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Reducing Surface Hot Shortness of Copper-Containing Steels Using Silicon Additions and Controlled Reheating Conditions

By Mark I. Copeland
Albany Metallurgy Research Center, Albany, Oreg.

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A study was conducted by the Bureau of Mines to determine the effect of steel reheating practices in burning natural gas on the amount of silicon required to prevent the formation of copper on steels containing up to 1 wt-pct Cu. Formation of copper, which causes surface hot shortness, was readily prevented by as little as 0.3 wt-pct Si and by 2 vol-pct excess oxygen in the furnace atmosphere when reheating steels containing up to 0.8 wt-pct Cu. Up to 0.8 wt-pct Si content and carefully controlled reheating conditions were necessary for steels containing 1 wt-pct Cu. Best conditions for these steels were reheating to 2,200° F (1,205° C) in burning gases containing 2 vol-pct excess oxygen and then to higher temperature in gases of 6 vol-pct excess oxygen. Slag and mold wash were not detrimental on steels reheated for 8 hr by a soaking-pit-type furnace schedule, but they were on steels heated for 2 hr by a pusher-type furnace schedule. The effect of silicon contents on scaling rates also were determined.

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REDUCING SURFACE HOT SHORTNESS OF COPPER-CONTAINING STEELS USING SILICON ADDITIONS AND CONTROLLED REHEATING CONDITIONS

by

Mark I. Copeland[1]

ABSTRACT

This study was conducted by the Bureau of Mines to determine the effect of steel reheating practices in burning natural gas on the amount of silicon required to prevent the formation of copper on steels containing up to 1 wt-pct Cu. Formation of copper, which causes surface hot shortness, was readily prevented by as little as 0.3 wt-pct Si and by 2 vol-pct excess oxygen in the furnace atmosphere when reheating steels containing up to 0.8 wt-pct Cu. Up to 0.8 wt-pct Si content and careful control of reheating conditions were necessary for steels containing 1 wt-pct Cu. Best conditions for these steels were reheating to 2,200° F (1,205° C) in burning gases containing 2 vol-pct excess oxygen, and then to higher temperatures in gases of 6 vol-pct excess oxygen. Slag and mold wash were not detrimental on steels reheated for 8 hr by a soaking-pit-type furnace schedule, but they were problematical on steels heated for 2 hr by a pusher-type furnace schedule. The effect of silicon contents on scaling rates also was determined.

INTRODUCTION

The Bureau of Mines sponsored this research effort to improve the recycling capability of copper-containing scrap steels by eliminating the major drawback to their use, the formation of surface cracks during hot working. Because the oxides of copper have a lesser, negative free energy of formation than iron oxides, copper-rich, copper-iron alloys normally form on the surface of steel when heated in oxidizing atmospheres. The molten copper alloy, melting at 2,001° F (1,094° C), penetrates the steel grain boundaries and causes deep surface cracks during hot working. This cracking condition has been referred to as "surface hot shortness."

It was demonstrated that silicon additions to steel can be used to prevent the formation of molten copper alloys on the surface of steels during reheating (<u>1</u>).[2] Silicon was beneficial because of the formation of fayalite (Fe_2SiO_4) on the steel surface by internal oxidation of iron and silicon.

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[1] Metallurgist.

[2] Underlined numbers in parentheses refer to items in the list of references preceding the appendixes.

Solid fayalite did not prevent solid, copper-rich, iron-copper alloys from forming on the steel surface during scaling. However, solid copper-rich alloys (the alloy being usually referred to hereafter as copper) did not stay on the steel surface, but they passed through the fayalite layer into the scale proper as the steel surface receded during scaling. At a temperature between the melting temperatures of the copper-rich alloy and of fayalite, 2,200° F (1,204° C), molten copper as well as iron-rich, iron-copper particles were formed. The molten copper remained on the steel surface within this temperature span, but the iron-rich particles passed into the scale where they oxidized to FeO and Cu. Molten copper in the scale does not cause hot shortness. When sufficient silicon was added to the steel, molten fayalite penetrated the scale layers, as illustrated in figure 1, which promoted the formation of only iron-rich, iron-copper particles and the removal of the copper formed at lower temperatures. Limited heating studies of steels, using simulated industrial reheating schedules, demonstrated that the silicon content required to prevent copper formation on steels containing 1 wt-pct copper could be reduced by the use of large excess oxygen contents in the heating atmosphere.

In the present report, the results of studies on the influence of steel reheating schedules and steel adherents on the amount of silicon necessary to prevent copper formation are presented. Surface sections of small ingots were largely used while in the previous study forged steels were reheated (1). Reheating studies were conducted on steels containing up to 1 wt-pct Cu and Si. Steels containing 1 wt-pct Cu were studied more extensively than steels with lower copper contents because of the greater difficulty in preventing copper formation on them (1), and because steels containing 1 wt-pct and more copper are of increasing importance in high-strength, low-alloy steels. The steels were heated to 2,282° F (1,250° C) or 2,372° F (1,300° C) in burnt, natural gas atmospheres by pusher (continuous)- and soaking-pit-type heating schedules which simulated industrial ingot reheating practice. The heating rates, oxygen contents, and

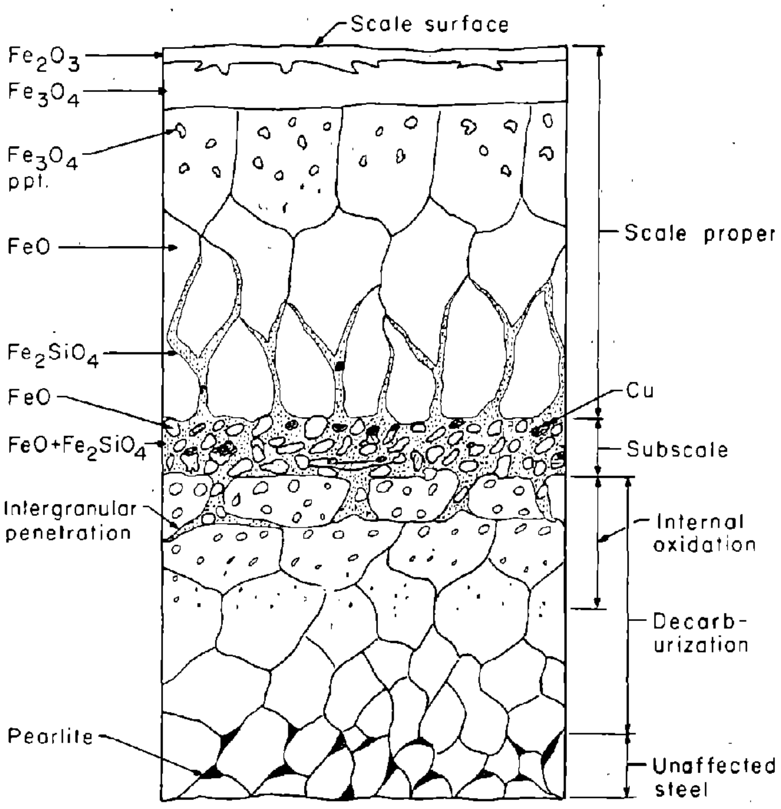

FIGURE 1. - Scale and steel structures at surface of steel heated to 2,372° F (1,300° C) and air cooled.

flow rates of the heating atmosphere, as well as the steel surface area heated were varied. Concurrently, the effect of coring (segregation), adherents (slag and mold wash) on the steel surface, and CO gas pores formed in the scale on the silicon contents necessary to prevent copper formation were evaluated. The effect of C, Cu, and Si additions on the scaling rate and on formation of copper on the steel surface were studied. Theoretical reasons for the beneficial action of molten fayalite in preventing copper formation were considered. Recommended reheating practices for preventing copper formation are presented.

ACKNOWLEDGMENT

The author wishes to acknowledge the laboratory and evaluation work conducted by Stephen A. O'Hare, metallurgist, during the scaling weight-gain determinations.

PROCEDURE

Small, 4-inch-square steel ingots were made and then sectioned, forged, and rolled. The 65-lb steel heats were induction melted, alloyed to desired content, aluminum-killed (1), and poured at 2,910° F (1,600° C) into alumina coated cast-iron molds. The chemical compositions of the steel heats are given in table 1. The 15-lb hot tops and two 5/8-inch-thick slices next to the hot top were cut from the ingots. The remaining ingot was hot forged and rolled to a 1/2-inch-thick plate by procedures previously described (1). Five-eighths-inch cubes were cut from the outside of the ingot slices for the scaling tests. Adhering mold wash, scale, and slag were removed by sandblasting the outside surface of a few cubes. Also, sanded 5/8-inch-square by 1/2-inch-thick specimens were prepared from the rolled plate.

TABLE 1. - Composition of steels

Heat No.	Content				Heat No.	Content			
	Cu	Si	C	Mn		Cu	Si	C	Mn
1............	1.08	0.17	0.22	0.43	11............	0.55	0.30	0.22	0.38
2............	1.08	.32	.20	.35	12............	.53	.58	.18	.46
3............	1.00	.42	.18	.42	13............	.57	.84	.20	.50
4............	1.02	.60	.20	.33	14............	1.09	.28	.18	.45
5............	1.12	1.08	.19	.37	15............	1.02	.72	.22	.52
6............	.83	.19	.22	.30	18............	1.01	.46	.32	.42
7............	.80	.27	.21	.42	17............	.28	.40	.32	.46
8............	.80	.58	.21	.46	16............	.12	.25	.22	.38
9............	.82	1.13	.21	.54	19............	.85	.35	.21	.45
10............	.56	.18	.21	.42					

The steel specimens were heated in air-natural gas combustion atmospheres using the electrically heated tube furnace previously described (1). The natural gas contained 97 vol-pct methane. Four specimens, placed together in a row, were spot welded on a type 310, stainless steel plate, which in turn was placed on a flat alumina plate with a round bottom to conform to the curvature of the furnace tube. The as-cast surface of specimens was placed on

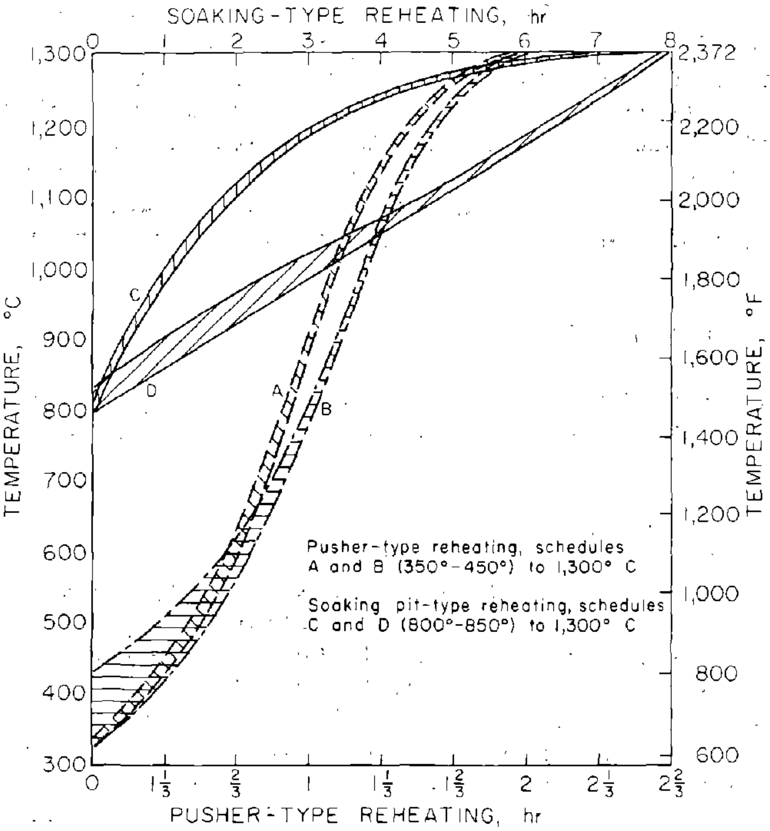

FIGURE 2. - Pusher- and soaking-pit-type reheating schedules.

the uppermost position of the assembly. The assembly, with the row of specimens perpendicular to the tube length, was placed in the tube at the location of the desired starting temperature. After reaching temperature, the assembly was advanced by hand pushing with an alumina rod into the hotter portion of the furnace tube. A Pt-Pt 13-pct Rh thermocouple spot welded to the top of one of the two center specimens was used for temperature measurement. Before inserting the assembly in the furnace, the air and natural-gas flow rates to the burner were adjusted to obtain the desired burnt-gas flow rate and excess oxygen content. The burnt gases, sampled at 2,282° F (1,250° C) near the furnace center, were analyzed for oxygen. The burnt-gas flow rates at 2,282° F (1,250° C) over the specimens were calculated from the natural-gas and airflow rates to the burner, the gas analyses, the temperature, and the cross-sectional area over the specimens in the tube.

The steel specimens were usually heated to 2,372° F (1,300° C) by pusher (continuous)- and soaking-pit-type schedules for 2 and 8 hr, respectively, which simulated industrial ingot reheating practices. These respective heating schedules are illustrated on curves B and D in figure 2. Curves A and C represent the pusher- and soaking-pit-type schedules, respectively, previously used (1) when the specimens were advanced in the furnace tube at a uniform rate with a motorized drive.

The scaled steel specimens were all evaluated metallographically. The scaled specimens were vacuum-pressure mounted in epon-type resin and then sectioned in a manner so that the leading and leeward edges (relative to burnt-gas flow) and top of the specimens could be examined. The specimens were remounted in Bakelite[3] and then sanded and polished by standard procedures using diamond abrasives. The polished specimens were examined microscopically

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[3] Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

for the presence of copper on the steel surface and for other structural features at the steel-scale interface. If copper was found any place at the steel's surface or interior, the heating experiment was judged to be negative, that is, the steel would be subject to surface hot shortness during hot working. Also, electron-beam microprobe analyses were conducted on several scaled and unscaled steels to determine the composition of the steel surface and the degree of coring (segregation).

The scaling rate of selected rolled steels was studied; the procedure and results are given in appendix A.

RESULTS AND DISCUSSION

Steels Heated to 2,372° F (1,300° C) by Two Reheating Schedules in Burnt Gases of the Same Oxygen Content and Flow Rate

The results of microscopic examination of cast and rolled steels heated to 2,372° F (1,300° C) by two pusher and two soaking-pit schedules are shown in figure 3. The surface of the cast steels was not sandblasted to remove adherents. The burnt gases in the furnace tube, at the 2,282° F (1,250° C) position, contained 2.0±0.2 vol-pct O_2 and had a flow rate of 2.23±0.10 ft/sec. From figure 3, the following are apparent:

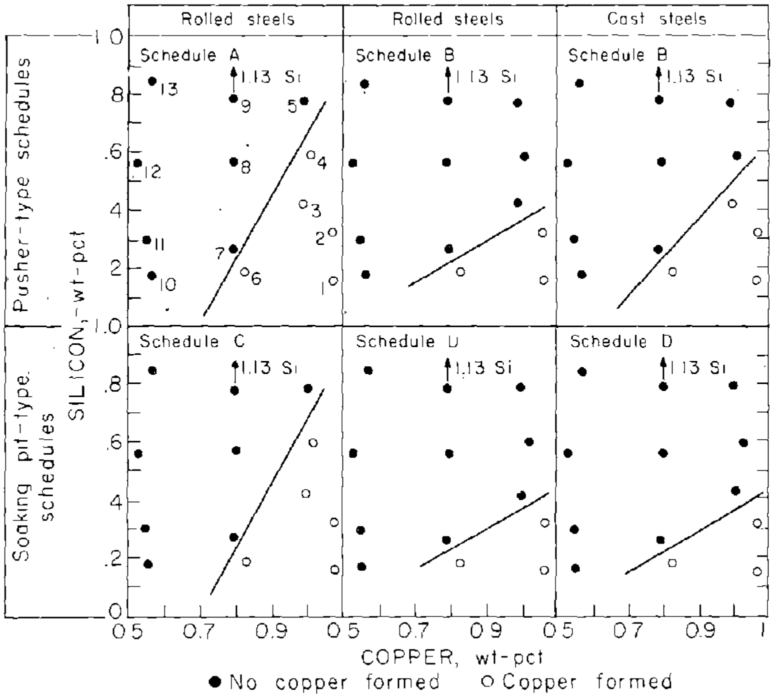

FIGURE 3. - Silicon contents required to prevent copper formation on steels when heated in burnt gases with oxygen content of 2.0 vol-pct and a velocity of 2.23 ft/sec.

1. Regardless of the heating method or rate or type of steel (cast or rolled), less than 0.18 wt-pct Si is required to prevent copper formation on steels containing about 0.6 wt-pct or less Cu. Between 0.19 and 0.27 wt-pct Si is necessary to prevent copper formation on 0.8 wt-pct Cu steels.

2. Considerably greater silicon content is necessary to prevent copper formation on steels containing about 1 wt-pct Cu. The amount of silicon required was dependent upon the type of steel as well as on the heating schedule, which is further discussed.

The amount of silicon necessary for rolled, 1 wt-pct Cu steels heated by schedules B and D was less than that required for heating by schedules A and C. By comparing these schedules in figure 2, it is apparent that the more linear the heating rate, the lower the silicon content required. The difference was believed to be due to the longer heating time and overheating occurring at the steel surface between 2,282° to 2,372° F (1,250° to 1,300° C) during heating by schedules A and C. When a temperature rise above the environment temperature occurs, copper as well as iron-rich, iron-copper particles form. Overheating was not detected by the thermocouple junctions spot welded to the specimens. As mentioned previously, the thermocouples remain on the outer portion of the scale, not on the steel surface, especially during the latter, higher-temperature portion of the scaling runs.

Less silicon was necessary to prevent copper formation on the unsanded, 1 wt-pct Cu, cast steels when heated by soaking-pit schedule D rather than by pusher schedule B. The difference was believed to be due to adherents and the much thicker scale formed on the steels heated by the soaking-pit schedule. The thicker scale resulted from the longer heating time. When the steels were heated by the pusher schedule, the copper was usually found under the adherents, which remained close to the steel surface. With the thicker scale, the adherents are at a greater distance from the steel surface; in this case, there is greater effective scale area present near the steel for transfer of oxygen from the scale surface to the steel.

Effect of Oxygen Content and Velocity of Heating Atmosphere on Preventing Copper Formation on 1 Wt-Pct Copper Steels Heated to 2,372° F (1,300° C)

The effect of burnt-gas flow rates and excess oxygen contents of the furnace atmosphere on the amount of silicon required to prevent copper formation on the surface of 1 wt-pct Cu steels is shown on the bar graph of figure 4. The surfaces of the cast specimens used were not sandblasted except for those in column 7. As determined at the 2,282° F (1,250° C) location in the furnace, burnt-gas flow rates of 1.23 to 4.57±0.10 ft/sec and of excess oxygen contents of 2.0 to 6.0±0.2 vol-pct were used. Four steel specimens were heated in each run except for those in columns 9 and 10, when two specimens were heated. The steels were heated to 2,372° F (1,300° C) by pusher schedule B and soaking-pit schedule D, as shown in figure 2.

Pusher Schedule Reheating of Cast Steels

The flow rate and excess oxygen content of the burnt gases affected the amount of silicon required to prevent copper formation on cast steels. The greater the flow rate and oxygen content of the burnt gases (columns 1 to 6 and 8), the less silicon was necessary. Simultaneously thicker scales on the steels were produced, which indicated that increasing the gas flow rates maintained a higher oxygen concentration at the scale surface. These factors indicated that steels heated by pusher-type schedules are very sensitive to oxygen contents at the steel surface.

With a burnt-gas flow rate of 2.23 ft/sec, the use of 2 vol-pct O_2 below 2,200° F (1,205° C) and 6 vol-pct O_2 above the temperature (column 8) appeared

Column		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
SILICON, wt-pct	Heat No. 4	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
0.6	3	○	○	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
.4	2	○	○	○	○	○	●	○	●	○	○	●	●	●	●	○	○	○	○
.2	1	○	○	○	○	○	●	○	●	○	○	○	●	●	●	○	○	○	○
Furnace gas	FLOW RATE, ft/sec	1.23	2.23	3.45	4.57	1.23	4.57	2.23 1/	2.23	2.23 4/	2.23 3/	1.52	4.57	1.52	4.57	1.52	4.57	1.52	4.57
	O_2, vol-pct	2				6		2	2+6 2/	2	2	2		6		2		6	
No. specimens heated		4								2		4				4			
Steel		Ingot section										Rolled section				Ingot, section			
Heating method		Pusher-type														Soaking pit-type			

● No Copper on surface ○ Copper on surface

1Sandblasted.
2Using 6 vol-pct O_2 above 1,200° C.
3Platinum cubes at first and fourth specimen positions.
4Two specimens per scaling run, placed in second and third positions.

FIGURE 4. - Effect of reheating schedule, furnace-gas oxygen content and velocity, and steel condition, surface area, and silicon content on preventing copper formation on 1 wt-pct copper steels.

to be as effective as when using 6 vol-pct O_2 and a high gas flow rate of 4.57 ft/sec during the entire heating operation (column 6). This observation would indicate that excess oxygen contents in the burnt gases are only effective above 2,200° F (1,205° C) when fayalite becomes molten.

The effect of exposed steel surface area on the amount of silicon required can be noted by comparing columns 2 and 9. In both columns, 2 vol-pct O_2 and a flow rate of 2.23 ft/sec of the burnt gas were used. Comparison of the columns showed that less silicon was necessary when the surface area of the steels heated were smaller (column 9). This observation and the thicker scales formed on the steels in column 9 indicated that more oxygen was available to the surface of the steels with a smaller surface area. To determine whether the lower silicon requirement for the steels with less surface area was due to a change in gas flow (turbulence) over the specimens, platinum cubes (made from foil) were placed in the missing positions (column 10). As can be observed by comparing columns 9 and 10, no change in the silicon content was required to prevent copper formation.

Pusher Schedule Reheating of Rolled Steels

The flow rate and oxygen content of the burnt natural gases did not significantly affect the quantity of silicon required to prevent copper formation on rolled steels. In fact the amount of silicon required was less than 0.2 wt-pct, except for the steels heated in the burnt gas (column 11) with a 2 vol-pct O_2 and a 1.52 ft/sec flow rate. The low silicon content necessary, in comparison to that for cast steels, was believed to be due to the lack of adherents on the steel surface.

Soaking-Pit-Schedule Reheating of Cast Steels

Variation in flow rate or oxygen content of the burnt gases did not affect the amount of silicon required to prevent copper formation on unsanded cast steels containing 1 wt-pct Cu (columns 15 to 18). The steel surface is not as sensitive to adherents, as explained earlier, or to variations in the oxygen concentration available at the steel surface when a thick scale is formed, a condition that was found in all steels heated by the soaking-pit schedules.

Heating Cast Steels to 2,282° F (1,250° C) Rather Than 2,372° F (1,300° C)

A limited number of reheating runs to 2,282° F (1,250° C), using both pusher schedule B and soaking-pit schedule D, were made on cast steels 1 to 5 (table 1) containing 1 wt-pct copper. The oxygen content and gas flow rate of the heating atmosphere were maintained at 2.0 vol-pct and 2.23 ft/sec, respectively. The heating runs were made because it may not always be desirable to reheat to as high as 2,372° F (1,300° C); and, holding for extensive times at this temperature (such as in soaking-pit furnaces), can cause the formation of copper as well as iron-rich, iron-copper particles at the steel surface.

The results of the heating tests are given in table 2. As can be noted, copper was present on all the steels when heated to 2,282° F (1,250° C). The presence of copper was believed to be due to the insufficient heating time above 2,200° F (1,205° C) to remove the copper formed between 2,000° F (1,094° C) and 2,200° F (1,205° C), and the fact that molten fayalite is not nearly as active in forming iron-rich, iron-copper particles between 2,200° F (1,205° C) and 2,282° F (1,250° C) as it is at higher temperatures. Holding for 30 minutes at 2,282° F (1,250° C) by either heating schedule removed the copper formed on steel 4 containing 0.6 wt-pct Si but not on those with lower silicon contents. When heating steels by pusher-type furnaces, holding at any temperature is not very practical. Therefore, steels heated by pusher furnaces should be heated above 2,282° F (1,250° C) to prevent copper formation. If it is necessary to heat steels in soaking-pit-type furnaces to above this temperature, the oxygen content of the furnace atmosphere should be reduced to low levels on reaching the desired temperature to prevent surface overheating due to excessive oxidation, which causes copper formation.

TABLE 2. - Metallographic observations of steels heated to 2,282° F (1,250° C)

Heating run	Reheating condition		Steels on which copper formed			
	Heating schedule	Time held at 2,282° F, min	1	2	3	4
19	Pusher schedule B.......	None	Yes	Yes	Yes	Yes
20	.....do.................	18	Yes	Yes	Yes	Yes
21	.....do.................	30	Yes	Yes	Yes	No
22	Soaking-pit schedule D..	None	Yes	Yes	Yes	Yes
23	.....do.................	30	Yes	Yes	Yes	No

Location of Copper on Steel Surfaces

Copper, when formed, was observed on the steel surface at sharp edges or corners, between grain boundaries on the steel surface, but never at the surface-grain boundary intersection.

The formation of copper at sharp edges or corners was believed to be due to a temperature rise occurring at these locations above its surroundings. As previously explained, copper, as well as iron-rich, iron-copper particles, could form when the heat of oxidation could not be dissipated, especially when heating above 2,282° F (1,250° C). The temperature rise at the sharp edges was probably caused by a high ratio of the surface area to the effective steel area with which to internally dissipate the heat. The formation of copper was found to be preventable by grinding a 1/8-inch-radius curve on the steel edges and corners, which was done on most of the work conducted in this report.

Copper was also found on the steel surface between prior austenite grain boundaries. The function of the steel adherents and scale thickness on copper formation was previously discussed. Also, copper was infrequently found under CO bubbles formed in the scale next to the steel surface. The CO bubbles were formed by oxidation of the steel's carbon content. The only detrimental function of the bubbles was believed to be restriction of transmittal of oxygen to the steel surface. Because a greater quantity of CO bubbles would be generated with steels containing higher carbon contents than those used (0.2 wt-pct), high carbon contents may become a restricting factor in preventing copper formation.

The copper occurring between the austenite grain boundaries on the steel surface was usually found to consist of groupings of molten copper and iron-rich, iron-copper particles. A typical grouping (copper being the lighter phase) is illustrated on the steel surface at the left side of figure 5; normal structures, when only iron-rich particles are forming, are shown on the right side. Cox (2) noted that steels with these surface groupings, which he referred to as "mushy" copper, are not subject to surface cracking. If this "mushy" copper does not cause cracking, then less silicon contents and less rigid heating conditions would be necessary than found in the present study. However, the author (Copeland) prefers to consider any molten copper on the steel surface to be potentially detrimental.

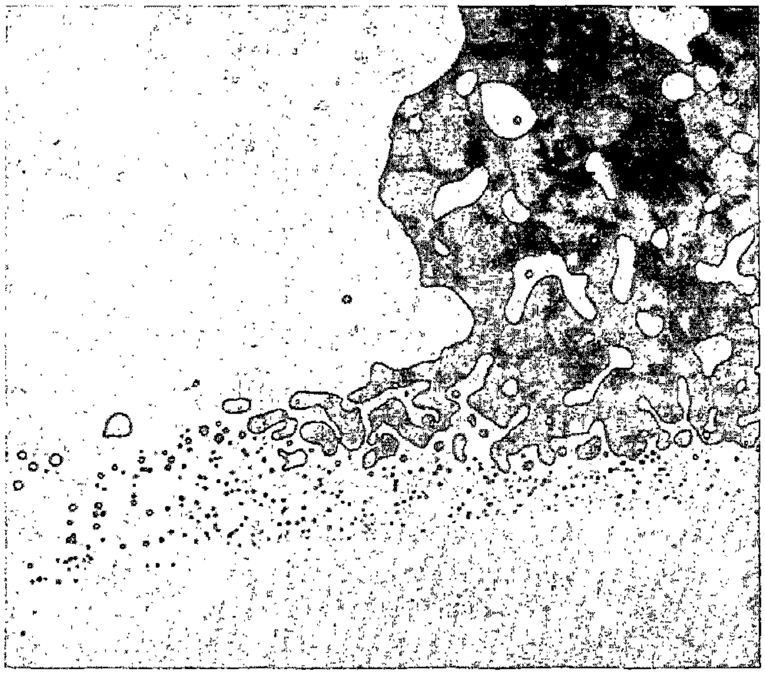

FIGURE 5. - Molten copper in a "mushy" state on the steel surface (X 500).

For the steels heated, coring (segregation) was not believed to be a significant factor in forming copper on the steel surface. Comparison in figure 2 of the amount of silicon required to prevent copper formation on rolled and cast, 1 wt-pct Cu steels after heating by soaking-pit schedule D would indicate this conclusion. This conclusion is further substantiated by comparison of cast (sandblasted) and rolled steels of the same copper content heated by pusher schedule B. Microprobe analyses were made near the surface of the cast ingots before and after heating, by pusher schedule B, to 2,200° F (1,205° C). Very little segregation was found after heating the steels. In contrast, considerable segregation, which is shown in table 3, was noted in unheated cast steels. As can be observed by comparing steels 15 and 19, increasing silicon contents decreased the amount of segregation. This may account for one of the beneficial aspects of increasing silicon contents.

TABLE 3. - Typical contents of ferrite and pearlite near surface of cast, 0.2 wt-pct carbon steels

Steel and location	Content by microprobe analysis, wt-pct		
	Si	Mn	Cu
Steel 19 analysis........	0.35	0.45	0.85
Ferrite...............	0.28-0.48	0.44-0.68	0.73-1.72
Pearlite..............	.36- .48	.44- .73	1.50-3.52
Steel 15 analysis........	0.72	0.52	1.02
Ferrite...............	0.58-0.80	0.42-0.75	0.89-1.15
Pearlite..............	.62- .89	.44- .80	.93-1.80

Action of Molten Fayalite

The method whereby molten fayalite promotes the formation of iron-rich, iron-copper alloys instead of copper on the steel surface is questionable. It is questionable because copper is removed from the steel surface at the same rate as iron after the copper content at the steel surface attains a value usually less than the solubility limit of copper in iron at high temperatures.

Certainly copper is not oxidized by contact with FeO, the oxide contacting the steel surface, since the negative free energy of formation of copper oxides is less than that for FeO.

The beneficial properties of molten fayalite may be due to electrolytic cell action which occurs in the scale and transports the copper and iron away from the steel surface, as illustrated in figure 6, of the following type is suggested:

FeCu alloy-molten fayalite-oxygen.

The anodic portion of the cell action would occur at the steel surface and the cathodic at the scale surface. For cell action to occur, oxygen ions as well as cations must exist in the molten fayalite. Cations were known to be present in molten silicates, but the occurrence of oxygen ions was not previously established. However, recent evidence, as summarized by Masson (5), indicates that they do occur by polymerization of silicate ions.

The cell action may be similar to that discussed by Ilschner-Gensch (3) for a nickel-molten borate-oxygen cell. When a piece of nickel was covered by molten borate under an oxygen atmosphere, virtually no oxidation occurred. The nickel was rapidly oxidized when a platinum conductor was extended from the oxygen-molten borate interface to the nickel. The accelerated nickel oxidation was explained by cell action whereby electron flow occurred in the platinum gauze, and ion migration occurred in the molten borate.

Potential for cell action of the same type as proposed by Ilschner-Gensch in scale containing molten fayalite can be observed in figure 1. This figure illustrates typical structures formed in unfractured scales when molten fayalite is present. Ionic mobility is afforded by the molten fayalite penetrating along iron-oxide grain boundaries, and electron flow by continuous contact of iron-oxide grains from the steel to scale surface. For the $1/2\ O_2 \longrightarrow O^{2-} + 2e$ cathode portion of the cell reaction to occur, the molten fayalite must penetrate the scale and contact the furnace atmosphere. And, contact was observed in all the scales examined for steels on which copper did not form. Penetration of the molten fayalite to the scale surface was observed on thin scales formed on steels heated for 2 hr by the simulated pusher-type heating schedule. However, usually the scale separated into two distinct scale layers. The separation occurred in the thicker FeO layer at the outer extremities of the

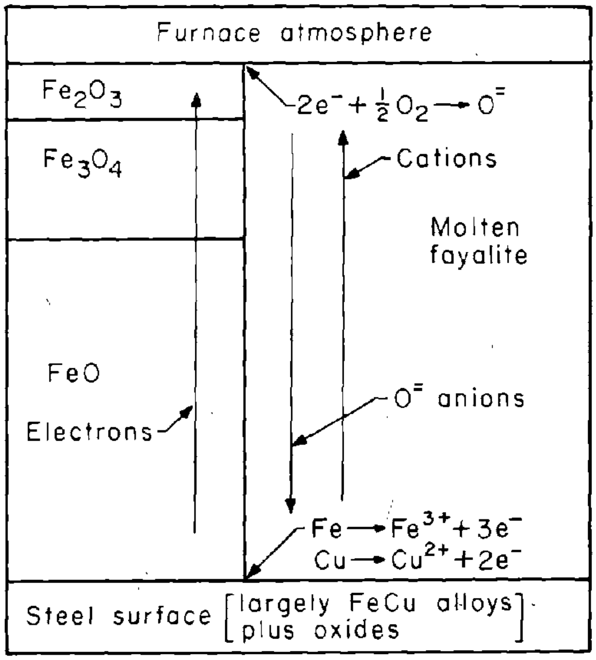

FIGURE 6. - Alloy FeCu-fayalite-oxygen local cells in scale.

molten fayalite penetrations in the FeO layer. During separation into two distinct layers, the inner layer remained continuous while the outer layer became fragmented. Fragmentation allowed access of the furnace atmosphere to the inner scale surface. Contact of the atmosphere with the inner scale was demonstrated by the Fe_2O_3 formed on its surface.

By electron-beam microprobe analysis of unbroken scales formed on steels containing 1 wt-pct copper, the same copper content as the steel was found immediately under the Fe_2O_3 layer while elsewhere it was less than 0.06 wt-pct. Also, copper silicate, determined by X-ray diffraction, was found to be the major constituent in a glassy formation occurring at times on the scale surface. Copper concentration at the scale surface of this large a value would be difficult to explain by any other method than cathodic reduction of cupric ions.

Other phenomena were observed during scaling which also may be explained by cell action, for instance, the accelerated scaling rates observed and the formation of copper at places on the steel surface when temperature increases occurred in the scale above the surrounding environment. The temperature increases occurred when stainless steel sheet sections were not spot welded to the steel specimens and when the steels were heated for long times above 1,250° C, such as by the simulated soaking-pit schedule for 8 hr. The temperature rise probably increases the fluidity of fayalite, which in turn increases the rate of oxidation due to the increased mobility of the ions in the fayalite. Copper formation at discrete locations on the steel surface may be due to local cell action along the steel surface becoming an important factor. Local cell action may be due to composition variations in the fayalite along the steel surface and/or differences in activities of exposed austinitic grains caused by crystallographic orientation or composition.

Scaling-Weight-Gain Measurements

The scaling-weight-gain measurements in appendix A were made largely to determine how silicon additions affected scaling rates and copper formation on steel surfaces when heated in oxidizing atmospheres. Of secondary importance was the affect of carbon and copper.

The scaling rates (the derivative of the equations in table A-1) for each of the steels at 1,922° to 2,282° F (1,050° to 1,250° C) are plotted in figure 7 on an Arrhenius type grid. From the figure, the following features predominate:

1. A minimum scaling rate occurs at 2,012° F (1,100° C), which is slightly above the melting point of copper. The minimum is probably due to molten copper-rich alloys forming on the steel, which restricts transfer of oxygen from the wustite (FeO) to the steel surface. Although the formation of molten copper is undesirable and unpreventable at this temperature, it does reduce the rate of further copper formation.

2. The scaling rates of steels increase with rising temperatures, which is normal. Also, the scaling rates at each temperature are similar, except

when runaway scaling rates occur [steel 15 at 2,102° F (1,150° C) and steels 15 and 18 at 2,192° F (1,200° C)].

3. The effect of silicon on the scaling rate is very pronounced. In general, increasing silicon contents lowers the scaling rate provided that the heat of oxidation can be dissipated. The lower scaling rate, especially below 2,200° F (1,205° C) when fayalite is solid, is believed to be due to a greater volume of fayalite forming on the steel surface and the poor oxygen- and/or iron-transport properties of fayalite. When platinum foil is not spot welded to the steels containing larger silicon contents to dissipate the heat of scaling, the steels with the greater silicon contents have the large scaling rates. Copper then forms on the steels.

The large scaling rate of steel 15 at 1,922° F (1,150° C) was not initially understood. However, when a thermocouple was spot welded to a small area ground through the scale to the steel, after scaling a specimen in CO_2 for 1 hr at 1,922° F (1,150° C) and then reheated at the same temperature, temperatures as high as 2,228° F (1,220° C) were recorded. At this temperature, fayalite would be molten.

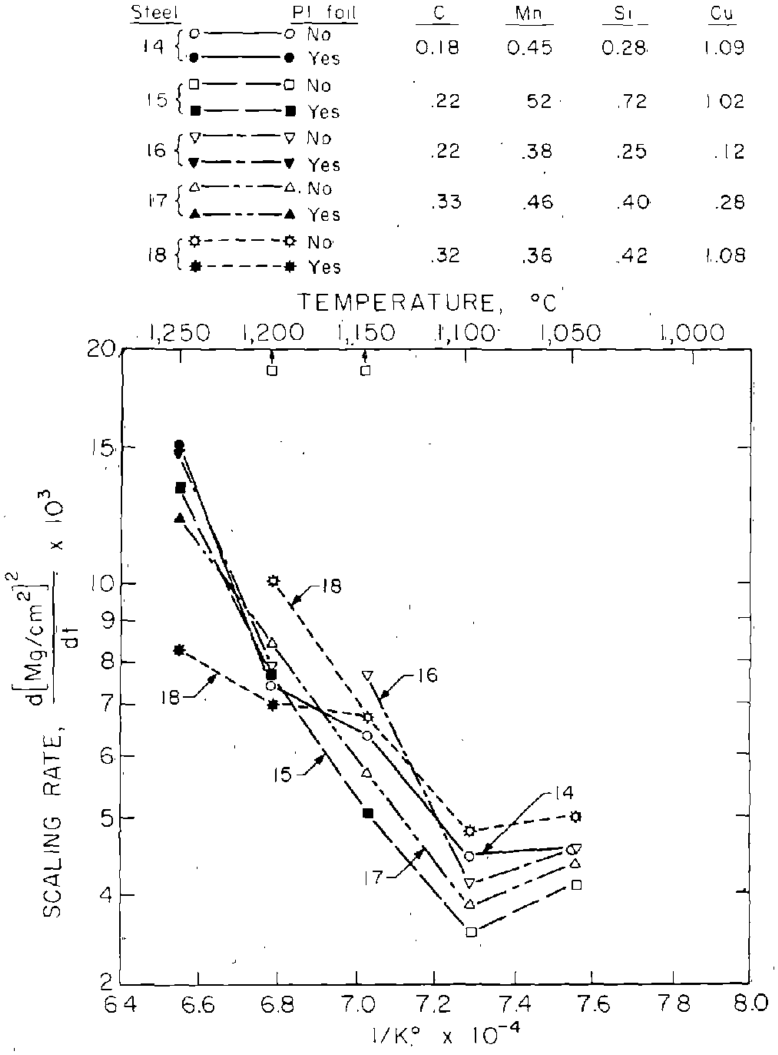

FIGURE 7. - Scaling rates of selected steels.

After making the observation described in the preceding paragraph, time-temperature measurements were made to determine whether the melting temperature of the fayalite formed on the steels used was near 2,200° F (1,205° C), the reported value for Fe_2SiO_4 (5). The ends of Chromel and Alumel wires were spot welded to opposite sides of sanded, 1/2-inch cubes made from the steels scaled. The assembly was suspended by the Alumel and Chromel wires in a furnace containing flowing CO_2. Then the specimens were heated at 2,012° F (1,100° C) for 6 hr to form a scale under the wires and sufficient fayalite to determine its melting temperature. The furnace was evacuated and the temperature of the Chromel-steel-Alumel junctions were recorded on a strip recorder while the furnace temperature was cycled between about 2,102° to 2,282° F (1,150° to 1,250° C). Thermal anomalies, indicating fayalite melting, occurred at 2,192° and 2,214° F (1,200° and 1,212° C) on cooling and heating, respectively. No other phase change could occur at these temperatures.

4. No definite effect of copper and carbon additions on the scaling rate could be observed. Variations in silicon contents overshadowed any effect of carbon and copper.

Effect of Fayalite on Steel Surface Quality and Copper Formation During Hot Working

The effect of adhering fayalite on the surface quality of the steels was studied during hot rolling of the ingots. Adherence of the fayalite was of concern since it is next to the steel surface and it may roll into the surface, which would cause surface roughness. But, fayalite adherence was not observed on the surfaces of the steel plates made, either by visual or metallographic examination. Scale formed during rolling and some surface roughness occurred on the rolled plates. However, the surface roughness probably could be minimized by spraying water on the hot steel just ahead of the roll entrance to remove the scale formed.

Copper concentration at the steel surface during hot rolling probably cannot be prevented. Prevention of copper concentration by fayalite during hot rolling is not possible for two reasons: (1) The fayalite formed appears to be almost completely removed during each rolling pass; and (2) the steel surface temperature usually decreases rapidly to temperatures where prevention of copper concentration by any fayalite formed is not complete. Whether molten copper forms or not depends upon the copper content at the steel surface at the start of rolling, as well as the rate at which the steel surface temperature is decreasing. As shown previously (1), the maximum amount of copper formed on 1 wt-pct copper steels was 7.5 wt-pct after heating to 2,372° F (1,300° C). This is considerably lower than the maximum solubility of copper, 12.2 wt-pct, in iron at 2,360° F (1,293° C), as shown in table 4. Molten copper may tend to form because of scaling and decreasing solubility of copper in iron, which is about 8.8 wt-pct at 2,020° F (1,105° C) and which is close to the melting temperature of copper-rich iron-copper alloys. However, there must be sufficient time for copper to diffuse to the steel surface and form metallic copper, even if the copper content near the steel surface exceeds its solubility in iron. Whether molten copper forms or not while using any particular rolling schedule would require study.

TABLE 4. - Solubility of copper in austenite[1]

Temperature		Copper, wt-pct
° F	° C	
2,020	1,105	8.8
2,170	1,191	10.5
2,360	1,293	12.1

[1] O'Hare, S. A., P. Romans, and M. I. Copeland. The Solubility of Copper in Iron From 1,094° C to 1,300° C. 9 pp.; available for consultation at Albany Metallurgy Research Center, Bureau of Mines, Albany, Oreg.

SUMMARY

Molten copper, which causes surface hot shortness during hot working, can be prevented from forming on the surface of steels containing up to about 1 wt-pct copper during reheating in burning gaseous atmospheres. Copper is readily prevented from forming on steels containing up to 0.8 wt-pct copper by use of up to 0.3 wt-pct silicon addition to the steel and 2 vol-pct excess oxygen in the furnace atmosphere. To prevent copper formation on steels containing more copper, silicon additions of up to 0.8 wt-pct and 6 vol-pct excess oxygen in the furnace gases are necessary on heating above 2,200° F (1,205° C).

The best reheating conditions to employ depend on the type of furnace used. However, regardless of the type of furnace used, use of low excess oxygen contents below 2,200° F (1,205° C) and uniform rates of heating are best to restrict scale and copper formation. When using pusher (continuous) type furnaces, it appears to be necessary to heat the steels to 2,372° F (1,300° C) to prevent formation of copper. Heating to 2,282° F (1,250° C) appears to be best when reheating steels in soaking-pit-type furnaces. Copper formation, which is due to overheating at the steel surface, is likely when holding ingots for lengthy times above this last temperature. If heating to and holding at 2,372° F (1,300° C) is necessary, the oxygen content of the furnace atmosphere should be maintained as low as possible upon reaching that temperature. Recommended reheating practices are outlined in appendix B.

Copper formation can occur under ingot adherents (mold wash and slag) during reheating. Formation of copper is most likely when thin scales are formed. The adherents remain close to the steel surface and restrict oxygen transfer to the steel surface, which promotes copper formation. Larger silicon contents, about 0.2 wt-pct more, are then necessary to offset their effect.

Like adherents, carbon monoxide bubbles formed in the scale by oxidation of the steel's carbon content, can restrict oxygen transfer to the steel surface. The larger the carbon content of the steel, the more likely that this action may occur. Bubble formation, however, was seldom observed during reheating of 0.2 wt-pct carbon steels.

Coring (segregation) on the steel surface presented no problem, insofar as promoting copper formation, during reheating of surface sections of 4-inch-square ingots. Coring, which should be studied, may present a problem for larger ingots.

Prevention of copper formation during reheating of steels by silicon additions is due to the formation of fayalite (Fe_2SiO_4) by internal oxidation of iron and silicon on the steel surface. Below the fayalite melting temperature, 2,200° F (1,205° C), when it remains on the steel surface, the benefit derived depends upon the temperature. The solid fayalite prevents solid copper from remaining on the steel surface. Solid fayalite does not prevent molten copper from forming on the steel surface, but it does restrict the amount formed because of the poor oxygen transport qualities of fayalite. Also, solid fayalite promotes the formation of iron-rich, iron-copper particles on the steel surface by agglomeration of FeO and Fe_2SiO_4 formed in the internal oxidation zone and by their encasement of iron-rich particles at the steel surface. Molten fayalite, which penetrates the scale grain boundaries to the scale surface, promotes the removal of copper formed below 2,200° F (1,205° C) and the formation of only iron-rich, iron-copper alloys on the steel surface. Larger fayalite contents are beneficial at all temperatures.

The beneficial properties of molten fayalite are believed to be due to FeCu alloy-fayalite-oxygen local cell action in the scale. In this cell action, oxygen concentration at the scale surface, amount of fayalite, and temperature are important factors in preventing copper formation. Oxygen concentration can be controlled by increasing the oxygen content, the velocity of the furnace gases, and by reducing the exposed steel surface area. With higher silicon contents, larger amounts of fayalite are produced; this action promotes oxygen transmittal by penetrating closer to the scale surface. Increasing temperatures are beneficial provided that the heat of scaling at the steel surface can be dissipated into the steel being heated. When the steel and heating-atmosphere temperatures become similar, copper can form if the steel is not removed from the furnace or if the heating atmosphere contains greater than 2 vol-pct excess oxygen.

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APPENDIX A.--SCALING-WEIGHT-GAIN MEASUREMENTS

Scaling studies were conducted on four hot-rolled steels. The following combinations of two steels were selected to evaluate the effect of varying C, Si, and Cu contents:

Element evaluated	Two steels used	Contents, wt-pct						
		Variable			Constants			
		Si	Cu	C	C	Mn	Si	Cu
Silicon	14	0.28	-	-	0.18	0.45	-	1.09
	15	.72	-	-	.22	.52	-	1.02
Copper	16	-	0.12	-	.22	.38	0.25	-
	14	-	1.09	-	.18	.45	.28	-
Carbon	14	-	-	0.18	-	.45	.28	1.09
	18	-	-	.32	-	.42	.4	1.01

Except when copper was the variable, steels with about 1 wt-pct Cu were selected, since steels with this copper content were the most difficult on which to prevent copper formation.

Test coupons for the scaling-rate tests were prepared from 0.2-inch-thick, hot-rolled steels. The coupons, measuring 1.00 by 0.50 by 0.15 inches, were prepared with a surface grinder, using a magnetic chuck and sufficient water to prevent "burning." After grinding, the surfaces of the coupons were lightly finished by hand on -600 grit paper. Platinum foil, 0.003 inch thick, was spot welded extensively to cover one large facet of a few of the coupons heated at 1,150° and 1,200° C and all the coupons heated at 1,250° C. The purpose of the platinum foil was to maintain the temperature of the steel specimen at about the same temperature as the surrounding furnace air. When this was not done, the temperature of the steel at the beginning of scaling runs was found to be greater by up to 70° C for steels with high silicon contents at 1,150° and 1,200° C and for all the steels at 1,250° C. The conductive foil accelerates equalization of the furnace atmosphere and steel temperatures by preventing a poorly conductive scale from forming. Normally when heating real ingots to temperature, the exothermic heat of scaling is dissipated into the steel.

The test coupons were suspended in a vertical tube furnace from an automatic-recording, thermogravimetric balance. For suspension, a platinum wire was spot welded to one edge of the specimen, which was positioned next to a thermocouple in the center of the furnace tube. The specimens were heated at temperatures of 1,050° to 1,250° C, in 50° C intervals, for up to 4 hr. The platinum-platinum 13-pct rhodium thermocouple was used to control the test-coupon temperature. By use of the same type of thermocouple spot welded to a few specimens, the temperature of the specimens was found to vary no more than ±10° C from the desired temperature, except when runaway scaling rates were found. Airflow in the furnace tube was restricted sufficiently to prevent measurable buoyancy of the specimens, but not enough to prevent scaling at a rate that occurs without the restrictions.

Scaling-rate equations, which were based on the original surface area of the specimens, were calculated from the parabolic-type curves found for each of the steels at all temperatures. Weight gains (mg/cm^2) were calculated, and the time in minutes was recorded for selected points on the parabolic curves. From the square of the weight gain and the time, linear equations of the form $[\mathrm{Mg/cm^2}]^2 = A + Bt$ were derived by least-squares analysis of the data. The equations derived are given in table A-1 and plotted in figure 7.

TABLE A-1. - Scaling-weight-gain equations, $[\mathrm{Mg/cm^2}]^2 = A + Bt$[1]

Temperature, ° C	Steel	A + Bt	Temperature, ° C	Steel	A + Bt
1,050	14	0.220 + 0.045 t	1,200	14	1.619 + 0.074 t
	15	-.271 + .040 t		15	2.966 + .367 t
	16	-.006 + .045 t		[2]15	.855 + .075 t
	18	-.032 + .050 t		16	.543 + .077 t
				18	1.005 + .102 t
1,100	14	-.259 + .044 t		[2]18	.098 + .069 t
	15	-.373 + .035 t			
	16	-.202 + .041 t	1,250	[2]14	.560 + .140 t
	18	-.333 + .048 t		[2]15	3.672 + .132 t
				[2]16	3.181 + .147 t
1,150	14	.621 + .063 t		[2]18	.135 + .082 t
	15	.386 + .238 t			
	[2]15	.166 + .050 t			
	16	.165 + .075 t			
	18	1.836 + .066 t			

[1] t is time in minutes, A and B are constants.
[2] Platinum foil spot welded to specimens.

APPENDIX B.--RECOMMENDED REHEATING PRACTICES

Based on the present and a previous (2)[1] study, the following reheating practices are recommended to prevent copper formation on up to 1 wt-pct copper steels when using burning gaseous atmospheres.

1. In both pusher (continuous) and soaking-pit-type furnaces--

a. Reheat at fairly uniform rate to the desired hot working temperature.

b. Expose all surfaces of steel to be hot worked to a heating atmosphere having good gas circulation.

c. Heat steels up to about 2,000° F (1,205° C) in burning gases containing 2 vol-pct excess oxygen before heating to higher temperatures.

2. In pusher-type furnaces--

a. Heat steels to 2,372° F (1,300° C) and then remove from the furnace.

b. On heating to temperatures above 2,000° F (1,205° C), use 2 vol-pct oxygen in the furnace atmospheres for steels containing up to 0.8 wt-pct copper and 6 vol-pct oxygen for steels containing more copper.

3. In soaking-pit-type furnaces--

a. Use the same amount of excess oxygen in furnace atmosphere as given in 2b when heating above 2,000° F (1,205° C).

b. Heat steels to 2,282° F (1,250° C) and hold at this temperature 30 minutes prior to removal, or heat steels to 2,372° F (1,300° C) and hold until removal.

c. Reduce excess oxygen content of furnace gases to 2 vol-pct, if not already at this level, when the furnace reaches the maximum temperature at which the holding period starts.

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[1] Underlined number in parentheses refers to item in the list of references preceding the appendixes.