and ladle treatments, a letter to designate the finished bar sizes and a suffixed number which identified the order of the bars produced from a particular ingot with reference to their relative position down from the top of that ingot. Steel types and ladle treatments were coded as follows:

			Ingot code number		
Alloy steel type........	Plain carbon	Mo	Low Ni,Cr,Mo		High Ni,Cr,Mo
Heat No.................	291	292	303		304

Rare-earth treatment	Casting order				
Mixed metals	1	1	4	7	10
Oxides	2	2	5	8	11
None	3	3	6	9	12

The letter code for bar size was needed primarily to identify chemical analysis and other test records to specific bar product. This code was as follows:

Bar size	Letter code
3-inch round	E
1-1/4-inch round	D
7/8-inch round	C
5/8-inch square	A

As an example, 12D1 referred to a bar produced from the high Ni,Cr,Mo steel without rare-earth treatment (12), rolled to a 1-1/4-inch round section (D), and that this bar represented the topmost portion of this product; similarly, 12D7 designated the seventh bar down of the same size from that ingot.

All 3-inch-diameter round bars were annealed directly from the mill while still hot. These bars were charged into a furnace previously heated to 1,200° F., held 4 hours at that temperature, furnace cooled to 600° F. and then were air cooled. Bars of smaller sizes of the high Ni-Cr-Mo type were drawn hot from the mill at 1,000 to 1,050° F., but bars of the other grades in these sizes were air cooled.

All bars were sandblasted and pickled before final inspection.

Bar Inspection

All bundles were opened and each bar was inspected separately. Inspection included the stamped identification, gauge and surface defects. The number of bars produced from a billet ranged from 1, in the case of the 3-inch diameter round bars, to 11, for some of the lots of 5/8-inch square bars.

Gage was checked by micrometer measurements taken at several diametrical positions around the bars. Surface defects were classified by their appearance. The depth of a defect was determined by filing the bar locally to remove the defect and then comparing the bar diameter at that location with

The diameter in the same axial plane adjacent to the filed area. The depths and lengths of individual surface defects in the 3-inch-diameter round bars were measured and reported bar by bar for comparison with the surface conditions of the respective billets. No attempt was made, however, to record this information on the smaller bars since it was quite apparent that the surface quality overall was good and the defects observed were usually shallow enough to be cleaned up within the AISI standard machining allowances applicable to the respective bar sizes.[38][39]

RESULTS AND DISCUSSION

Melting and Casting

Detailed planning, a studied attempt to adapt sound industrial practice to the 4-ton open-hearth furnace, and preliminary trials of many details during operations upon other projects were rewarded by the successful melting and casting of the four heats required in a run of only six heats. Before this final run, a first run of four heats had been melted to determine the optimum casting arrangement.

A typical heat log is shown in figure 5. Chemical compositions of the ingot and bars produced are listed in table 4.

Melting and Refining

Bath Composition at Melt

The compositions of the six heats shortly after melt are listed in table 5. The uniformity in carbon and in manganese concentrations among these heats is striking. Iron contents of the slags were in the range expected for cold-charge heats except heat 303. This general pattern of uniformity from heat to heat was helpful in establishing and maintaining a consistent refining practice.

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[38] American Iron and Steel Institute, Hot Rolled Carbon Steel Bars: Sec. 8 in Steel Products Manual. New York, N.Y., 1952, p. 58.
[39] _____. Hot Rolled Alloy Steels: Sec. 10 in Steel Products Manual. New York, N.Y., 1949, p. 11.

Heat No. OH-304 Date tapped 4-14-55 Project 1307 Watertown Co-op.
Supervisor E. J. Ostrowski Purpose Rare Earth Metal & Metal Oxide
Recorder E. C. Coup Treatment of Exp. No. 1 Grade

RESULTS OF CHEMICAL ANALYSIS

MATERIALS CHARGED

Kind	Description / Composition	Size	Lb. chgd. / Lb. added
Pig iron	USBM / .02 S, .14 P, 1.1 Mn, 1.8 Si	100 ≈	5600
Scrap	Bruceton Plate / C 1020	4 x 4 / x 1	1600 / -
Scrap	USS Punchings / C 1015	1"	700 / -
Ferro Si	Electromet. 4922 / 48.81 Si	5" x / 2"	- / 55
Ferro Mn	U. S. Steel / 72.85 Mn, 6.99 C	4" down	- / 50
Silico Mn	Ohio 2.33 C, / 15.85 Si, 68.9 Mn	4" x / 1"	- / 110
Rare Earth Metals	AMP Lanceramp 1 / La >30, Ce (45-50)	4 oz. balls	- / 2.4
Rare Earth Oxides	MCA Raremet 5-C / 14.6 La, 29.1 Ce	40 mesh	- / 4.1
Pebble Lime	Tom Brown / Max. S-.05%	1" x / 3/8"	240 / 285
Lime-stone	U. S. Steel / 52% CaO	3" x / 1"	150 / -
CaSi	Electromet. 4947 / 29.9 Ca, 62.7 Si	4" x / 1"	- / 20.7
Alumina ore	Harbison-Walker / 49 Al2O3, 20 SiO2	2" down	29 / -
Al	Alloy & Chem. Co. / Virgin Alloy, 2 S	1 lb. stars	- / 7
Coke			
Ferro Mo	MCA No. 9275 / 72.84 Mo.	1½" down	- / 39¼
FeCr	Electromet 4926 / 68.57 Cr	5 lb. x 1"	- / 75

MATERIALS PRODUCED

Pigs No. 1	290	Slag 1	
Ingots No. 6	6111	Front 2	502
Pit	1097	Back 3	525
Drain Back	-	4	
Ladle skull	-	5	
Total	7498	Total	1027

FUELS

	Gas	Oil	Oxy
Rate			
Time			
Total			

Nickel oxide Nat'l Lead - 1"
96.6 NiO 110

Metallurgical oxygen 163.4 lb.

Ingots Produced:
No. 1	1497 lb.
2	1484
3	1701
1A	475
2A	475
3A	479
Total	6111

No skull
All ingots full in hot-tops.
Molds coated with aluminum.
Started stripping at 1:40 PM.
All ingots in sand bin and covered by 2:30 PM.
Sand dry.

SPECIFIC LOG OF HEAT

TIME	AMT.	Description
7:30 AM		Closed taphole
7:35		Began charging
	150	Limestone
	240	Pebble Lime
	5600	Pig Iron, USBM experimental furnace
	1600	Scrap plate, C 1020, Bruceton
	700	Scrap, boiler punchings, C 1015
	100	Nickel oxide
	36	Ferromolybdenum
8:00		Finished charging
10:35		Melted Slag No. 1, Metal No. 1
10:37	44.9	O2 injected by lance: 77 cfm at 45 psig for 6' 55"
10:44		Slag foamy Slag No. 2, Metal No. 2
10:45		Bath temp. by immersion TC, 2740° F. (Unit No. 1)
10:47	51.4	O2 injected by lance: 77 cfm at 45 psig for 7' 55"
10:58		Slag thinning—not so foamy; Slag No. 3, Metal No. 3
10:59		Bath temp. 2830° F. (Unit No. 4)
11:01	27.6	O2 injected by lance: 64 cfm at 55 psig for 5' 24"
11:09		Slag fluid, action picking up; Slag No. 4, Metal No. 4, 1.12 C
11:10		Bath temp. 2840° F. (Unit No. 1)
11:11	18.1	O2 injected by lance: 64 cfm at 55 psig for 3' 23"
11:16		Slag fluid Slag No. 5, Metal No. 5; .75 C
11:17	20.7	Bath temp. 2915° F. (Unit No. 2)
11:19		Slag off thru front door, 3½ minutes
11:24	30	Ferrosilicon
	29	Alumina ore } mixed beforehand
	180	Pebble lime }
11:27	14.4	O2 injected by lance: 83 cfm at 55 psig for 2' 03"
11:30	25	Pebble lime
	7.0	O2 injected by lance: 83 cfm at 55 psig for 1'
11:32		Slag No. 6, Metal No. 6; .48 C
11:33		Bath temp. 2940° F. (Unit No. 3)
11:49		Slag viscous Slag No. 7, Metal No. 7; .39 C
11:50		Bath temp. 2975° F. (Unit No. 4)
11:51	10	Nickel oxide
	3¼	Ferromolybdenum
12:01 PM		Slag viscous Slag No. 8, Metal No. 8; .27 C
12:10		Slag creamy Slag No. 9, Metal No. 9; .25 C
12:11		Bath temp. 2960° F. (Unit No. 4)
12:14		Metal No. 10
12:14		Blocked
	110	Silicomanganese
	75	Ferrochromium
	25	Ferrosilicon
	80	Pebble lime—spread over slag
12:26		Metal No. 11
12:29		Started tap into large ladle 2850° F. (optical)
	7	Aluminum stars—plunged on rod
	17.3	Calcium silicon—in can—plunged on rod
12:32		Finish tap 2' 55" to tap
		Start teeming into ladle No. 1
	1.7	Calcium silicon—in can on rod, plunged into No. 1 ladle
	2.4	Lanceramp No. 1—in can on rod, plunged into No. 1 ladle
12:32		Finish teeming into No.1 ladle—0' 23" to fill
		Start teeming molds No. 1 and 1A from No. 1 ladle
12:33		Finish teeming molds No. 1 and 1A—0' 35"
		Start teeming into No. 2 ladle
	1.7	Calcium silicon—in can on rod, plunged into No. 2 ladle
	4.1	Rareme T No. 5-C—in can on rod, plunged into No. 2 ladle
		Finished teeming into No. 2 ladle—0' 22" to fill
		Start teeming into molds No. 2 and 2A from No. 2 ladle
12:34		Finished teeming into molds No. 2 and 2A – 0' 45"
		Start teeming into mold No. 3 from big ladle
12:35		Start teeming into mold No. 3A from big ladle
12:36		Finished No. 3A. Back poured hot top of No. 3
		Metal No. 12 – Large ladle at tap
		Metal No. 13 – Stream pouring No. 1 ingot
		Metal No. 14 – Stream pouring No. 2 ingot
		Metal No. 15 – Stream pouring No. 3 ingot

RESULTS OF CHEMICAL ANALYSIS

METAL

Time	No.	Lot	C	Mn	P	S	Si
		Experimental No. 1 Grade					
	Range		.33	.85 Max.	Max.		.30
			.38	1.10	.025	.025	.45
	Aim		.35	.95			.35
10:35	1	5150	2.28	.61			
10:44	2	5135	2.17	.24			.024
					Ni	Mo	Cr
10:58	3	5136	1.58	.21	.96	.39	.05
11:09	4	5151	1.17	.19			
					S		Cr
11:16	5	5152	.88	.17		.022	.04
11:32	6	5137	.57	.17			
							Cr
11:49	7	5138	.46	.16			.05
12:01	8	5139	.36				
12:10	9	5140	.33				
							Cr
12:14	10	5153	.31	.16		.020	.06
					P		Si
12:26	11	5154	.39	1.04	.026	.019	.24
					Ni	Cr	Mo
					1.04	.69	.43

SLAG

No.	Lot	Fe	CaO	MgO	SiO2	Al2O3	R2O3	P	S
		Ni	Cr	Mo					
		.90	.60	.30					
		1.10	.80	.40					
		1.00	.70	.35					
1	5141	4.37							
2	5142	7.05							
3	5143	6.84							
4	5144	8.86							
5	5145	9.55	30.7	18.4	27.0		15.7	.45	.06
6	5146	5.64							
7	5147	8.74							
8	5148	9.03							
9	5149	8.74	46.5	15.3	17.5		17.7	.60	.06

FIGURE 5. - Typical Heat Log.

TABLE 4. - <u>Chemical composition of molten steel, ingots, and bars</u>

Product identity	Chemical composition, weight-percent										
	C	Mn	P	S	Si	Ni	Cr	Mo	Ce	La	N_2
OH-291:											
Ladle 291-1....	0.32	1.11	0.014	0.013	0.28	-	-	-	-	-	-
Ingot 291-1A...	.32	1.15	.026	.015	.28	0.02	0.09	Nil	0.024	0.008	0.007
Bar 1E1 top....	.29	1.17	.01	.015	.29	.04	.05	-	-	-	-
Ladle 291-2....	.39	1.16	.010	.013	.29	-	-	-	-	-	-
Ingot 291-2A...	.36	1.16	.025	.013	.31	-	-	-	.006	.002	.005
Bar 2E1 top....	.34	1.15	.02	.016	.31	.04	.07	-	-	-	-
Ladle 291-3....	.44	1.19	.013	.014	.29	-	-	-	-	-	-
Ingot 291-3A...	.38	1.14	.026	.014	.30	-	-	-	.003	.001	.006
Bar 3E1 top....	.33	1.18	.01	.020	.30	.04	.07	-	-	-	-
Bar 3E2 top....	.33	1.17	.03	.016	.31	.05	.07	0.003	-	-	-
Bar 3E2 bottom.	.32	1.16	.03	.020	.31	.04	.06	.003	-	-	-
OH-292:											
Ladle 292-1....	.31	.72	.048	.016	.23	-	-	.23	-	-	-
Ingot 292-1A...	.38	.69	.040	.015	.21	.01	.09	.22	.023	.009	.006
Bar 4E1 top....	.29	.69	.05	.014	.23	.03	.07	.26	-	-	-
Ladle 292-2....	.31	.69	.048	.021	.24	-	-	.22	-	-	-
Ingot 292-2A...	.38	.69	.047	.021	.22	-	-	.25	.006	.002	.006
Bar 5E1 top....	.29	.68	.04	.020	.23	.03	.07	.25	-	-	-
Bar 5E2 top....	.28	.68	.05	.021	.24	.02	.07	.25	-	-	-
Bar 5E2 bottom.	.28	.69	.05	.021	.23	.02	.07	.24	-	-	-
Ladle 292-3....	.31	-	-	.018	.25	-	-	.22	-	-	-
Ingot 292-3A...	.39	.68	.043	.019	.22	-	-	.20	.002	.001	.005
Bar 6E1 top....	.29	.68	.04	.020	.22	.02	.08	.25	-	-	-
OH-303:											
Ladle 303-1....	.34	.84	.024	.010	.31	.51	.50	.20	.024	.008	-
Bar 7E1........	.38	.88	.03	.009	.29	.54	.50	.21	-	-	-
Ladle 303-2....	.34	.81	.023	.015	.30	.52	.50	.20	.004	.001	-
Bar 8E1........	.38	.88	.03	.017	.31	.54	.51	.20	-	-	-
Ladle 303-3....	.34	.85	.024	.015	.24	.51	.51	.21	.002	.001	-
Bar 9E1 top....	.38	.88	.04	.019	.24	.54	.50	.22	-	-	-
OH-304:											
Ladle 304-1....	.39	1.01	.028	.013	.39	1.03	.72	.41	.028	.010	-
Bar 10E1 top...	.41	1.03	.04	.013	.39	1.05	.72	.37	-	-	-
Ladle 304-2....	.39	1.04	.029	.016	.41	1.03	.72	.39	.005	.002	-
Bar 11E1 top...	.41	1.03	.03	.018	.40	1.06	.73	.40	-	-	-
Ladle 304-3....	.38	1.06	.030	.014	.41	1.03	.72	.40	.004	.001	-
Bar 12E1 top...	.43	1.03	.03	.019	.35	1.05	.72	.41	-	-	-

TABLE 5. - Composition of heats at melt

Heat	291	292	293	294	303	304
Melting period..........hours	2.6	3.0	3.1	2.5	2.5	2.6
Melt composition, metal:						
Carbon........weight-percent	2.63	2.44	2.53	2.36	2.50	2.28
Manganese...............do...	.68	.61	.61	.53	.68	.61
Sulfur..................do...	,023	.024	.021	.025	.021	.024
Melt composition, slag:						
Iron....................do...	4.15	2.88	-	3.59	8.97	4.37

Thermal Effects of Oxygen Injections

Perhaps the most interesting effect of the initial oxygen injection was a precipitous rise in metal temperature. This rise is graphically shown in figure 6 where the temperature of the molten metal and the roof are plotted as a function of carbon concentration during refining. For comparison, the estimated relations between carbon and the liquidus temperature of iron-carbon solutions is also shown. This temperature increase resulting from the initial oxygen injection ranged up to 400° F. although the percentage of carbon oxidized was not large. Neither did any extensive oxidation of iron occur as measured by the iron content of slag samples. This great increase in metal temperature resulted, the investigators believe, principally from mechanical agitation of the metal by the force of the oxygen stream which exposed the metal that had
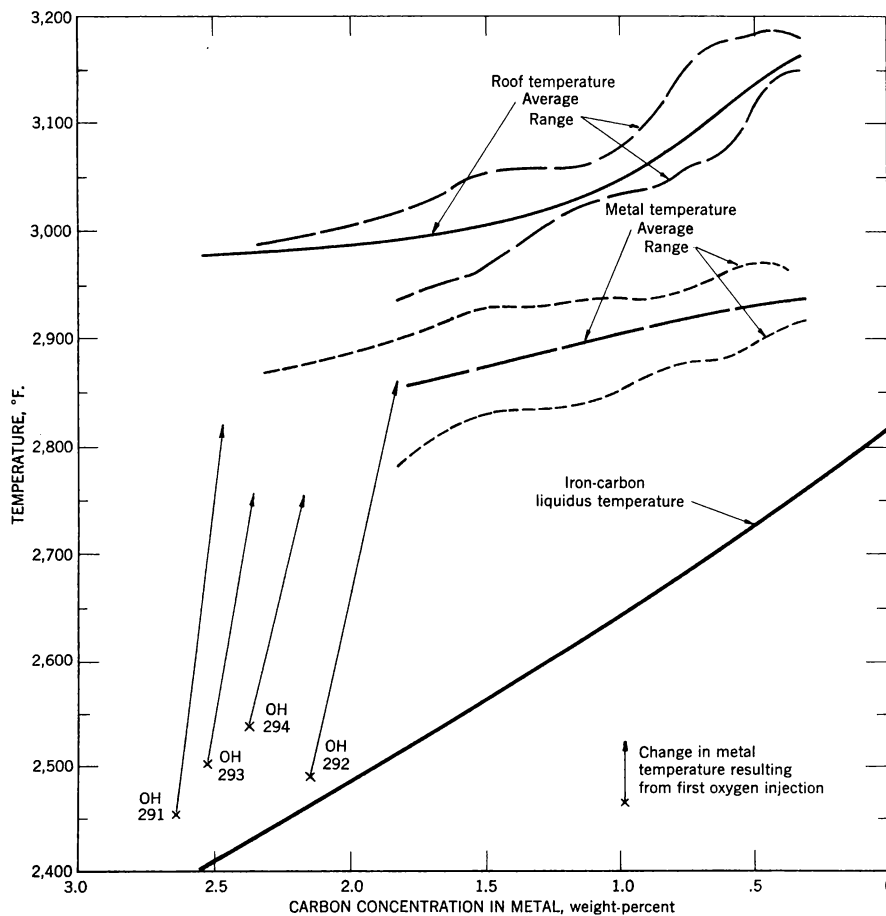

FIGURE 6. - Relations Between Temperatures of Iron-Carbon Liquidus, Metal and Roof, and Carbon Concentration in Metal.
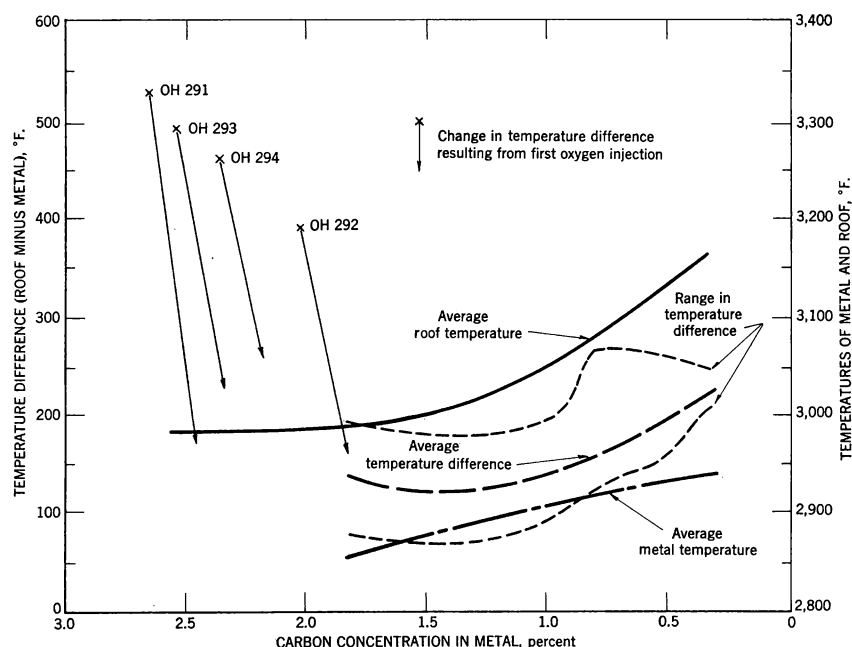
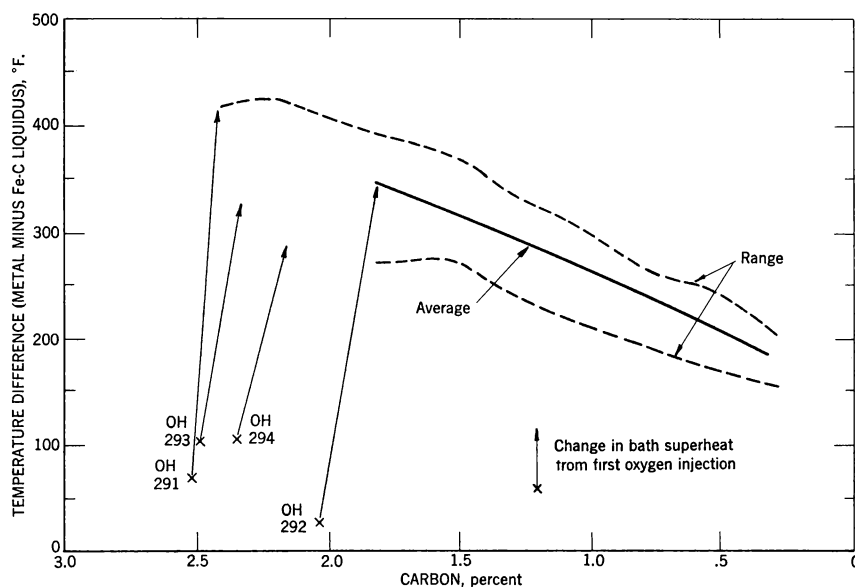FIGURE 7. - Temperature Difference Between Roof and Metal as a Function of Metal Carbon Concentration.

FIGURE 8. - Relation Between Metal Carbon Content and Superheat.

been covered by a quiescent slag (note the low iron oxide concentration, hence low oxygen potential, in the slag before the initial oxygen injection) to the much hotter roof. Melting had taken place from the top of the charge downward and although the slag temperature at the top of the slag layer was undoubtedly rather high through radiation from the flame and the roof, the temperature gradient through it to the metal must have been very great. At the instant when the bath became completely molten, the metal temperature at the hearth surface (upper surface of the furnace bottom) was roughly 2,400° F., and at the top of the metal layer it probably was no more than 50° F. hotter, because of the high thermal diffusivity of the metal. Thus, the temperature gradient from the exposed slag surface to the hearth was concentrated in the slag layer (see figure 7). By contrast, the violent agitation of the metal which accompanied the oxygen injection produced a two-fold benefit: (1) It increased the thermal potential by exposing the metal to the relatively high temperature of the roof, and (2) it increased greatly the thermal gradient in the metal layer during the injection period by forming drops and films of metal a fraction of an inch in thickness compared to a layer of metal one foot or more in depth in a quiet bath.
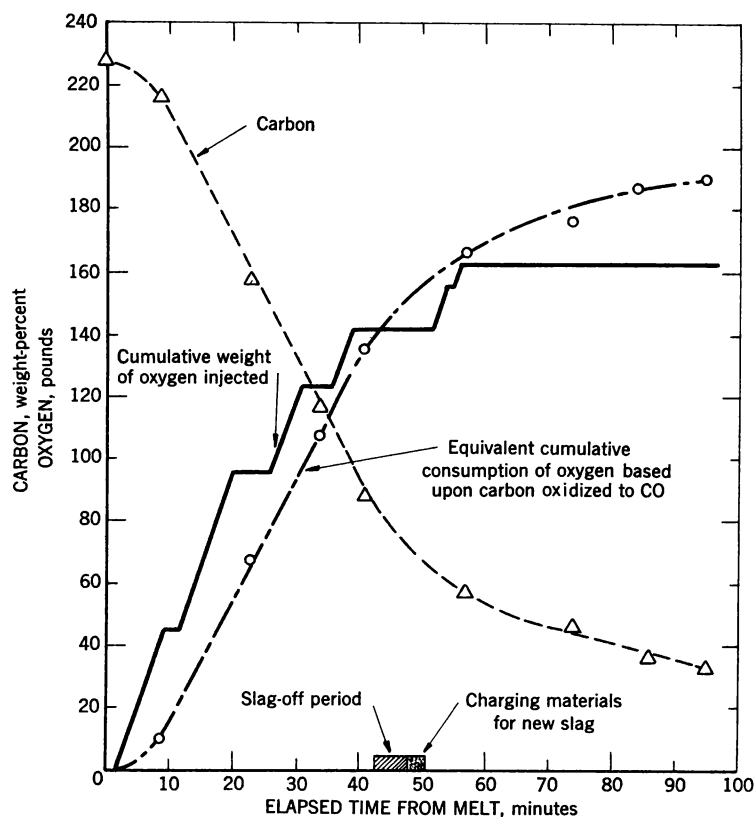
FIGURE 9. - Oxygen Injection and Carbon Oxidation, Heat 304.

After this initial rise in metal temperature, the remainder was obtained only by increasing the temperature level of the entire system. Figure 6 illustrates how the plot of metal temperature paralleled the rise in roof temperature. In the latter stage of the refining period, after 1.0 percent carbon, the roof temperature increased faster than the metal temperature. In this stage the oxygen injections were briefer and less frequent and in consequence, the insulating effect of the slag layer was operative for a greater proportion of the time. Figure 6 also depicts how slowly the metal temperature rose from 0.50 percent carbon when no oxygen was injected.

Superheat (the temperature difference between the molten metal and its liquidus) is plotted as a function of metal carbon concentration, see figure 8. The authors observed, first, that the range among the six heats was slightly less than 100° F. from 1.80 percent down to 1.0 percent carbon, but that as refining progressed and temperature level approached the limit attainable, the spread diminished progressively. Second, and perhaps more striking, is the progressive diminution in superheat as the refining period progressed. The level and slope of this relation is the heart of bath temperature control, for the liquidus temperature rises inexorably while the metal temperature is a direct result of furnace condition and the refining practice. Near the end of the refining period, at 0.30 percent carbon, superheat ranged from 165° to 210° F. This was much higher than industrial practice (see fig. 3) but as explained previously, was needed to compensate for the temperature loss experienced during teeming. A few temperature measurements taken in the blocking period indicated that roughly half of the cooling effect of the blocking and alloying additions had been recovered before tap.

Rates of Oxygen Injection and Carbon Oxidation

The course of oxygen injections and carbon oxidation for a typical heat is presented in figure 9 where cumulative weight of oxygen injected, percent carbon removed, and its oxygen equivalent are plotted with respect to elapsed time after melt. The first period of oxygen injection (from 2 to 9 minutes)

was not efficient in oxidizing carbon (although, as previously discussed, this initial injection was effective thermally), but the subsequent closely-spaced injections up to 39 minutes after the melt were quite effective. From that point injection periods were shorter and less frequent; the bulk of the oxygen for decarburization then was supplied from the furnace atmosphere.

Figure 10 is an analysis of the variation in the rate of carbon removal. This is a cumulative type chart that is particularly useful in studying variations in rates. The intersection of the experience curve at any point with one of the family of rate curves signifies the overall rate from the beginning
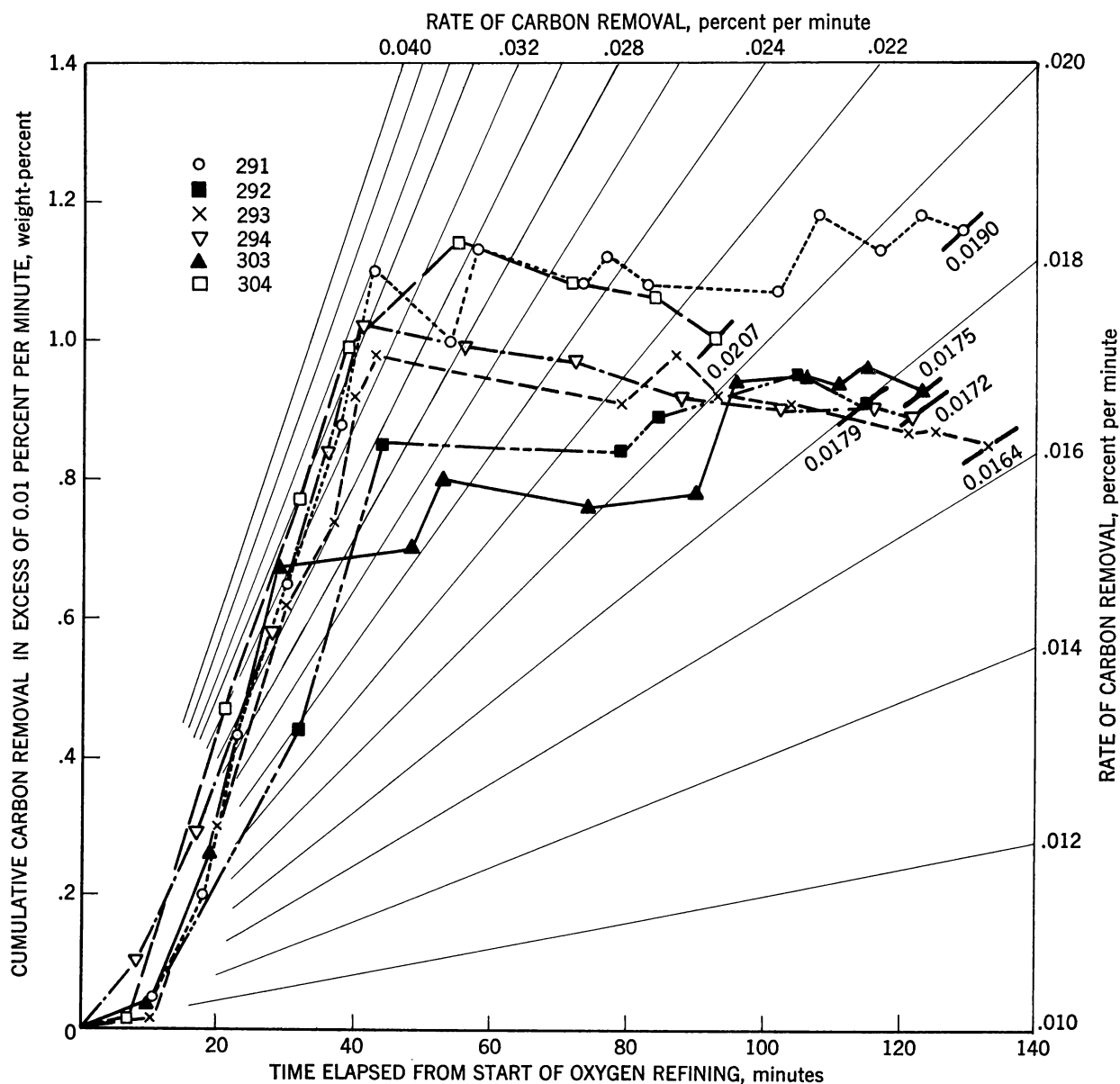

FIGURE 10. - Rates of Carbon Oxidation.

of the experience curve to that time. Any segment of the experience curve represents a rate equal to the rate signified by the rate curve that is parallel to the segment. This curve has the general characteristics of a growth curve; the induction stage, the stage of maximum growth rate, the leveling off, and lastly, the turning down as the supply of one reactant becomes depleted. In the period of fastest carbon removal, from 10 to 45 minutes after melt, the carbon drop averaged as much as 0.036 percent per minute, then it slowed to approximately 0.014 percent per minute, and finally to 0.009 percent per minute.

Furnace Deoxidation

The prescribed practices were carried out without difficulty. The silicomanganese furnace block immediately terminated the bubbling action in the bath that characterized normal oxidation at that carbon content. This addition combined with the pebble lime addition to the slag after block resulted in silicon levels above 0.10 percent as shown in table 6. The effectiveness of the furnace deoxidation also could be gaged by the above-normal recoveries of manganese and chromium and in particular the unusual consistency of these recoveries.

TABLE 6. - Recoveries of alloying elements in the steels

Alloying element	Forms of alloys added	Heat No.					
		291	292	293	303	294	304
Manganese.........	Si-Mn and Fe-Mn:						
	Aim........percent	0.75	0.80	0.90	0.90	0.95	0.95
	Added.........do...	1.16	.88	.97	.85	.91	1.02
	Recovered.....do...	83.	64.	84.	83.	84.	87.
Silicon:							
Block..........	Si-Mn and Fe-Si:						
	Aim...........do...	.25	.25	.25	.25	.35	.35
	Added.........do...	.19	.17	.18	.22	.35	.41
	Recovered.....do...	58.	[1]70.	-	-	-	-
First ladle.....	Ca-Si:						
	Added.........do...	.07	.07	.07	.16	.16	.16
	Recovered.....do...	[2]64.	[2]7.	[2]80.	65.	91.	64.
Second ladle....	Ca-Si:						
	Added.........do...	-	-	-	.05	.05	.05
	Recovered.....do...	-	-	-	128.	107.	96.
Both ladles.....	Ca-Si:						
	Added.........do...	.19	.19	.19	.21	.21	.21
	Recovered.....do...	89.	68.	87.	79.	95.	73.
Nickel...........	NiO pellets:						
	Aim...........do...	-	-	.55	.55	1.00	1.00
	Added.........do...	-	-	.55	.55	1.02	1.11
	Recovered.....do...	-	-	86.	89.	86.	92.
Chromium..........	Fe-Cr:						
	Aim...........do...	-	-	.50	.50	.70	.70
	Added.........do...	-	-	.57	.46	.66	.69
Molybdenum........	Fe-Mo:						
	Aim...........do...	-	.25	.20	.20	.35	.35
	Added.........do...	-	.26	.20	.21	.35	.38
	Recovered.....do...	-	97.	103.	97.	94.	104.

[1]Samples 12 minutes after blocking addition. Heat tapped 13 minutes later.

[2]Based on assumed 100-percent recovery from calcium-silicon addition to second ladles.

In the ladle practice, low recoveries were expected from the calcium-silicon additions compared to industrial practice, because the natural tendency for oxidation of silicon during tapping and teeming would be accentuated by the large surface of metal exposed to oxidation per unit of volume in the small amounts handled and, further, the second teeming operation would present an additional opportunity for such oxidation losses. Despite these factors a satisfactory recovery of silicon was experienced in tapping and in the second ladles it was recovered almost completely (table 6).

These results were considered significant because each supplier of rare-earth materials had emphasized that a thoroughly deoxidized metal was essential to the proper reaction of their materials. This condition was confirmed by the consistent recoveries of lanthanum and cerium (the only two rare-earth elements determined) from the rare-earth metal mixtures (Lanceramp No. 1). This point will be discussed later.

Tapping and Teeming

Except for an electrical failure that delayed the tap in heat 292, the tapping operation proceeded smoothly. The stiff slag resulting from the pebble lime treatment did not run into the tap hole when the furnace was tilted to start the tap. There was ample time to plunge the aluminum and calcium-silicon alloy additions, and there was little evidence that any deoxidizing material rose unreacted to the top of the metal. The tapping ladle was pulled away from the furnace before the slag began to run, and little metal was lost. This procedure was important in preventing a reaction of the rare-earth materials with furnace slag.

A cover of pebble lime shovelled on top of the metal in each ladle after filling proved beneficial in retarding radiant heat loss from the molten steel.

Teeming to a mark on the second ladle lining provided the requisite amount of metal for each ladle treatment, and teeming into the molds from the double-nozzle second ladles was generally satisfactory. Figure 11 illustrates the second ladles set up over the ingot molds. The teeming operation is portrayed graphically in figure 12 where the steel from ladle 1 has been teemed, teeming is in progress from ladle 2, and ladle 3 is being filled. The entire tapping and teeming operation took less than 6 minutes.

Ladle Treatments with Rare-Earth Materials

The results of spectrographic determinations for lanthanum and cerium upon ingot drillings are listed in table 4. When no rare-earth materials were added, a residual level of 0.003 percent cerium and 0.001 percent lanthanum was nonetheless reported. An addition of 0.10 percent rare-earth metals (2 pounds per ton) as oxides resulted on the average in 0.006 percent cerium and 0.002 percent lanthanum, for a net rare-earth recovery of approximately 4 percent. A similar amount of rare-earth metals resulted in average levels of 0.024 percent cerium and 0.008 percent lanthanum, a net rare-earth recovery of 28 percent.
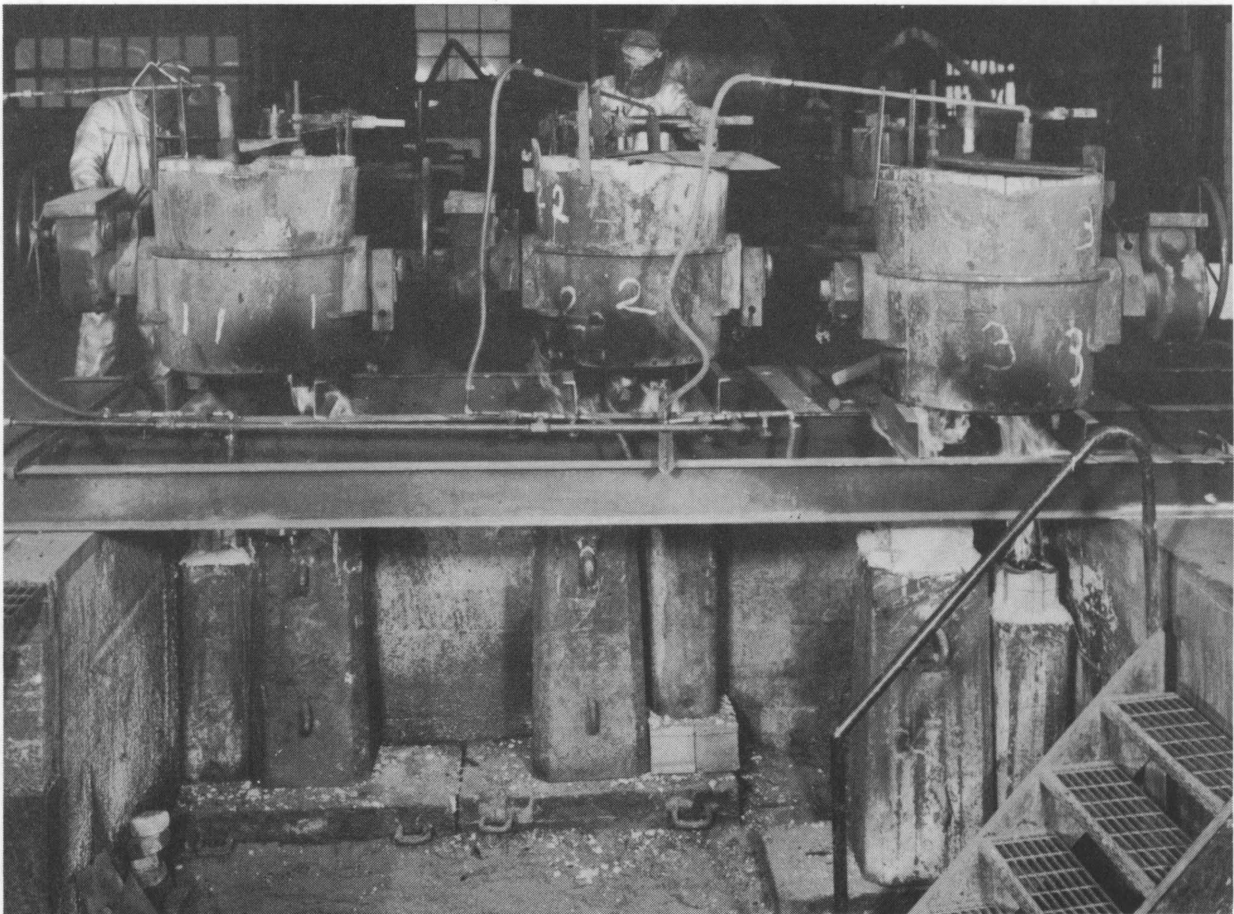
FIGURE 11. - Arrangement of Second Ladles and Ingot Molds.

Apparently, only a small fraction of the oxide material was retained in the steel, but a substantial part of the rare-earth metal additions was recovered. These recoveries from the metal mixture were significantly greater than had been anticipated, for several plants had reported recoveries ranging from 10 to 30 percent with 20 percent as an overall average. Further, the recoveries in this work were remarkably consistent from heat to heat.

Also observed was the fact that either treatment resulted in a cerium to lanthanum ratio of approximately 3:1 although the ratios of these elements were 1.5:1 in the metal and 2:1 in the oxide material. The cause is not known, and it was beyond the scope of this work to inquire further. To the authors it seems likely to have resulted from the relative sulfide-forming tendencies of the two elements.

Ingot Cooling

The procedure described was followed for each heat. No evidence of thermal cracking or flaking was detected in either the ingots or the rolled
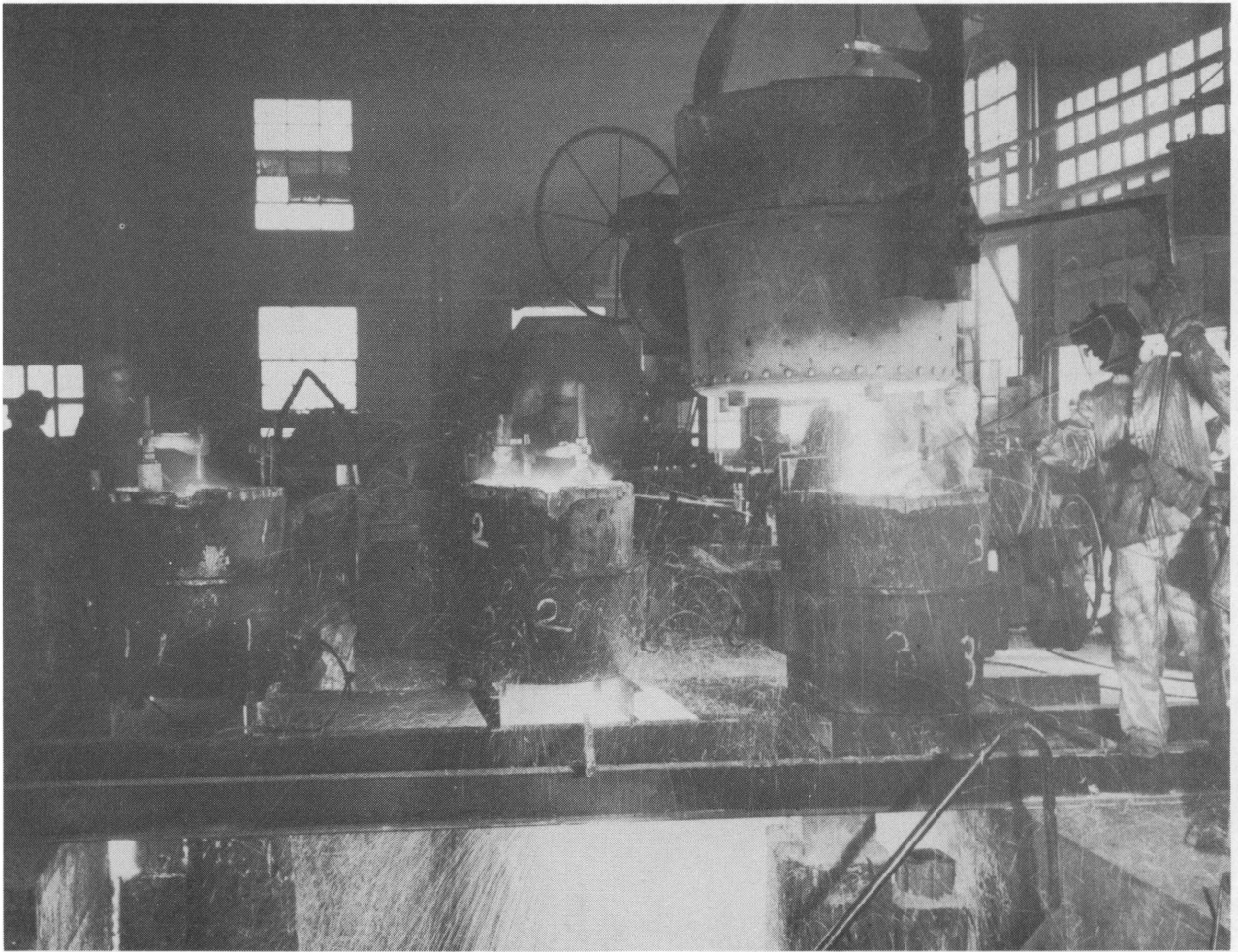
FIGURE 12. - Teeming the Ingots.

product, indicating that this practice had been entirely effective in retarding the transformation from austenite.

Rolling and Finishing

The mill arrangements had been set up to accomplish two purposes--to produce high quality steel in soundness and mechanical properties, and to produce the best surface quality possible.

Billet Production

All the ingots were bloomed without difficulty. During the initial passes, evidences of folds were observed in most of the ingots, particularly at the corners. Very few ingot cracks were visible. The surface could best be described as typical for the four grades represented without any visible defects attributable specially to the casting practice, that is, nothing apart from the folds, scabs and hanger cracks usually observed in industrial practice.

These observations proved that the casting practice devised had produced ingots of representative surface quality by industrial standards. Consequently, any characteristic differences in the surface defects observed in the steels treated with rare-earth metals or metal oxides could properly be attributed to such treatments.

Identification of the billets was established as specified, and the billet cooling cycle specified was performed completely.

Billet Testing, Inspection, and Preparation

Very high yields of billet product had been cut purposely from the ingot product to avoid wasting any sound steel. See table 7. As a result, several of the original cross-sectional macroetch slices that had been cut from the topmost and bottommost locations in the billet product (relating to the position in the ingot) showed indications of insufficient cropping. In most instances retests secured after cutting back 6 inches (roughly 27 additional pounds, equivalent to 1.7 percent less yield from an average ingot) were rated satisfactory. The macroetched specimens which were rated satisfactory indicated a soundness equivalent to industrial product in the judgments of both the authors and the mill metallurgist. Figure 13 shows specimens cut from ingot 304-2, which were typical of those examined from the tops of the following six ingots:

291-2		303-2	304-2
	292-3	303-3	304-3

The -2 ingots had been treated with rare-earth metal oxides; the -3 ingots were untreated.

TABLE 7. - Yields of rolled product from ingots

Form	Weight, pounds	Yield, percent		
		Ingots	Tested billets	Ground billets
Ingots..........................	18,570	-	-	-
Billets from mill................	15,265	82.2	-	-
Tested billets...................	14,800	79.7	-	-
Ground billets...................	14,040	75.6	94.9	-
Bars shipped.....................	12,838	69.1	86.7	91.4

The billets rolled from the remaining two ingots in these treatment classes, 291-3 and 292-2, had severe center porosity extending down a substantial distance from the top. The condition failed to improve after twice cutting the topmost product back 6 inches, a total of 12 inches. Even at the bottom end of the T cut, roughly 30 percent of the ingot product, the center condition was not up to commercial requirements. Therefore, the adjacent billet, the D cut, from these ingots was rolled to 3-inch-diameter round bars to provide some sound product in this size. The cause for this deep-seated porosity was evident; the reservoir of metal in the hot top failed to feed enough metal to the ingot body for filling the shrinkage cavity that otherwise would form during solidification. Ingot 291-3 had a partly filled hot top;
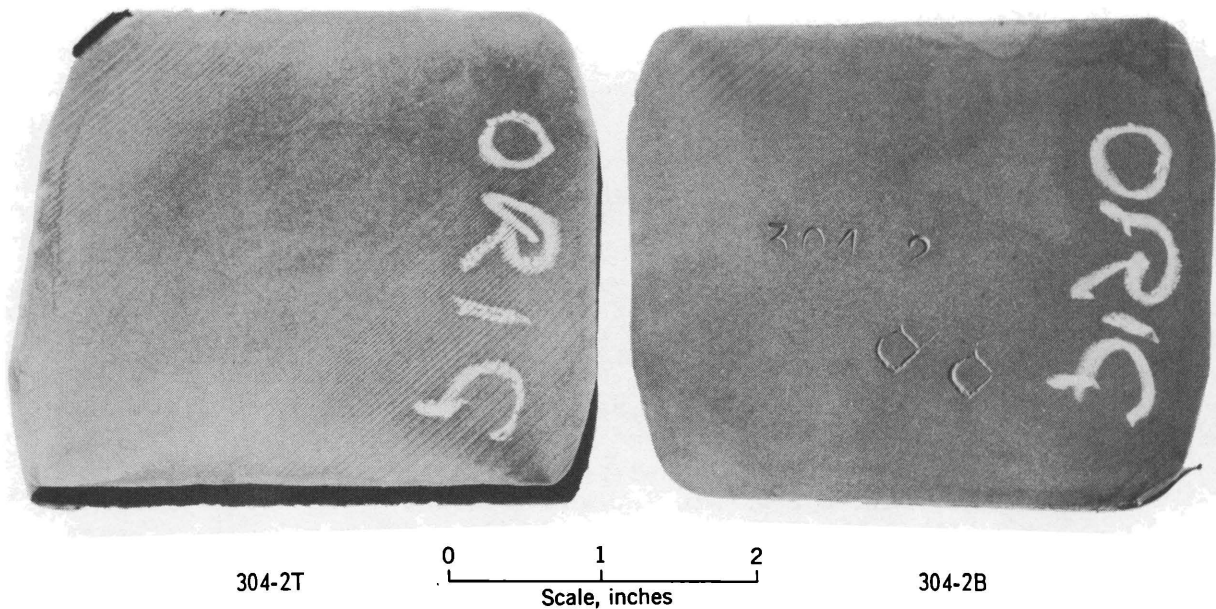
FIGURE 13. - Macroetched Specimens From Product of Ingot 304-2.
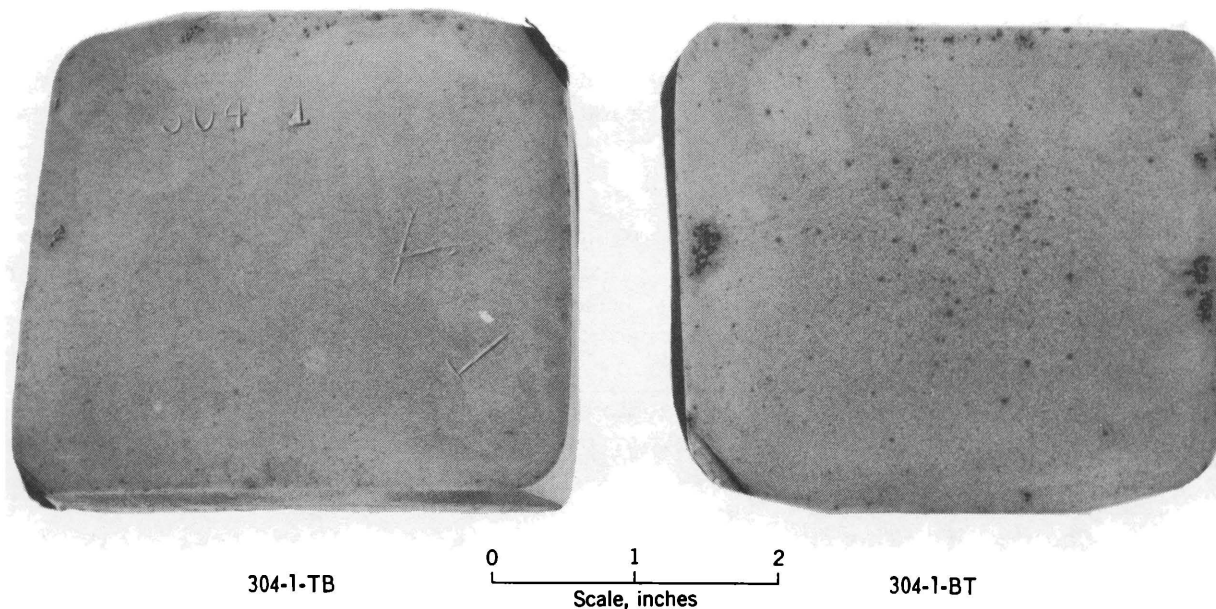
FIGURE 14. - Macroetched Specimens From Product of Ingot 304-1.

291-2 had a full hot top, but it became bridged at the hot-top junction and failed to feed the needed quantity of metal into the ingot body.

The remaining four sets of macroetch specimens exhibited a characteristic pattern exemplified by figure 14. The specimens pictured represented the condition at the bottom of the T cut, some 375 pounds down from the

hot-top junction, and the top of the B cut, 175 pounds up from the bottom of the product. Considering only the normal billet yield, these test positions represented locations 30 percent down from the top and 14 percent up from the bottom. This pattern of voids irregular in size and distribution, but concentrated under the ingot skin in the upper portion of the ingot length, was observed in all four ingots that had been treated with rare-earth metals, but was not detected in any of the product treated with rare-earth oxides, nor in any of the untreated product.

Other investigators have observed this type of defect in steels similarly treated. It was observed in stainless steel slab ingots by Henke and Lula,[40] and Russell[41] published a photograph of a 0.20 percent plain-carbon macroetch specimen that exhibited this pattern. Briggs[42] described a porous condition under the cope surface in heavy sections of castings and attributed it to rare-earth sulfides. The desulfurizing power of rare-earth metals in steels is well established, having been studied and reported by Russell,[43] Boulger,[44] and Berger and Snellman.[45] Although no direct data are available, it seems reasonable in the light of the work cited to infer that the voids observed had resulted from sulfide inclusions which had been trapped early in the solidification period, and which were etched out of the macroetch specimens.

Results of a detailed surface inspection of the T and the M billets are listed in table 8. The data presented express the total lengths of seams in pieces of different lengths as feet of light seams and inches of deep seams per lineal foot of billet length. This quantity is a direct measure of the amount of surface preparation required and its cost. For steels of the types rolled, the percentage of the billet product rejected for poor surface is usually small, so the determining factor when evaluating surface quality is the footage of defects to be removed per foot of billet length.

Only seams are presented in this tabulation. The other major classes of steel defects, ingot cracks and scabs, occurred too infrequently to affect the overall surface quality significantly. The authors recognized that scabs can result in seams, and where such occurred their lengths were included in the seam tallies.

[40]Henke, R. H., and Lula, R. A., Rare-Earths Counteract Hot Rolling Defects in Stainless Steel: Jour. Metals, vol. 6, 1954, p. 887.

[41]Russell, J. V., Rare-Earth Additions Affect Surface Quality of Low Carbon Steel: Jour. Metals, vol. 6, 1954, p. 439.

[42]Briggs, Charles W., The Effect of Rare-Earth Metals on Cast Steel. Part II. The Production of Commercial Cast Steel Containing Rare-Earth Additions: Steel Founders' Soc. of Am., Cleveland, Ohio, 1954, p. 49.

[43]Work cited in footnote 41, p. 440.

[44]Boulger, F. W., Udy, M. C., Wahll, M. J., and Frazier, R. H., The Effect of Rare-Earth Metals in Cast Steels. Part I. Laboratory Studies at Battelle Memorial Institute: Steel Founders' Soc. of Am., Cleveland, Ohio, 1954, pp. 9-11.

[45]Berger, J. Alfred, and Snellman, Matts G., Desulphurization with Rare-Earths: Steel, vol. 134, No. 15, (Apr. 12), 1954, pp. 110, 112, 117.

TABLE 8. - <u>Comparative density of seams classified between faces,</u>
<u>among heats and steel types, and among ladle treatments</u>

	Seam lengths per face per running foot of billet			
Seam depth...........	Light seams, feet		Deep seams, inches	
Billet cut...........	T	M	T	M
Between faces:				
Top and bottom.....................	1.3	0.1	0.8	1.5
Left and right sides...............	1.9	.2	1.1	1.0
Among heats and steel types (left and right sides only):				
Heat 291 | Plain carbon............	1.8	0.2		
Heat 292 | Mo alloy................	1.0	.1		
Heat 303 | Low Ni-Cr-Mo alloy......	2.3	.3		
Heat 304 | High Ni-Cr-Mo alloy.....	2.5	.2		
Among ladle treatments (left and right sides only):				
Rare-earth metals..................	1.5	0.2		
Rare-earth oxides..................	2.1	.1		
None..............................	2.1	.3		

For this tabulation the surface defects were classified between the two
pairs of opposite sides of the billet, described respectively as top plus
bottom, and left plus right. These descriptions refer to the orientation of
the billet in the last pass of the blooming mill when viewed from the entering
side of the mill. There is no significance to be attached to any one side as
such, but identification of the defects to the pairs of opposite faces was
important to a precise evaluation of surface quality. The open pass in the
rolls of the universal blooming mill subjected the billet faces in contact
with the rolls, (the top and bottom faces), to compressive plastic flow at the
surface that was predominately longitudinal since the roll collars that formed
the shoulders in the pass prevented any significant transverse flow. As a
result, seams in these faces would have a tight, narrow appearance. Slippage
in the rolls also would tend to smooth the surface metal over some defects and
thus conceal them. By contrast, the side faces, unsupported by working rolls,
would experience transverse as well as longitudinal deformation at the surface,
and therefore tend to open up and expose any seams that were present.

The data presented in table 8 indicate the magnitude of the billet face
effect in masking the appearance of seams. The apparent footage of light
seams in the T billets averaged 1.3 on the top and bottom faces, one-third
less than the 1.9 value on the sides. A similar difference was observed in
the M cuts but the magnitude of this difference between faces was less relia-
ble for estimating the magnitude of the face effect because the billets exam-
ined had only one-tenth the seam density, 0.1 to 0.2 against 1.3 to 1.9 feet
per lineal foot of billet face, and represented scarcely more than one-quarter
of the length of the T billets. As no other basis was available for inferring
a difference in seaminess between the pairs of faces, a rough estimate showed
that one-third of the surface seams would be concealed in the top and bottom
faces, therefore, a comparative study of seam occurrence should be limited to
only the side faces.

Deep seams should not be as sensitive to the face effect as light seams, since the billet upon cooling from the rolling temperature would have a stronger tendency to shrink away from the walls of the seam, thus exposing it. Actually, this class of defect was only a minor factor in the steels investigated, as it ranged from 0.8 to 1.1 inch per running surface foot, scarcely 6 percent of the light seam footage. The average total seam length per lineal foot of billet length, presented in table 8, was confined to measurements of light seams from the left and right sides of the T and M billets. Overall, the seam density in the T cuts averaged 1.9 feet per foot and in the M cuts, 0.2 feet per foot. These levels indicated that the incidence of defects was concentrated in the billets produced from the topmost part of the ingots. Against these overall averages, the molybdenum steel, heat 292, with averages of 1.0 and 0.1 feet per foot, respectively, showed a distinctly better surface, and the two Ni-Cr-Mo alloys were decidedly poorer at 2.3 and 2.5 feet per foot in the T billets. A billet of this size (4 inches square) that would require from 3 to 4 feet per foot of surface conditioning would, in effect, have to be skinned. By this standard the Ni-Cr-Mo alloys probably would have required skinning while the molybdenum alloy could have been prepared by spot conditioning. The common knowledge is that heat-to-heat variation in surface quality is very great and the data cited represent only single heats of four different types of steel. For this reason no claim is made that these results show any basic difference in billet surface condition as a function of steel type. They do, however, demonstrate the precision of the method of measurement adopted in attributing the variation in surface condition which was experienced to a rational system of causes.

The effect of the rare-earth ladle treatments on surface condition is given in the last series in table 8, which indicate that the T cuts of steels treated with rare-earth metals had significantly fewer light seams than either the untreated steels or those treated with rare-earth metal oxides. Both of the latter groups were substantially equivalent in surface condition. Apparently, the rare-earth metal treatment resulted in far fewer seams as a general effect of its use because in this classification the data represented four different types of steel. However, each T billet that had been treated with rare-earth metals also contained a large number of tiny longitudinal discontinuities ranging in length from three-sixteenths to one-half of an inch and averaging roughly one-fourth of an inch. These defects were not true seams and were not tallied as such. They were dispersed over the entire surface and a T billet 7 feet long might exhibit a hundred or more on a side. To remove the greater part of this type of defect, all billets representing rare-earth metal treatment were completely ground. Although no such defects were observed in either the untreated steels nor those treated with rare-earth oxides, these billets also were completely ground to provide a comparable surface for bar rolling. Metal loss data from grinding were analyzed but were not useful in evaluating surface quality because the overall grinding effectively determined the metal loss. When the 3-inch-diameter round bars produced from the T billets were inspected after sandblasting and pickling, numerous short, scattered, longitudinal defects were again observed in the product of all four steel types that had been treated with rare-earth metals. When filed to the sound metal underneath, these defects were 0.004 to 0.008 inches deep. By comparison, all the scattered seams observed were much deeper, and much longer.

As in the billet product, the 3-inch round bars representing the untreated ingots were comparable in surface characteristics to those treated with the rare-earth metal oxides and none contained any of the distinctive short, shallow defects found in the bars treated with rare-earth metals.

A natural question was whether the characteristic subsurface voids in the macroetched specimens from the T billets of all four steels treated with rare-earth metals were somehow related to the tiny surface breaks observed in the billets and bars produced. Without attempting to describe the origin of the subsurface porosity, it is suggested that these conditions were related in a manner similar to the effect which shallow blow holes in rimming steel ingots have upon the resulting billet surfaces. The shallow blowholes are exposed by scaling during heating and the well-known alligator-hide condition results from rolling the honeycombed skin structure of the ingot. Similarly, the authors believe that voids (or sulphide inclusions) lying close to the skin of the steels treated with rare-earth metals became exposed by scaling during the ingot heating period, and that the concavities so formed were elongated into longitudinal defects by rolling. Despite overall grinding of the billets, a reheating for bar rolling would only serve to scale the surface anew, and therefore expose a fresh set of discontinuities at the ingot surface.

The effects upon the rolled surface that were observed could be produced from the operation of this suggested mechanism upon even relatively small discontinuities owing to the magnitude of the plastic deformation forces involved when reducing the cross-sectional area by at least two-thirds in normal hot rolling practice. The originating defects in the 12-11/16-inch square ingots must have been very small to have only resulted in defects one-fourth of an inch long, as these ingots were reduced by blooming to a billet cross-section of approximately one-tenth the ingot area while being lengthened by an equal factor. Without allowing for any tearing, an ingot defect less than one-thirty second of an inch long would result in a billet defect approximately one-fourth of an inch long.

Controlling the Metal Composition

Specifications

The composition ranges listed in table 1 had the practical effect of establishing the typical variation in chemical composition among heats of industrial product as the criterion for the composition limits of the steels produced. The two main exceptions to the standard limits are a maximum of 0.025 percent phosphorus and sulfur. These limits are very restrictive, but producers themselves oftentimes impose limits for these elements well below the standard limits of 0.040 percent to provide alloy steels that will develop the mechanical properties required for satisfactory performance when used in the heat-treated condition.

Performance to Specifications

In General

An industrial producer who has accepted an order for a non-standard grade
of steel is presumed to have less experience, hence, less control over compo-
sition compared to standard grades; accordingly, the AISI has established
tables of standard ranges for nonstandard grades that are generally broader
than the corresponding ranges for standard steels.[46] [47] In furnace opera-
tions, the laboratory personnel concerned with melting these heats were in a
similar position. Therefore, melting and casting ingots to commercial speci-
fications were not standard operations. Despite this condition, and the inher-
ent risk of greater error when alloying such relatively small weights of
open-hearth steel, the specifications for these heats were based on the stand-
ard steel production ranges. A comparison between these specifications,
listed in table 1, and the compositions of the steels produced, listed in
table 4, showed that all the steels produced were within the standard grade
ranges for silicon, nickel and molybdenum, and were within the restrictive
limit for sulphur. The other four elements specified, namely, carbon, manga-
nese, chromium, and phosphorus, fell outside the limits of table 1 in one or
more instances. A discussion of each of these elements follows.

Carbon

On the basis of ladle samples, only two heats of the six produced (heats
293 and 303) fell within the carbon specifications for standard grades, and
one additional heat (304) fell within the limits for nonstandard grades.
When the bars were sampled, a fourth heat (291) was found to be within the
AISI standard limits for check analysis[48] [49] with respect to the basic speci-
fication for nonstandard steels. The other two heats, 292 and 294, were
entirely out of range on the low and the high sides, respectively.

The problems encountered in meeting the carbon aim were fourfold:

1. The difficulty of estimating carbon content with sufficient preci-
sion by magnetic testing, using pencil specimens cast from melt samples that
differed in alloy contents, and therefore in magnetic properties, among the
various heats.

2. The need of blocking the melt on the basis of a magnetic determina-
tion of carbon at a level of carbon (0.25 to .30 percent), where the magnetic
method is less reliable compared to higher carbon levels.

3. The problem of halting carbon oxidation by blocking addition at the
proper carbon content, that is, at the proper moment. On the average, the

[46]American Iron and Steel Institute, Hot Rolled Carbon Steel Bars; Sec. 8 in
Steel Products Manual. New York, N.Y., 1952, p. 46.
[47]_____. Hot Rolled Alloy Steels; Sec. 10 in Steel Products Manual.
New York, N.Y., 1949, pp. 37-38.
[48]Work cited in footnote 46, p. 47.
[49]Work cited in footnote 47, p. 42.

period of refining equivalent in carbon drop to the entire range of carbon was only 7 minutes, roughly one-half to one-fourth of the equivalent period in industrial-size furnaces.[50] [51] [52]

4. Variability in the net recovery of carbon from anthracite that was added to the first ladle, especially since the metal was tapped much hotter than in normal practice.

Manganese

This element finished outside the standard range in only one heat: Above the range in heat 291, the first one melted. The percentage of the element actually recovered from the furnace additions was much greater than had been expected from experience with manganese additions to smaller heats in this furnace. The percentage recovery calculated from heat 291 was used in calculating the additions for all subsequent heats, and all finished within the specifications. Manganese recovery was remarkably uniform, as shown in the discussion to follow.

Chromium

Similar to manganese, this element finished above the specified range in heat 293, the first heat melted to a chromium specification. Likewise, the chromium additions to all three subsequent heats where this element was specified were based upon the percentage of recovery calculated from this heat, and all finished within the respective ranges for standard steels.

Phosphorus

Although effective control over this element was recognized from the outset as a serious problem in view of the high temperature, oxygen refining practice that was necessary, the counter-measure of slagging off midway in the refining period successfully controlled this element in four heats of the six melted. Heats 291, 293, 294, and 303 indicated excellent control over this element. Heat 304 exceeded the restrictive specification slightly; the authors believe that the extra-fast refining practice for this heat was less effective in dephosphorizing the metal prior to slagoff. Very high levels of phosphorus that were observed in product samples from heat 292 resulted principally from the abnormal 25 minute block caused by a power failure, although the 160 pound lime charge for this heat probably did not effect as much dephosphorization before slagoff as the 240 pound charge which was used in the other heats.

[50] Larsen, B. M., Rates of Open-Hearth Reactions: Ch. 22 in Basic Open-Hearth Steelmaking. AIME, New York, N.Y., rev. ed. 1951, p. 901.
[51] Work, H. K., and Webb, W. R., Operation of an Experimental Open-Hearth Furnace: Open Hearth Proc., AIME, vol. 28, 1945, P. 29.
[52] Philbrook, W. O., Tenenbaum, M., and Washburn, F. M., Refining Practice: Ch. 8 in Basic Open-Hearth Steelmaking. AIME, New York, N.Y., rev. ed. 1951, p. 311.

Recovering Alloying Elements from Additions

Molybdenum, Nickel, Manganese and Chromium

A complete list of the percentage recoveries of alloying elements from the amounts added to the melts is exhibited in table 6. The amounts of alloying elements added, expressed as weight percentages of the weight of metal to which they were added, were estimated because the molten metal was not weighed during processing. Table 9 presents a comparison between the average recoveries of molybdenum, nickel, manganese and chromium in these experimental heats and typical industrial experience cited by Belding and Kulp.[53] This tabulation shows that the recovery of molybdenum experienced was approximately the same as in industrial practice, and that in all instances the recovery was essentially complete, the losses observed being attributable to errors in estimating the metal weights. The recovery of nickel, like molybdenum, should be high. However, the low values experienced were believed to have resulted from using a falsely high value of nickel content in the pellets for calculating the additions. Opinion is that the recovery of nickel approached that of molybdenum. Both manganese and chromium were recovered to a significantly greater degree than would have been expected on the basis of industrial experience. These differences are viewed as a measure of the effectiveness of the lime addition that was made after the block in preventing reoxidation of the slag. Actually, it had been anticipated that the recoveries of these elements would be poorer than typical industrial experience, rather than better, for the amount of oxygen that would diffuse into a unit weight of metal during the block would depend directly on the specific interfacial area between metal and slag, that is, the area per unit weight of metal, and this factor was at least twice as great as the specific interfacial area of industrial furnaces.[54] [55]

The variation in alloy recovery between heats as presented in table 6 would indicate at first glance that the alloying practice was quite erratic. For example, the range of molybdenum recovery from 94 to 104 percent appeared inconsistent with the notion that this element was recovered quantitatively or else betrayed an apparent lack of control over weighings, sampling techniques and analytical procedures. For these reasons, a study of the magnitude of the variations in recovery from furnace additions was undertaken for each of the alloying elements added with the exception of silicon. Study of the latter element was precluded by the silicon addition to the metal during tapping. Table 10 presents an analysis of the performance in meeting the chemical compositions desired--the basic objective of the alloying practice. The first six lines of this table are concerned with estimating typical amounts of the respective elements that were to be recovered in the metal, expressed as

[53]Belding, H. Ross, and Kulp, R. K., Finishing and Deoxidation Practice: Ch. in Basic Open-Hearth Steelmaking. AIME, New York, N.Y., 1951, rev. ed., pp. 380-381, 388-389.

[54]Work cited in footnote 51.

[55]A mean hearth area of 0.87 ft.^{2} per ft.^{3} of metal was calculated from the data presented on 160 furnaces tapping from 180 to 225 tons. American Iron and Steel Institute, Determination and Comparison of Furnace Performance and Capacity: Contributions to the Metallurgy of Steel, No. 20. New York, N.Y., 1948, pp. 73-109.

weight percentages of it. The typical amounts <u>to be added</u>, also in weight-percent, listed in line 11, were calculated by dividing the amounts to be recovered in line 6 by the average recovery efficiencies shown in line 10. Amounts expected to be recovered based upon the maximum and minimum efficiencies of recovery (shown in lines 8 and 9) are listed in lines 13 and 14, respectively. The range in composition resulting, shown in line 15, deserves comment for it expresses the total variation in chemical composition experienced in either four or in five heats, taking into account actual variations in recovery resulting from oxidation losses of manganese and chromium, and errors in weighings of the alloy addition agents, in sampling the melts, in sampling the melt samples for the drillings used in chemical analysis, in the analytical procedure, in sampling and analyzing the addition agents themselves, and other unknown sources of error. When it is considered, for example, that errors of plus or minus 2 percent of the concentration of the element determined could be expected in routine chemical analyses,[56] the ranges listed in line 15 may be viewed as reflecting an alloying practice that was quite uniform.

TABLE 9. - <u>Comparative alloy recoveries from furnace additions</u>

Element	Ferroalloy and analysis[2]	Typical industrial experience[1]			Average of experimental results, percent
		Expected recovery, percent	Hot-metal heat, grade 4340, percent	Cold-charged heat, grade 8640, percent	
Molybdenum	Molybdenum oxide (Mo 60)	95	96	100	None added
	Ferromolybdenum (Mo 73)	95	None added	None added	99
Nickel	Nickel electrodes (Ni 100)	95	97	do.	None added
	Nickel oxide pellets (Ni 78)	None added	None added	do.	88
Manganese	Ferromanganese (Mn 80)	80	} 81	77	} 84
	Silicomanganese (Mn 66)	80		None added	
Chromium	Ferrochromium (Cr 68)	85	89	83	93

[1]Work cited in footnote 53.
[2]Approximate weight percentages of elements contained are listed in parentheses.
[3]Metallurgical grade of MoO_3 (pure chemical would contain 66.65-percent molybdenum). Supplied in cans containing a stated amount of the element.

These data (table 10, line 15) not only indicated that a relatively uniform alloying practice had been achieved, but they also provide a starting point for answering two questions of broader interest: What tolerances in alloy composition for the respective elements would be required for successful melting in this furnace, especially to produce products within tolerance 95 percent of the time, and how would such tolerances compare to the natural tolerances of industrial open-hearth practice, also for 95 percent chemistry performance? Both of these queries are essentially statistical.

[56]Work cited in footnote 53, p. 374.

TABLE 10. - Chemical composition performance

Line		Alloying element			
		Molybdenum	Nickel	Manganese[1]	Chromium
1	Nominal concentrations specified among heats:				
2	Maximum...weight-percent	0.35	1.00	0.95	0.70
3	Minimum...do.......	.20	.55	.75	.50
4	Average...do.......	.27	.78	.88	.60
5	Usual residual content in bath at time of block............do.......	None	.01	.17	.08
6	Typical amount to be recovered from addition................do.......	.27	.77	.71	.52
7	Efficiencies of recovery from alloying additions:				
8	Maximum...percent	104.	92.	87.	98.
9	Minimum...do.......	94.	86.	83.	88.
10	Average...do.......	99.	88.	84.	93.
11	Typical amount to be added, line 6 ÷ line 10...........weight-percent	.273	.875	.845	.559
12	Amounts expected to be recovered from typical additions:				
13	At maximum yield, line 11 x line 8.......................do.......	.284	.805	.735	.548
14	At minimum yield, line 11 x line 9.......................do.......	.257	.753	.701	.492
15	Range in amount recovered, R, line 13 - line 14............do.......	.027	.053	.034	.056
16	Number of heats, n...	5.	4.	5.	4.
17	Ratio of mean range in samples of size n, to the standard deviation σ, d_2...	2.33	2.06	2.33	2.06
18	Estimated standard deviation of the amount recovered, (S), $(R \div d_2)$..weight-percent	.012	.025	.015	.027
19	Standard error of R in samples of size n, E............................	.864	.880	.864	.880
20	Standard error of S in samples of size n, s, $(E \div d_2)$...weight-percent	.37 x S	.43 x S	.37 x S	.43 x S
21	Expected maximum value of s, (1.61 x s).....................do.......	.60 x S	.69 x S	.60 x S	.69 x S
22	Expected maximum value of S, S + (1.61 x s)................do.......	1.60 x S	1.69 x S	1.60 x S	1.69 x S
23	or ....do.......	.019	.042	.024	.046
24	Estimated composition range for 95 percent performance (1.96 x 2 x line 23)..do.......	.07	.16	.09	.18
25	Industrial ranges for 95-percent performance:				
26	All grades and practices.....................................do.......	.06	.20	.23	.18
27	Detailed study of A8620:				
	(a) 832 heats from 12 practices.....................do.......	.06	.19	.24	.17
	(b) Practices having minimum spreads for the respective elements...............................do.......	.03	.12	.17	.13

[1]Heat 292 not included.

Variation between heats in the recoveries of the alloying elements listed in table 10 resulted from the joint influence of a number of factors, principally those discussed two paragraphs earlier. The pattern was very similar to industrial experience where studies of this nature have indicated an approximately normal distribution of errors.[57]

The experimentally determined composition ranges of line 15 were employed to estimate the standard deviation, σ, of each alloying element by taking these ranges as estimates of the mean ranges for the respective number of heats (line 16), then consulting published tables of the number of standard deviations encompassed by the mean range of samples from a normal population (line 17).[58] The practical significance of this statistic (d_2) is that for small samples such as these, it provides a good estimate of σ.[59] [60] Line 18 lists the respective estimates of σ, denoted by S. As an estimate, S itself was distributed; values of s, the standard error of S, were calculated by reference to Tippett,[61] using values of the standard error of R for a sample of size n[62] (line 19) to obtain the values of s listed in line 20.

In repeated meltings, S would not be expected to exceed $[S + (1.61 \times s)]$ more than 5 percent of the time,[63] so the values of (1.61 x s) listed in line 21 were used to develop the maximum values of S shown in lines 22 and 23. In turn, a 95-percent performance in repeated meltings would be expected to encompass a range of chemical compositions that would straddle rather symmetrically the average composition that was obtained. Therefore, each tolerance limit would be at the p = .025 level, which in a normal distribution would be equivalent to (1.96 x S). The total tolerance then would be 2(1.96 x S), and ranges so calculated from values of maximum S are listed in line 24.

[57] American Iron and Steel Institute, Chemistry Performance Survey of Open-Hearth Alloy Steels: Contributions to the Metallurgy of Steel, No. 28. New York, N.Y., 1949, 75 pp.

[58] Pearson, Karl, Tables for Statisticians and Biometricians, Part II: Biometric Laboratory, University College, London, 1st ed., 1931, p. 167.

[59] Tippett, L. H. C., The Methods of Statistics: Williams and Norgate, London, 3d ed., 1941, pp. 31-32.
Pearson, Karl, Tables for Statisticians and Biometricians, Part II: Biometric Laboratory, University College, London, 1st ed., 1931, p. cxvii.

[60] Some may object that the range is not as efficient a statistic for estimating the parameter σ compared to a second-moment calculation, in that the same number of data yields a less precise estimate of σ. Where only a single, small sample is available, however, the estimate derived from range is less affected by an occurrence of an isolated point separated from the other data values. In this instance, also, the choice of range is defended because it takes the heart of the problem--the range in composition itself--and uses it as a meaningful statistic. Efficient statistics are discussed by Fisher, R. A., Statistical Methods for Research Workers: Oliver and Boyd, Edinburg, 8th ed., 1941, pp. 300-308.

[61] Work cited in footnote 59, p. 84.

[62] Work cited in footnote 58, p. 76.

[63] The probability is .05 that the ratio of the standard error, s, for groups of four heats to the standard error, s, for a large number of heats would not exceed 1.61. This is the square root of the variance ratio F for 3 and 1,000 degrees of freedom respectively.

It is interesting to compare these estimates with industrial experience, also for 95-percent performance, over an 18-month period, as published by AISI.[64] Comparative data for all grades and alloying practices (in reality, producing plants) are listed in line 26; averages from a detailed study of one grade, A8620, in line 27, and in line 28, the minimum ranges for the respective elements. Although the carbon content of A8620 would be significantly less than the experimental steels, the concentration of the four alloying elements under discussion would be quite comparable, hence, spreads in composition should also be comparable. The ranges estimated from the experimental steels agreed closely with the industrial experience except for manganese, which, in the authors' experience was recovered with a precision that would not be met industrially. This comparison demonstrated that even on the very conservative basis shown in the previous paragraph, the experimental open-hearth furnace could produce these alloy steels within composition ranges at least as close as industrial producers. Further, the range for nickel would have been narrowed considerably if nickel electrodes had been used; the industrial range for nickel no doubt also would have been smaller if only heats requiring a nickel addition were studied, as the bulk of the nickel content was gained from charging alloy scrap at the time of that study, and occasionally the concentration in the resulting melt would approach the high side of the specification.

Silicon

Silicon recoveries from the alloys added at block could not be calculated directly for it was impossible to secure a representative sample of tapped metal prior to the ladle addition of calcium-silicon alloys. Although some samples were taken from the furnace during the block period, these could only be used to estimate silicon losses over the blocking period to the time of sampling, and would leave undetermined the subsequent losses in the remainder of the blocking period and from oxidation during tapping. Thus, these samples would be indicative only of a maximum level of silicon recovery that might be experienced from the furnace blocking practice.

Furnace samples taken approximately 12 minutes after the block in heats 291, 292, and 304 contained 0.12, 0.13 and 0.24 percent silicon, respectively. The first two heats had been blocked with silicomanganese and showed recoveries of 58 and 70 percent. See table 6. Heat 304, where the silicomanganese block was followed immediately by an addition of 50 percent ferrosilicon to meet a higher silicon specification, showed 56 percent recovery of silicon in the furnace, the least of the three heats sampled. It is difficult to perceive why the silicon recovery in heat 304, as measured by the furnace sample, was not substantially better than in the other two heats as a much larger amount of silicon was added to a bath that apparently was equivalent to the other two heats in weight and oxygen concentration. However, the authors believe that the alloys added at block probably were not distributed uniformly throughout the quiet baths. At the concentration levels of silicon that were reported, an error of 0.01 percent in the reported composition also would have changed the recovery by 8 percent in heats 291 and 292, and by 4 percent in heat 304. Thus, it was concluded that a fair estimate of silicon recovery in

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[64]Work cited in footnote 57.

the furnace 12 minutes after block would be roughly 58 percent, the median of the three values reported. These samples were taken at a time shortly before the tap would begin in normal practice, therefore, this estimate of 58 percent was regarded as essentially the recovery at the beginning of tapping. The following paragraphs show that the recovery of silicon in heat 292 was undoubtedly far less when the heat finally was tapped 13 minutes after the furnace sample had been secured.

Silicon recoveries from ladle additions of calcium-silicon alloy, also listed in table 5, were calculated on the assumption that 58 percent of the block addition had been recovered and that 6,800 pounds of metal was tapped into the first ladle. This estimate of tapped weight was developed from weighings of ingots and casting pit scrap and is believed accurate to within plus or minus 4 percent. First-ladle recoveries could be calculated directly for heats 294, 303 and 304, since the third ingot from each was cast directly from the first ladle. Using these data as typical for the respective heats, it was then possible to calculate second ladle recoveries from the ladle samples secured while casting the treated ingots, that is, the first and second pairs, in these heats. These second-ladle values were so close to 100 percent that it seemed justifiable to use that value to back-calculate the first-ladle recoveries for heats 291, 292 and 293. Table 6 shows first-ladle recoveries ranging from 64 to 91 percent if heat 292 is excluded. Based on the median value, the best estimate of recovery was 65 percent with a range of plus 0.04, minus 0.00 percent silicon. Since second ladle recoveries were so close to being complete, the values of more than 100 percent that appear in the table were attributed to errors in weighings and samplings, as an error amounting to 0.01-percent silicon concentration would be equivalent to a 20 percent error in recovery, considering that only 0.05 percent silicon was added. The net recovery from calcium-silicon additions in both ladles ranged from 73 to 95 percent, again excluding heat 292. The 95 percent value reported for heat 294 is thought to be unreasonably high, but there was no definite basis in the record for rejecting it. In the first three heats, (291, 292 and 293), two-thirds of the calcium-silicon alloy was added to the second ladle where its efficiency was higher, but only one-fourth was so added in heats 294, 303 and 304. Although the first-ladle recoveries were likewise comparable, adding the bulk of the calcium-silicon in the second ladle where the recovery was naturally greater, gave rise to overall recoveries that averaged 12 percent better in heats 291 and 293 compared to heats 303 and 304.

The pattern of silicon recovery resulting from the 25-minute block in heat 292 deserves comment. The overall recovery of 68 percent from the calcium-silicon additions to this heat was close to that experienced in heats 303 and 304. Naturally the recovery of silicon should have increased with each successive addition, so that something close to the final treatment (second-ladle) recoveries observed in heats 303 and 304 would be experienced. In those heats the second-ladle recoveries averaged better than 100 percent, and complete recovery of silicon at this stage seemed a reasonable assumption for heat 292. On this basis, and if 58 percent recovery from the block were maintained, the first-ladle addition efficiency could have been no more than 7 percent. Although some oxidation of silicon would occur in tapping, and

more so in this heat in view of the long blocking period, it was obvious that these apparent recovery values of 58 percent followed by 7 percent were inconsistent, especially since the first-ladle recoveries of 65 and 64 percent, had been observed in heats 303 and 304 based on the same 58 percent furnace recovery. Therefore, it was evident that the recovery of silicon in the furnace at the time of the tap was far less than this estimate, as a result of a substantial oxidation of silicon that had occurred in the furnace in the 13-minute interval from the furnace sampling to the tap. The amount was unknown, but even on an assumption of only 50 percent recovery from the first-ladle addition, the furnace recovery could not have exceeded 42 percent.

To summarize, silicon recovery in the furnace from a block of at least 0.10 percent silicon averaged close to 60 percent for blocking periods as much as 15 minutes duration when a lime-freeze was used upon the slag, but diminished considerably when a substantially longer blocking period was experienced. After a normal blocking period, heats that were treated with calcium-silicon alloy in the ladle during tapping showed a fairly uniform recovery of 65 percent from this agent, and if further subjected to a second addition during teeming into a second ladle, the recovery of silicon for that stage was close to 100 percent. The high levels of recoveries and the narrow spreads in the silicon concentrations resulting from the ladle additions suggested that the plunge-bomb technique by which the calcium-silicon alloy was added had operated successfully.

Carbon

The amounts of carbon that were contained as incidental carbon in the ferroalloys were apparently recovered completely, judging by calculations upon bath and ladle metal samples. This is in line with industrial experience.

Recoveries from ladle additions of anthracite could not be calculated precisely because the calculations depended in turn on estimates of carbon drop over the period from the last preliminary sample to the instant when the furnace was blocked. A reasoned evaluation of the data indicated that close to 80 percent recovery of carbon from anthracite probably would be experienced for the types of heats described in this report.