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# Preventing Formation of Copper Alloys of Tin, Antimony, and Arsenic on Steel Surfaces During Reheating To Reduce Hot Shortness

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Bureau of Mines scientists discovered that up to 1.0 pct silicon and 0.1 pct Ni additions to steel would prevent the formation of copper alloys of tin, antimony, and arsenic on the surface when reheating to 1,300° C. The steels containing up to 1.0 pct Cu and 0.3 Sn, 0.2 Sb, or 0.1 As, were reheated in natural gas-air combustion atmospheres containing 2 vol pct excess oxygen. Molten copper alloys are detrimental as they penetrate the steel surface grain boundries during hot working which can result in the formation of deep surface cracks. Theories for the beneficial properties of silicon and nickel additions were discussed.

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# PREVENTING FORMATION OF COPPER ALLOYS OF TIN, ANTIMONY, AND ARSENIC ON STEEL SURFACES DURING REHEATING TO REDUCE HOT SHORTNESS

by

Mark I. Copeland[1] and John S. Howe[2]

## ABSTRACT

The Bureau of Mines discovered that silicon and nickel additions can prevent the formation of copper alloys of Sn, Sb, and As on the surface of steel during reheating to hot-working temperatures. When molten, these copper alloys cause surface hot shortness during hot working. Wrought steels were reheated isothermally and by simulated industrial practice; the resulting surfaces were metallographically evaluated. The steels contained, in weight-percent, 0.20 C, 0.45 Mn, and up to 1.00 Si, 1.00 Cu, and 0.15 Ni, and up to 0.30 Sn, Sb, or As. The larger the Cu, Sn, Sb, and As content of the steels, the greater the amount of silicon necessary to prevent copper alloy formation. A content of 0.10 Ni considerably decreased the amount of silicon necessary for copper steels containing tin and antimony, but not for those containing arsenic. Theories for the beneficial effect of silicon and nickel additions are presented.

## INTRODUCTION

The segregation of the residual elements Cu, Sn, Sb, As, and Ni on the steel surface during scaling has received increasing attention. As a result of their nobility, they concentrate next to the steel surface and segregate as copper-rich alloys on the surface as the steel scales. In steel scrap processing, copper-rich alloys usually form because the copper content is greater than Sn, Sb, or As. The molten copper alloys tend to penetrate the austenite grain boundaries during hot working and cause surface fissures, commonly referred to as surface hot shortness.

Studies have been conducted on the surface concentration behavior of the residual elements during scaling, on the effect of Sn, Sb, and As on the solubility of copper in austenite, and on the surface energy of molten copper and its alloys in contact with iron. The residual elements all concentrate at the steel surface in a similar manner, as shown by Kosec (4).[3] When copper

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[1] Metallurgist.

[2] Physical science technician.

[3] Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

forms on the steel surface, Kosec also found that tin and antimony preferentially concentrate in the copper, but arsenic tends to concentrate more in the internal oxidation zone (IOZ) between the copper-rich phase and the steel matrix. Salter (7) and Melford (5) observed that tin lowered the solubility of copper in austenite. Antimony and arsenic also lowered the solubility of copper (6), although not as extensively as tin. Nickel, also a residual element, tended to slightly offset the effect of antimony or arsenic. Salter (7) also found that the dihedral wetting angle of molten copper at the austenite grain boundaries was affected by Sn, Sb, and As. Grain boundary penetration is inversely proportional to the dihedral angles. The measurements also indicated that the dihedral angle tended to be minimum at about 2,012° F (1,100° C) for molten copper-iron alloys and molten copper-rich alloys of Sn, Sb, As, and Ni.

Silicon additions were observed by Copeland and Kelley (2) and Cox (3) to reduce copper-rich, iron-copper alloy formation (usually referred to hereafter as copper) on steel during reheating to 2,012° to 2,372° F (1,100° to 1,300° C). Silicon was beneficial because of the formation of fayalite (the mineralogical name for $Fe_2SiO_4$) on the steel surface. All of the fayalite, formed by internal oxidation of iron and silicon, remained on the steel surface except when molten. Copeland and Kelley (2) and Cox (3) found that solid fayalite did not prevent the formation of copper, but it did reduce the amount formed. On the other hand, Copeland and Kelley found that molten fayalite (mp 2,200° F [1,205° C]) would completely prevent copper formation, provided sufficient silicon was added to the steel. Typical structures observed at the steel-scale interface in these previous studies are illustrated in figure 1. Iron-rich, iron-copper particles, but no copper, were found on a steel containing 0.8 Cu and 0.6 Si after heating in air at 1,220° C for 4 hours.[4] The amount of silicon required depended upon the copper content of the steel. Subsequently, Copeland (1) found that uniform rates of reheating and control of the oxygen in the heating atmosphere were important factors in reducing the silicon content necessary to prevent copper formation.

In the previous work (1), it was theorized that the beneficial properties of molten fayalite in forming iron-rich alloys was due to the establishment of electrolytic cells in the scale of the following type: Iron alloy-molten fayalite-oxygen. Formation of cells of this type is possible because the molten fayalite penetrates the scale grain boundaries and extends to the furnace atmosphere where the $1/2\ O_2 + 2e \rightarrow O^{2-}$ reaction occurs. The anodic half cell occurs at the steel surface and the cathodic half cell at the scale-furnace atmosphere interface. Ionic mobility is provided by the molten fayalite and electronic mobility is provided largely by the iron oxides.

The present study was conducted to determine if copper alloys of Sn, Sb, or As could be prevented from forming on steels containing these elements as readily as on steel containing only copper as a residual element.

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[4] Compositions are in weight-percent unless otherwise indicated.

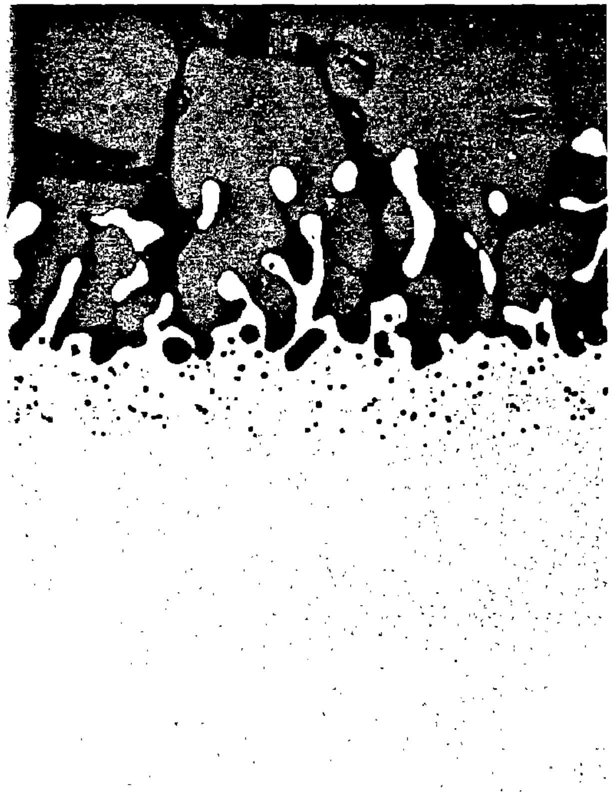


FIGURE 1. - Iron-rich, iron-copper particles forming on scaled steel. The steel portion (light colored) is at the bottom half of the photomicrograph, and the internal oxidation (peppered) zone is at the upper portion of the steel. The mozaic scale structure above the steel consists of voids (black), fayalite (dark gray), FeO (light gray), and iron-rich particles. This figure and all others in this report are at a magnification of 500.

## PROCEDURE

Four series of steels were made for conducting the experiments. The nominal contents of the steel series are given in table 1, and the analysis of the individual steels of series I, II, III, and IV are listed in appendix tables A-1, A-2, A-3, and A-4, respectively. All the series contained 0.20 C, 0.45 Mn, up to 1.00 Cu, and up to 1.00 Si. In addition, series I steels contained nominal contents of up to about 0.15 Ni and 0.30 Sn, Sb, or As. Series II, III, and IV steels contained nominally 0.15 or 0.30 Sn, 0.10 or 0.20 Sb, and 0.10 As, respectively, and actual nickel contents up to 0.15. The carbon and manganese contents were not varied since it was previously found (2) that these elements did not influence copper alloy formation by fayalite. The 0.20 C and 0.45 Mn contents, which are not given in the tables, varied no more than ±0.02 and ±0.05 wt-pct, respectively.

Forged, elongated buttons were made for conducting the experiments. The steel buttons, weighing 100 grams, were made by nonconsumable-electrode arc melting of electrolytic iron powder, spectrographic-grade graphite powder, and high-purity powders of electrolytic Mn, Cu, Si, Ni, Sn, Sb, and As. The buttons were forged to 1/2-inch-square bars after heating to 2,282° F (1,250° C) in an argon atmosphere. The bars were sandblasted, and sanded (150-mesh grit). Sections 5/8-inch long were prepared from the center portion of the bars for the scaling tests.

TABLE 1. - Nominal content of series I, II, III, and IV steels

| Steel Nos. | Content | | | | | |
|---|---|---|---|---|---|---|
| | Si | Cu | Sn | Sb | As | Ni |
| STEEL SERIES I, ISOTHERMAL HEATING | | | | | | |
| 1-1 to 1-3 | 0.2 or 0.9 | 0 or 1.0 | 0.30 | - | - | 0.05 |
| 1-4 to 1-6 | .2 or .9 | 0 or 1.0 | - | 0.30 | - | .05 |
| 1-7 to 1-9 | .2 or .9 | 0 or 1.0 | - | - | 0.30 | .05 |
| 1-10 to 1-12 | .4 or .7 | 0.6 | .30 | - | - | 0.05 or 0.15 |
| STEEL SERIES II, PUSHER AND SOAKING METHOD | | | | | | |
| 2-1 to 2-11 | 0.2 to 1.0 | 0.3 to 0.9 | 0.15 | - | - | 0.05 |
| 2-12 to 2-23 | .2 to 1.0 | .4 to 1.0 | .15 | - | - | .10 |
| 2-24 to 2-36 | .2 to 1.0 | .2 to 1.0 | .30 | - | - | .05 |
| 2-37 to 2-48 | .2 to 1.0 | .2 to 1.0 | .30 | - | - | .10 |
| STEEL SERIES III, PUSHER AND SOAKING METHOD | | | | | | |
| 3-1 to 3-14 | 0.2 to 1.0 | 0.2 to 1.0 | - | 0.10 | - | 0.05 |
| 3-15 to 3-23 | .2 to .8 | .4 to 1.0 | - | .10 | - | .10 |
| 3-24 to 3-32 | .2 to .9 | .2 to .9 | - | .20 | - | .05 |
| 3-33 to 3-44 | .2 to .9 | .4 to 1.0 | - | .20 | - | .10 |
| STEEL SERIES IV, PUSHER AND SOAKING METHOD | | | | | | |
| 4-1 to 4-14 | 0.2 to 0.8 | 0.2 to 1.0 | - | - | 0.10 | 0.05 |
| 4-15 to 4-28 | .2 to 1.0 | .2 to 1.0 | - | - | .10 | .10 |

The prepared steel sections were reheated by two different methods. Series I steels were made to determine the concentration behavior of Sn, Sb, and As on the steel surface when scaled, and to determine the effect of copper and nickel on this behavior. This series of steels was reheated in air at 2,228°±18° F (1,220°±10° C) for 4 hours by using an electrically heated box-type furnace previously described (2). The 2,228° F temperature is slightly above the melting temperature of fayalite (2,200° F). Series II, III, and IV were reheated by procedures simulating as closely as possible pusher (continuous) and soaking-pit furnaces. The steels were reheated at a fairly uniform rate in a tube-type furnace by the pusher schedule from 707°±100° F (375°±55° C) to 2,372°±18° F (1,300°±10° C) in 2 hours and by the soaking-pit schedule from 1,508°±36° F (820°±20° C) to 2,372°±18° F (1,300°±10° C). Steel ingots are normally charged cold into pusher furnaces rather than charged at 600° to 800° F. However, since steels hardly scale when heated up to these temperatures, the investigators believed the final results would not be affected. The 1,508° F starting temperature in the soaking-pit furnace schedule represents a compromise temperature, which furnace operators verbally reported to the investigators that they use when charging ingots into their furnaces. A 2-vol-pct oxygen level was maintained in the natural gas-air combustion atmosphere at the 2,282° F (1,250° C) temperature position in the tube; the calculated flow rate of the combustion atmosphere in the furnace tube was about 2 ft/sec. The electrically heated tube furnace used and techniques employed were described previously (1-2).

Several techniques were used in preparing and evaluating the scaled specimens. The specimens were vacuum-pressure mounted in epon-type resin, sectioned through their center with a water-cooled diamond saw, and then any cracks and pores in the scale were vacuum-pressure filled with epon. The section was remounted, and the sawed surface was ground and polished by standard procedures using diamond paste abrasives. The scale-steel interface was examined for structures by visual microscopy. The presence of any copper alloys on the steel surface was considered detrimental; that is, the steels would be subject to surface hot shortness when hot worked. Electron-beam-microprobe analyses of the oxidized steel surface layer of metallographically prepared mounts were obtained.

## RESULTS AND DISCUSSION

### Studies of the Surface of Isothermally Heated Steels

Initially, we examined the concentration behavior, individually, of Sn, Sb, and As at the steel surface after scaling and the effects of these elements on the surface structure. The steels contained 0.3 of one of these residual elements and 0.2 Si, a silicon content representing the amount normally added to steels. Compared with these initial specimens were steels containing 1.00 Cu and 0.20 or 0.90 Si additions and one of the other residual elements. For the comparisons, steels 1-1 through 1-9 (table A-1) were isothermally heated in air for 4 hours at 2,228±18° F (1,220±10° C).

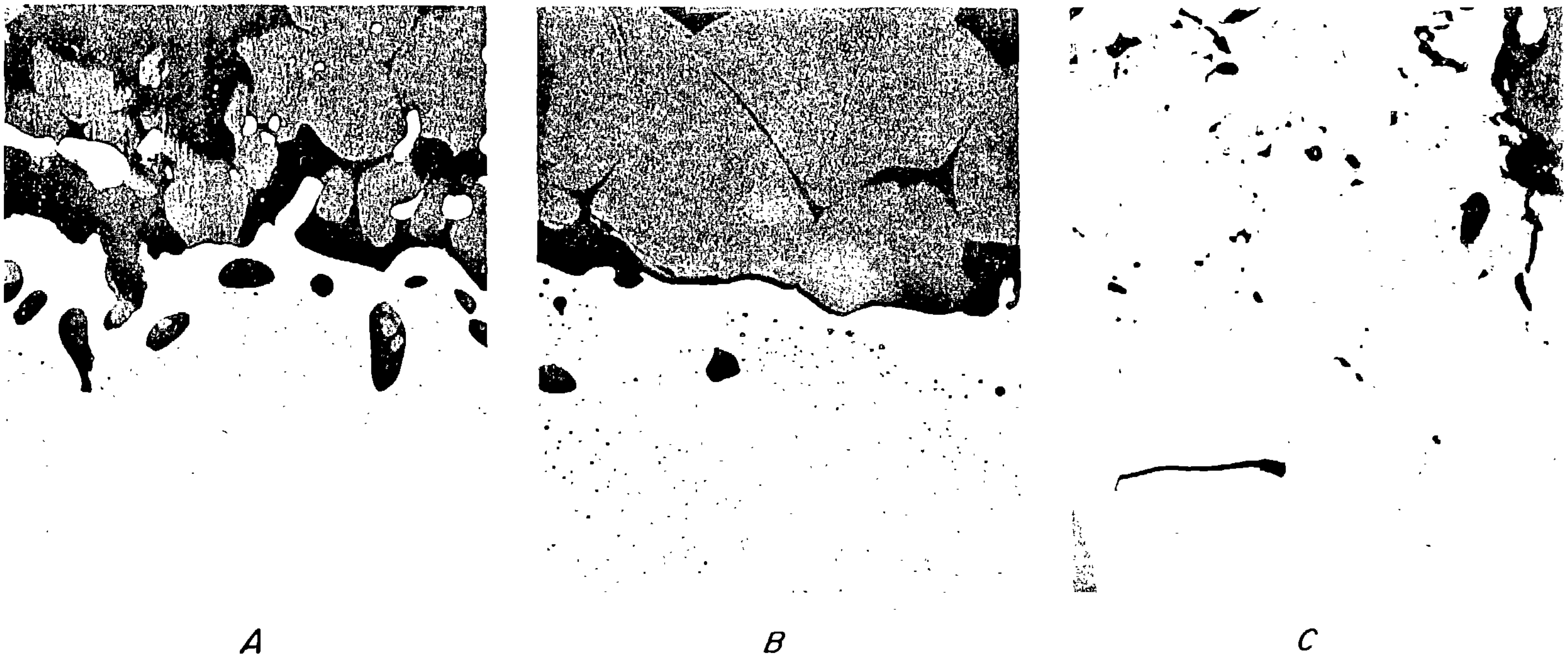
The surface structures observed and the surface concentrations of the residuals as found by microprobe analyses after scaling steel containing Sn, Sb, and As are illustrated in figures 2, 3, and 4, respectively. From the analytical values and photomicrographs, the following conclusions were made.

### Steels Containing Tin

Figure 2A.--A discontinuous, narrow tin concentration zone, with a tin enrichment ratio of 5.5 to 1 over the steel matrix, occurs at the surface of a steel containing 0.30 Sn and 0.20 Si. Iron-rich, iron-tin particles are forming and breaking away from the steel surface as oxides in the IOZ are coalescing and encasing them.

Figure 2B.--In the presence of 1.00 Cu, the tin concentrates largely in the copper formed at the steel surface, in agreement with Kosec (4). The slight tin enrichment at the steel surface lowers the copper solubility in iron from 9.7 (1) to 6.8 at the scaling temperature. No iron-rich particles are forming.

Figure 2C.--In the presence of 0.90 Si and 1.00 Cu, the tin again concentrates in the copper formed at the steel surface (not shown) and only slightly in the surface enrichment layer. However, the copper content of the copper alloy is higher and the enrichment layer is lower than in figure 2C. The composition change may be caused by the increased amount of fayalite formed by the high silicon content. The morphology of the steel surface is similar to that observed (fig. 1) when molten fayalite prevents the formation of copper on steels containing no tin.



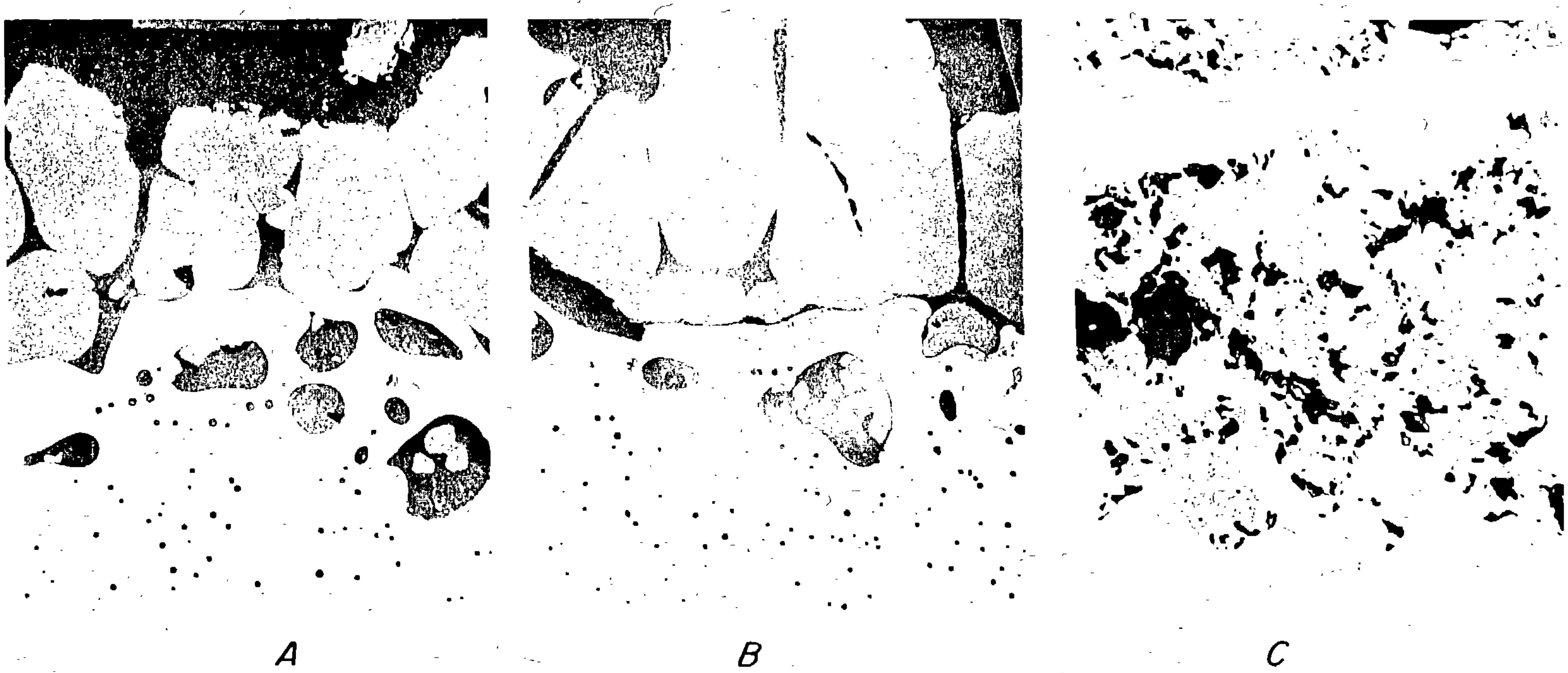
| Location | Si | Cu | Sn | N |
|---|---|---|---|---|
| Matrix | 0.22 | — | 0.33 | 0.04 |
| Mid IOZ | 1/ | — | 0.50 | 2/ |
| Steel surface | 1/ | — | 1.80 | 2/ |

| Location | Si | Cu | Sn | Ni |
|---|---|---|---|---|
| Matrix | 0.20 | 1.02 | 0.32 | 0.05 |
| Mid IOZ | 1/ | 1.80 | 0.40 | 2/ |
| Steel surface | 1/ | 6.80 | 0.60 | 2/ |
| Cu alloy | 1/ | 66 | 32 | 2/ |

| Location | Si | Cu | Sn | Ni |
|---|---|---|---|---|
| Matrix | 0.91 | 1.00 | 0.28 | 0.04 |
| Mid IOZ | 1/ | 2.50 | 0.60 | 2/ |
| Steel surface | 1/ | 6.00 | 0.90 | 2/ |
| Cu alloy | 1/ | 73 | 25 | 2/ |

1/ Silicon oxidized. 2/ No analysis.

FIGURE 2. - Steel-scale interface structures and surface microprobe analyses of steels containing ≈0.30 Sn and *A*, ≈0.20 Si; *B*, ≈0.20 Si and ≈1.00 Cu; and *C*, ≈0.90 Si and ≈1.00 Cu.



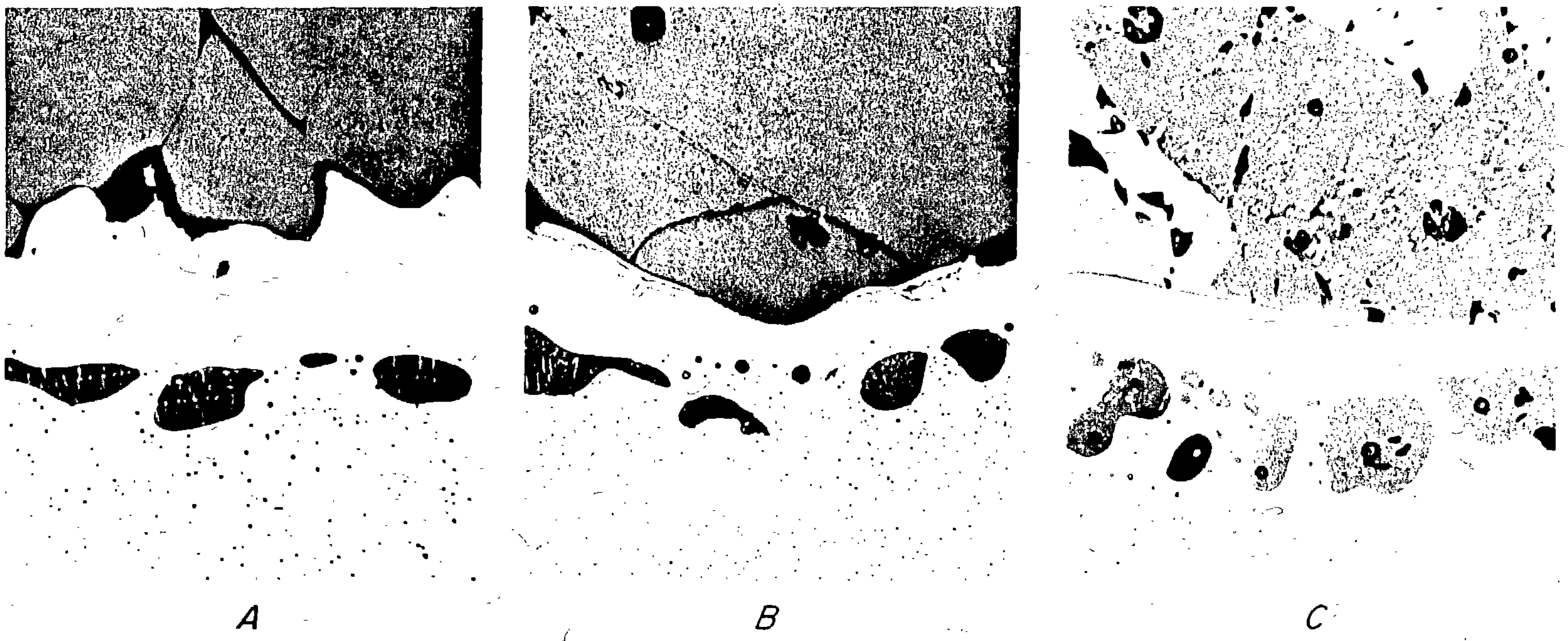
| Location | Si | Cu | Sb | Ni |
|---|---|---|---|---|
| Matrix | 0.21 | — | 0.29 | 0.04 |
| Mid IOZ | 1/ | — | 0.70 | 2/ |
| Steel surface | 1/ | — | 3.90 | 2/ |

| Location | Si | Cu | Sb | Ni |
|---|---|---|---|---|
| Matrix | 0.20 | 1.02 | 0.28 | 0.05 |
| Mid IOZ | 1/ | — | 0.40 | 2/ |
| Steel surface | 1/ | 5.70 | 0.90 | 2/ |
| Cu alloy | 1/ | 63 | 34 | 2/ |

| Location | Si | Cu | Sb | Ni |
|---|---|---|---|---|
| Matrix | 0.89 | 0.96 | 0.28 | 0.03 |
| Mid IOZ | 1/ | 1.40 | 0.50 | 2/ |
| Steel surface | 1/ | 6.50 | 0.90 | 2/ |
| Cu alloy | 1/ | 62 | 30 | 2/ |

1/ Silicon oxidized. 2/ No analysis.

FIGURE 3. - Steel-scale interface structures and surface microprobe analyses of steels containing 0.30 Sb and *A*, 0.20 Si; *B*, 0.20 Si and 1.00 Cu; and *C*, 0.90 Si and 1.00 Cu.



| Location | Si | Cu | As | Ni |
|---|---|---|---|---|
| Matrix | 0.21 | — | 0.26 | 0.04 |
| Mid IOZ | 1/ | — | 1.20 | 2/ |
| Steel surface | 1/ | — | 3.10 | 2/ |

| Location | Si | Cu | As | Ni |
|---|---|---|---|---|
| Matrix | 0.22 | 1.02 | 0.25 | 0.05 |
| Mid IOZ | 1/ | 1.50 | 1.70 | 2/ |
| Steel surface | 1/ | 7.10 | 5.40 | 2/ |
| Cu alloy |  | 2/ | 2/ |  |

| Location | Si | Cu | As | Ni |
|---|---|---|---|---|
| Matrix | 0.92 | 0.98 | 0.26 | 0.05 |
| Mid IOZ | 1/ | 2.50 | 0.50 | 2/ |
| Steel surface | 1/ | 7.00 | 3.00 | 2/ |
| Cu alloy | 1/ | 85 | 4.00 | 2/ |

1/ Silicon oxidized. 2/ No analysis.

FIGURE 4. - Steel-scale interface structures and surface microprobe analyses of steels containing 0.30 As and *A*, 0.20 Si; *B*, ≈0.20 Si and 1.00 Cu; and *C*, 0.90 Si and 1.00 Cu.

## Steels Containing Antimony

Figure 3A.--The structures observed at the surface of steels containing 0.30 Sb and 0.20 Si are similar to that for steels containing 0.30 Sn and 0.20 Si (fig. 2A). However, the surface concentration of antimony is greater, 13.5 times the matrix, than for tin.

Figure 3B.--As with steels containing copper and tin (fig. 2B), the antimony largely concentrates in the copper (darker than steel) formed on the surface and slightly in the enrichment layer of steels containing 0.30 Sb and 1.00 Cu. The slight antimony enrichment lowers the solubility of copper in iron from 9.7 (1) to 5.7.

Figure 3C.--When 0.90 Si is added to steels containing 0.30 Sb and 1.00 Cu, the morphology of the scaled steel surface and iron-rich particle surface is entirely different. The oxides in the IOZ tend to coalesce under the enrichment layer, which causes the enrichment layer to break away from the steel surface as the oxide layer becomes continuous. As the enriched layer oxidizes in the scale, alternative FeO and FeO + $Fe_2SiO_4$ bands (not shown) parallel to the steel surface occur in the inner portion of the scale.

## Steels Containing Arsenic

The morphology of the surface of scaled steels containing 0.3 arsenic is similar, whether containing (1) 0.20 Si, (2) 0.20 Si and 1.00 Cu, or (3) 0.90 Si and 1.00 Cu, as illustrated in figure 4. The oxides forming in the IOZ coalesce under the enrichment zone, which causes this zone to break away from the steel surface in a manner similar to that of the steel containing 0.30 Sb, 0.90 Si, and 1.00 Cu (fig. 3C). As noted by Kosec (4), the enrichment zone formed is much wider and more uniform in arsenic content than the zone formed on steels containing tin or antimony. Silicon or copper additions do not lower the content of arsenic in the enrichment zone, and arsenic does not lower the solubility of copper in iron as much as tin or antimony, the latter result being in agreement with Salter (7).

## Effect of Nickel Additions

Steels 1-10 through 1-12 in table A-1, which contained 0.30 Sn and 0.55 Cu, were then scaled in the same manner as the alloys discussed previously. A smaller amount of copper was used than in the prior steels because it was concluded that copper alloys may not be prevented from forming on steels containing 1.00 Cu in the presence of 0.30 Sn. To one steel, 1-11, enough nickel was added to bring the nominal content to 0.15. Nickel was added because (1) it concentrates like copper on the steel surface during scaling, (2) it may change the oxidation characteristics of the steel surface, and (3) it slightly increases the solubility of copper in iron (7).

The morphology and content of the scaled surface of the steels containing 0.55 Cu are presented in figure 5. From this figure, the following can be observed:

| Location | Si | Cu | Sn | Ni |
|---|---|---|---|---|
| Matrix | 0.37 | 0.54 | 0.29 | 0.04 |
| Steel surface | [1] | 4.70 | 1.40 | 2.20 |

| Location | Si | Cu | Sn | Ni |
|---|---|---|---|---|
| Matrix | 0.37 | 0.56 | 0.30 | 0.12 |
| Steel surface | [1] | 4.50 | 1.50 | 4.00 |

| Location | Si | Cu | Sn | Ni |
|---|---|---|---|---|
| Matrix | 0.73 | 0.56 | 0.28 | 0.05 |
| Steel surface |  | 4.80 | 1.30 | 2.60 |

[1] Silicon oxidized.

FIGURE 5. - Steel-scale interface structures and surface microprobe analyses of steels containing 0.30 Sn and 0.55 Cu and A, 0.40 Si; B, 0.40 Si and 0.10 Ni; and C, 0.90 Si.

1. No copper alloys formed on the steel (fig. 5B) containing 0.37 Si and 0.12 Ni, and the scale morphology is very similar to that of figure 1.

2. Copper alloys did form on the steels containing 0.37 and 0.73 Si (figs. 5A and 5C, respectively) and only 0.05 Ni, the residual content of the electrolytic iron used to prepare the steels. Note the unusual concentration of molten fayalite on the steel surface in figure 5C with very little penetration into FeO layer.

3. The copper and tin contents of the enriched surfaces were all similar except for nickel. This indicates that nickel did not significantly change the solubility of copper in iron, at least in the presence of tin.

## Steels Heated by Simulated Industrial Heating Schedules

Because 0.12 Ni and 0.40 Si prevented the formation of copper alloys on an isothermally heated steel containing 0.55 Cu and 0.30 Sn (steel 1-11 as shown in figure 5B), a study was conducted to determine the amounts of nickel and silicon that would prevent the formation of copper alloys of Sn, Sb, and As on steels when heated by the simulated heating schedules. The steels, series II, III, and IV, contained 0.20 to 1.00 Si and Cu, 0.05, 0.10, or 0.15 Ni, and 0.15 or 0.30 Sn, 0.10 or 0.20 Sb, or 0.10 As. The maximum content of the steels containing antimony and arsenic was maintained at 0.20 and 0.10, respectively, because of the difficulty in obtaining composition control at higher contents during arc melting. The investigators feel that larger contents seldom would be encountered in melting scrap steel. The analysis of the steels containing 0.05 and 0.10 Ni, used in the study, are given in appendix tables A-2, A-3, and A-4.[5] The steels of series II, III, and IV were all initially heated by the simulated pusher schedule, and then the steel containing the lower Sn, Sb, and As contents (0.15, 0.10, and 0.10, respectively) were heated by the simulated soaking-pit schedule.

### Steels Containing Tin and Nickel

The results of scaling the tin-containing steels in table A-2 are shown in figure 6. The lines in figure 6 (and 7 and 8) separate the composition regions between where copper alloys were formed or not formed (left-hand side). Solid and broken lines separate regions for steels heated by pusher and soaking-pit schedules, respectively. At the top of the figures, the results of a previous study (1) of copper-containing steels (without Sn, Sb, or As additions) are presented for comparison purposes. As can be observed, the greater the amount of copper and tin and the lower the nickel content of the steels, the greater the difficulty in preventing copper-tin alloys from forming on the steels. For the steels containing 0.05 Ni, a drastic increase in silicon content is necessary in order to prevent copper alloy formation when the tin content is increased from 0 to 0.15, but no significant change in silicon content

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[5] Steels also containing 0.15 Ni were made and reheated to 2,372° F (1,300° C). Because the amounts of silicon necessary to prevent copper alloy formation were nearly the same as steels containing 0.10 Ni described in figures 6, 7, and 8, the compositions and scaling observations were not included.

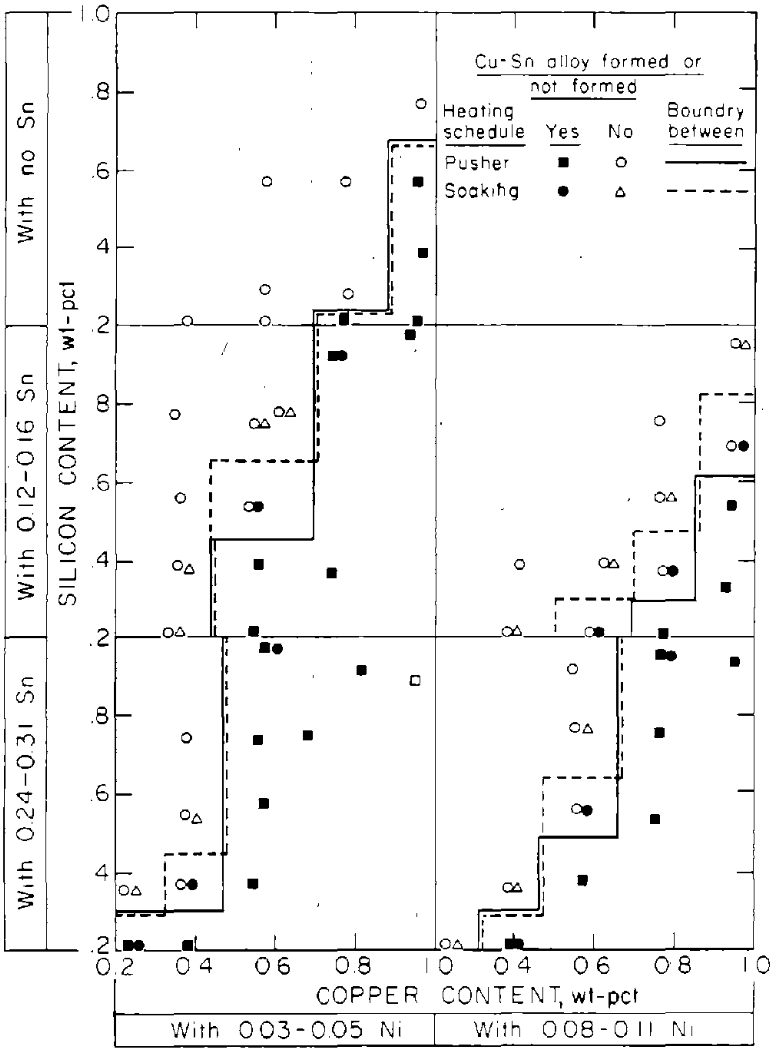

FIGURE 6. - Silicon and nickel contents necessary to prevent Cu-Sn alloy formation on series II steels containing copper and tin.

is necessary when the tin content is increased from 0.15 to 0.30. The amount of silicon necessary is decreased drastically when the nickel content of the steels increased from 0.05 to 0.10. In fact, the amount of silicon necessary for steels containing 0.10 Ni and 0.15 Sn is very similar to the steels containing no tin when heated by the pusher schedule. The amount of silicon required to prevent copper-tin alloy formation in figure 6 is slightly lower for the steels heated by the pusher schedule. The reason for the lower silicon content was believed due to a slight increase in oxidation resistance imparted by tin. A longer time above 2,200° F (1,205° C) was then necessary for copper alloys to form. Because of the oxidation resistance imparted and the probability that steels would scale more when heated by actual commercial, continuous pusher furnaces than by our pusher schedule, the investigators believe that the silicon and nickel contents in figure 6 (and figures 7 and 8 for steels containing antimony and arsenic, respectively) for steels heated by the soaking pit schedule are a better guide than the same steels heated in the pusher schedule.

### Steels Containing Antimony and Nickel

The silicon contents necessary to prevent copper-antimony alloys from forming on the series III steels (table A-3) containing 0.10 or 0.20 Sb and 0.05 or 0.10 Ni are shown in figure 7. By comparison with the steels containing tin (fig. 6), it is more difficult to prevent copper alloy formation on steels containing antimony than tin. In fact, copper-antimony alloy formation could not be prevented on steels containing 0.20 Sb and 0.05 Ni regardless of their silicon or copper contents. From observation of the 0.10 Sb steels (the

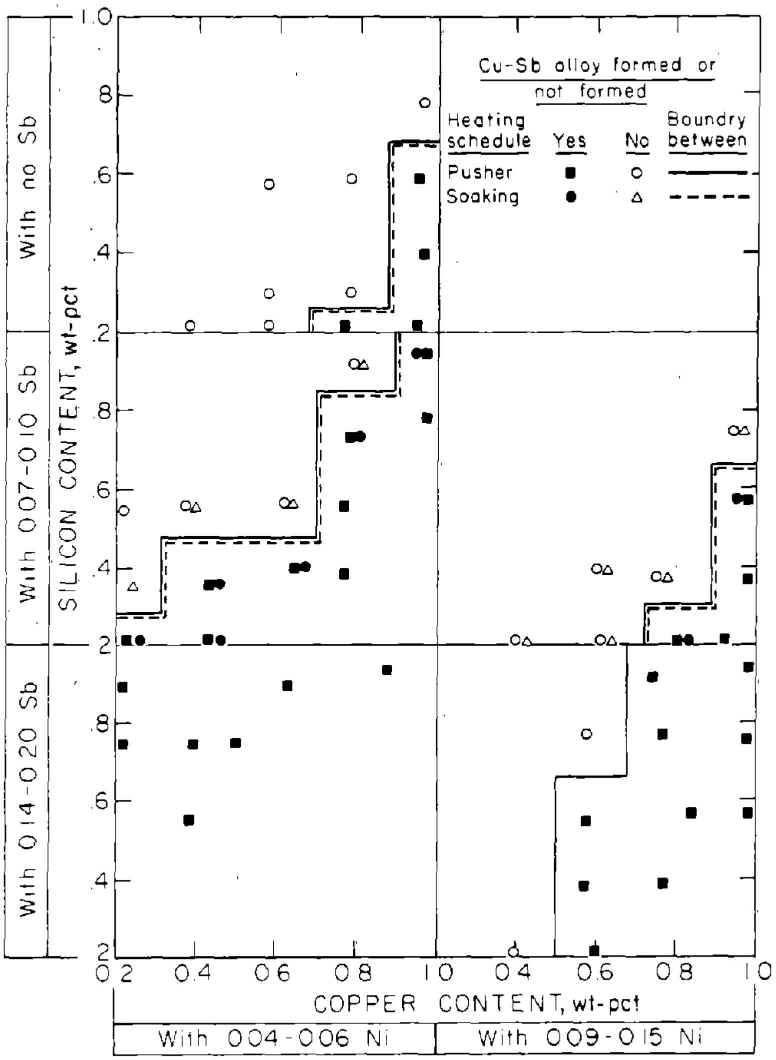

FIGURE 7. - Silicon and nickel contents necessary to prevent Cu-Sb alloy formation on series III steels containing copper and antimony.

only ones heated by both heating schedules), it also is apparent that the same amount of silicon was required for either type of reheating schedule. This observation indicates that antimony additions do not influence the oxidation resistance of the copper-bearing steels. The amount of silicon required for steels containing 0.10 Sb and 0.10 Ni were the same as for steels containing no antimony.

## Steel Containing Arsenic and Nickel

The amount of silicon required to prevent copper-arsenic alloy formation on the surface of the 0.10 As steels in table A-4 is illustrated in figure 8. Most obvious is the fact that copper alloys could be easily prevented from forming when heated by the pusher schedule; in fact, only 0.20 Si was necessary on the steels containing 0.10 Ni. The small quantity of silicon necessary was due to the excellent oxidation resistance imparted by the arsenic addition and the insufficient time to form copper-arsenic alloys when only heated for 2 hours to 2,372° F (1,300° C). When the steels were heated by the soaking-pit schedule for 8 hours and much thicker scales were formed, increased silicon was necessary for a given copper content. A significant difference between these steels containing arsenic and those containing tin or antimony, figures 6 and 7, respectively, was the fact that 0.10 Ni was of no help over steels containing 0.5 Ni when heated by the soaking-pit schedule.

## Structures of Steel-Scale Interface

The structures noted at the steel-scale interface varied after heating by the pusher or soaking pit schedule. The structures were the same, as illustrated in figures 1 or 5B, when copper did not form. Similar structures

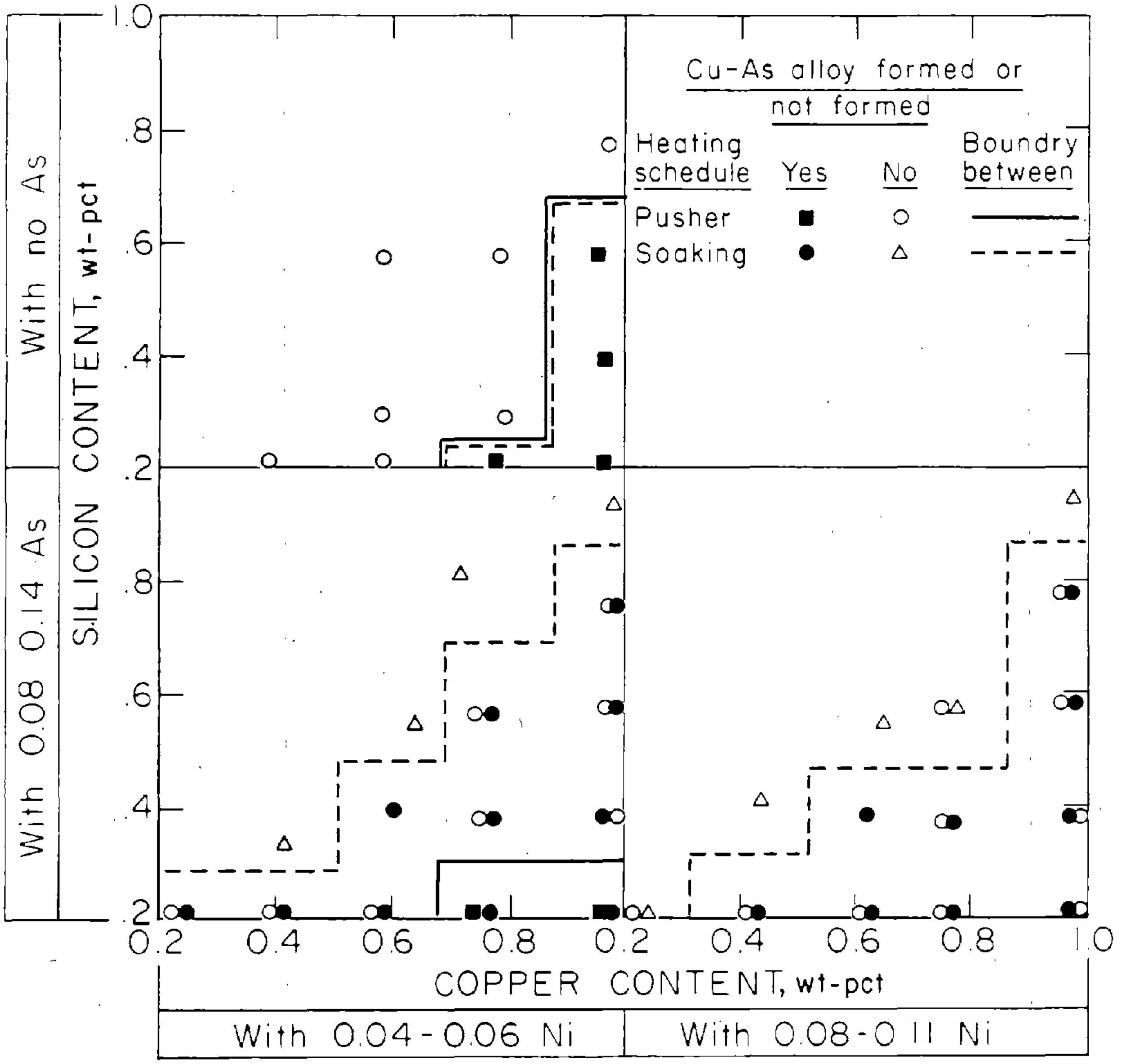

FIGURE 8. - Silicon and nickel contents necessary to prevent Cu-As alloy formation on series IV steels containing copper and arsenic.

were present for steels with silicon contents slightly less than the boundary lines in figures 6-8, but copper alloys or copper plus iron-rich alloys (fig. 9) appeared at intervals. The structures approached those illustrated in figures 2B, 3B, and 4B, with increasing copper and decreasing silicon contents. By comparing these latter figures with figure 1, it can be noted that iron-rich particles are not being formed at the steel surface and entrapped in the scale as the surface recedes during scaling.

When molten copper-antimony alloys formed on steels, they always penetrated the austenite grain boundaries, even throughout the 1/2-inch thickness of the scaled specimens. Molten copper-tin or copper-arsenic alloys did not penetrate the grain boundaries of the scale steels except when hot forged.

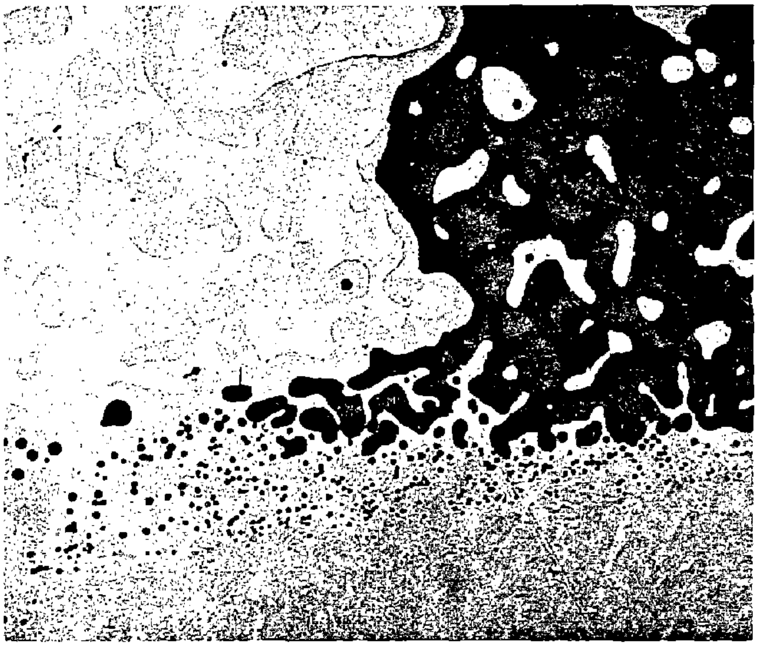

FIGURE 9. - Copper- and iron-rich particles in cells of these phases occurring on steel surface.

## Chemical Composition of Scaled Steel Surfaces

The average Cu, Ni, and Sn, Sb, or As solid solution content of the iron at the very outside scaled surface of selected steels of series II, III, and IV reheated by the soaking-pit schedule were determined. Steels of each series were selected that contained similar copper and silicon contents but different nickel contents. Copper alloys formed on the steels containing 0.05 Ni but not on those containing 0.10 Ni. Sections of the scaled specimens were metallographically prepared and analyzed by the electron-beam microprobe scanning technique. The chemical analyses of the steel matrixes and scaled surfaces are given in table 2. The following conclusions were apparent by comparison of the analyses:

1. The residual elements all concentrate at the steel surface during scaling, as previously observed for isothermally heated steels. They concentrate because the residuals oxidize less readily than iron and also probably because the scaling rate is more rapid than diffusion back into the matrix. The oxide particles formed in the internal oxidation zone also probably reduce diffusion to the steel matrix. The particles restrict diffusion by reducing the effective iron cross-sectional area for diffusion.

2. As a result of increasing the nickel content of the steels from 0.05 to 0.10, the Cu, Sn, Sb, and As contents at the outside surface decreased except for the slight copper increase for the steels containing arsenic. In contrast, the nickel content increased. The reasons for the nickel content increasing was not known except that the nickel content of the matrix was larger.

TABLE 2. - Composition of matrix and surface layers of scaled steels

| | Ni | Cu | Sn | Sb | As | Si | Fe[1] |
|---|---|---|---|---|---|---|---|
| Series II, 0.15 Sn: | | | | | | | |
| No. 2-9, with copper alloy: | | | | | | | |
| Matrix........................ | 0.03 | 0.75 | 0.15 | - | - | 0.37 | (2) |
| Surface........................ | 1.8 | 6.9 | 3.2 | - | - | (3) | 88.1 |
| No. 2-17, no copper alloy: | | | | | | | |
| Matrix........................ | .11 | .77 | .13 | - | - | .37 | (2) |
| Surface........................ | 3.0 | 6.0 | .5 | - | - | (3) | 90.5 |
| Series III, 0.10 Sb: | | | | | | | |
| No. 3-9, with copper alloy: | | | | | | | |
| Matrix........................ | .4 | .79 | - | 0.09 | - | .38 | (2) |
| Surface........................ | 1.3 | 6.5 | - | 2.2 | - | (3) | 90.9 |
| No. 3-19, no copper alloy: | | | | | | | |
| Matrix........................ | .14 | .76 | - | .07 | - | .37 | (2) |
| Surface........................ | 2.2 | 5.8 | - | .9 | - | (3) | 91.1 |
| Series IV, 0.10 As: | | | | | | | |
| No. 4-10, with copper alloy: | | | | | | | |
| Matrix........................ | .04 | .74 | - | - | 0.11 | .56 | (2) |
| Surface........................ | .2 | 4.3 | - | - | 1.6 | (3) | 93.9 |
| No. 4-73, no copper alloy: | | | | | | | |
| Matrix........................ | .09 | .75 | - | - | .10 | .58 | (2) |
| Surface........................ | .3 | 4.7 | - | - | .9 | (3) | 94.1 |

[1] Iron in surface layer calculated.

[2] Not determined.

[3] Silicon oxidized and combined with FeO to form $Fe_2SiO_4$.

## Scaling Action and Beneficial Properties of Nickel and Fayalite

The scaling mechanism occurring when a solid fayalite plus wustite structure forms on the steel surface during reheating is believed to be the same as when no silicon is contained in the steel. In that mechanism, iron ions diffuse through the wustite layer and iron and/or oxygen diffuse through the outer magnetite and hematite layers. Wustite is normally the scaling-rate-controlling phase for steels containing up to 0.2 Si because it is usually by far the thicker structural layer of the scale. As the solid fayalite plus wustite conglomerate becomes thicker with increasing silicon contents and scaling time, it becomes the rate-controlling structure (1).

We theorize that two scaling mechanisms occur simultaneously when a molten fayalite (mp 1,205° C) plus wustite structure forms on the steel and the fayalite penetrates the scale grain boundries to the furnace atmosphere. These mechanisms are diffusion and electrolytic cell action; the latter was discussed in the introduction. The type of mechanism controlling the scaling rate depends upon the temperature at the steel-scale interface relative to its surrounding environment and the amount of fayalite formed. When the steel-scale interface and surrounding environment temperatures are similar, diffusion is believed to be the major controlling mechanism. The wustite layer is replaced by the molten-fayalite-plus-wustite structure as the rate controlling structure with increasing fayalite contents (1).

Electrolytic cell action becomes the scaling-rate-controlling mechanism when the scale-steel interface temperature is allowed to become significantly larger than the surrounding environment. This action can become catastrophic, an action that can be considered analogous to the accelerated corrosion of steels exposed to burning fuels containing vanadium. When cell action becomes the major mechanism, formation of copper alloys then occurs. However, we found (1) that a significant temperature rise of the steel surface above its surroundings can be prevented by dissipating the heat of scaling. Dissipation is achieved by not allowing the steel mass being heated to equilibrate in temperature with the heating environment or by cladding a portion of the surface with an oxidation resistant material. Overheating of the specimens during this investigation was prevented by cladding one surface with type 310 stainless steel. However, the latter approach is not very practical for real ingots. If it is desirable to hold the ingots at the same temperature as the atmosphere (after reaching hot-working temperature), catastrophic scaling can also be prevented by reducing the oxidation potential of the heating atmosphere to low values.

The reasons that 0.08 to 0.15 Ni prevented copper alloy formation during reheating of copper steels containing tin and antimony were not established. When critical amounts of tin and antimony concentrated on the steel surface during scaling, the surface became passive. The increasingly lower oxidation rates, as shown by thinner scale thickness, of steels containing greater amounts of these elements would tend to confirm the imparted passivity. We theorize that the benefit of nickel is due to its rendering the steel surface nonpassive to electrolytic cell action as it concentrates on the steel. Thus, nickel promotes the formation of iron-rich alloys on the surface, rather than copper alloys. Further studies on the effect of nickel additions should be conducted.

It was noted that the larger the silicon content, the greater the number of wustite grains penetrated by the molten fayalite, and the wider the penetrations. The larger number of penetrations would allow a greater number of electrolytic cells to be established along the steel surface, thus preventing inactive sites to be established. With wider fayalite penetrations, ionic mobility would be easier. This may explain why large silicon contents would more readily prevent copper or copper alloy formation than smaller silicon contents.

Although the present work was not extended to study the reheating of cast steels containing Cu, Sn, Sb, and As, the authors believe that the results of the previous work (1) on reheating surface sections of copper-bearing ingots applies. The effect of ingot adherents (slag and mold wash), surface segregation, oxygen content of furnace atmosphere, and temperature to which steels are heated are specifics in mind. A previous publication (1) may be consulted for recommended reheating practices.

## CONCLUSIONS

Copper alloys of Sn, Sb, and As could be prevented from forming on wrought steels reheated by simulated industrial practice provided sufficient amounts of silicon and nickel were alloyed with the steel. The steels studied contained 0.20 C, 0.45 Mn, up to 1.00 Si, up to 1.00 Cu, up to 0.15 Ni, and up to 0.30 Sn, 0.20 Sb, or 0.10 As. In general, the larger the amount of Cu, Sn, Sb, or As contained in the steel, the larger the amount of silicon required to promote the formation of iron-rich alloys, instead of copper alloys, on the steel surface as it scaled. The required amount of silicon was reduced considerably by increasing the nickel content from 0.05 to 0.10 for steels containing tin and antimony but not for those containing arsenic.

Silicon and nickel additions, when present in the proper amounts, were theorized to promote the formation of iron-rich alloys on the steel surface because of the part they participate in electrolytic cell action in the scale formed. The electrolytic cells (iron alloy-molten fayalite-oxygen) are formed in the scale along the steel surface by intergranular penetrations of molten fayalite through the scale to the scale-furnace atmosphere interface. Fayalite forms on the steel surface by internal oxidation of silicon and iron. While tin and antimony concentrations at the steel surface tend to make the surface passive to the electrolytic cells formed, a content of 0.10 Ni offsets this tendency.

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## APPENDIX.--CONTENT OF STEELS

TABLE A-1. - Content of series I steels containing Cu and Sn, Sb, or As, weight-percent

| Steel No. | Si | Cu | Sn | Sb | As | Ni |
|---|---|---|---|---|---|---|
| 1-1 | 0.22 | - | 0.33 | - | - | 0.04 |
| 1-2 | .20 | 1.02 | .32 | - | - | .05 |
| 1-3 | .91 | 1.00 | .28 | - | - | .04 |
| 1-4 | .21 | - | - | 0.29 | - | .04 |
| 1-5 | .20 | 1.02 | - | .28 | - | .05 |
| 1-6 | .89 | .96 | - | .28 | - | .03 |
| 1-7 | .21 | - | - | - | 0.26 | .04 |
| 1-8 | .22 | 1.02 | - | - | .25 | .05 |
| 1-9 | .92 | .98 | - | - | .26 | .05 |
| 1-10 | .37 | .54 | .29 | - | - | .04 |
| 1-11 | .37 | .56 | .30 | - | - | .12 |
| 1-12 | .73 | .56 | .26 | - | - | .05 |

TABLE A-2. - Content of series II steels containing ≈0.15 and 0.30 Sn

| Steel No. | Cu | Si | Sn | Ni |
|---|---|---|---|---|
| 2- | CONTAINING ≈0.05 Ni | | | |
| 2-1 | 0.35 | 0.18 | 0.16 | 0.03 |
| 2-2 | .36 | .37 | .16 | .04 |
| 2-3 | .36 | .55 | .12 | .03 |
| 2-4 | .35 | .77 | .13 | .03 |
| 2-5 | .55 | .19 | .16 | .03 |
| 2-6 | .58 | .38 | .16 | .04 |
| 2-7 | .57 | .57 | .15 | .03 |
| 2-8 | .55 | .75 | .15 | .03 |
| 2-9 | .75 | .37 | .15 | .03 |
| 2-10 | .75 | .92 | .13 | .03 |
| 2-11 | .75 | .99 | .12 | .03 |
| | CONTAINING ≈0.10 Ni | | | |
| 2-12 | 0.39 | 0.17 | 0.14 | 0.09 |
| 2-13 | .41 | .38 | .15 | .11 |
| 2-14 | .60 | .17 | .15 | .09 |
| 2-15 | .63 | .40 | .15 | .11 |
| 2-16 | .78 | .18 | .15 | .09 |
| 2-17 | .77 | .37 | .13 | .11 |
| 2-18 | .77 | .57 | .13 | .09 |
| 2-19 | .77 | .76 | .13 | .10 |
| 2-20 | .95 | .35 | .15 | .10 |
| 2-21 | .94 | .53 | .13 | .09 |
| 2-22 | .96 | .70 | .15 | .10 |
| 2-23 | .96 | .99 | .15 | .11 |

TABLE A-2. - Content of series II steels containing ≈0.15 and 0.30 Sn--Continued

| Steel No. | Cu | Si | Sn | Ni |
|---|---|---|---|---|
| CONTAINING ≈0.05 Ni | | | | |
| 2-24 | 0.20 | 0.18 | 0.28 | 0.03 |
| 2-25 | .20 | .37 | .27 | .03 |
| 2-26 | .39 | .17 | .26 | .04 |
| 2-27 | .40 | .37 | .26 | .04 |
| 2-28 | .38 | .54 | .29 | .03 |
| 2-29 | .37 | .74 | .28 | .04 |
| 2-30 | .54 | .37 | .29 | .04 |
| 2-31 | .58 | .58 | .27 | .03 |
| 2-32 | .56 | .73 | .28 | .05 |
| 2-33 | .58 | .97 | .26 | .03 |
| 2-34 | .76 | .75 | .31 | .04 |
| 2-35 | .82 | .91 | .24 | .04 |
| 2-36 | .95 | .88 | .25 | .03 |
| CONTAINING ≈0.10 Ni | | | | |
| 2-37 | 0.17 | 0.19 | 0.29 | 0.10 |
| 2-38 | .40 | .17 | .27 | .09 |
| 2-39 | .40 | .36 | .26 | .09 |
| 2-40 | .60 | .17 | .28 | .09 |
| 2-41 | .58 | .37 | .28 | .09 |
| 2-42 | .56 | .55 | .24 | .10 |
| 2-43 | .56 | .76 | .26 | .08 |
| 2-44 | .55 | .91 | .25 | .08 |
| 2-45 | .76 | .53 | .25 | .09 |
| 2-46 | .77 | .75 | .28 | .09 |
| 2-47 | .77 | .95 | .28 | .10 |
| 2-48 | .96 | .93 | .29 | .09 |

TABLE A-3. - Content of series III steels containing $\approx$0.10 and 0.20 Sb

| Steel No. | Cu | Si | Sb | Ni |
|---|---|---|---|---|
| CONTAINING $\approx$0.05 Ni | | | | |
| 3-1 | 0.24 | 0.17 | 0.07 | 0.04 |
| 3-2 | .22 | .36 | .10 | .04 |
| 3-3 | .22 | .55 | .09 | .03 |
| 3-4 | .44 | .17 | .08 | .04 |
| 3-5 | .44 | .36 | .07 | .04 |
| 3-6 | .38 | .56 | .09 | .03 |
| 3-7 | .66 | .40 | .08 | .05 |
| 3-8 | .63 | .56 | .08 | .04 |
| 3-9 | .79 | .38 | .09 | .04 |
| 3-10 | .78 | .55 | .09 | .04 |
| 3-11 | .79 | .74 | .08 | .05 |
| 3-12 | .80 | .92 | .07 | .05 |
| 3-13 | 1.00 | .78 | .08 | .04 |
| 3-14 | 1.00 | .95 | .10 | .04 |
| CONTAINING $\approx$0.10 Ni | | | | |
| 3-15 | 0.40 | 0.18 | 0.08 | 0.11 |
| 3-16 | .62 | .18 | .07 | .12 |
| 3-17 | .60 | .39 | .07 | .12 |
| 3-18 | .81 | .17 | .07 | .13 |
| 3-19 | .76 | .37 | .07 | .14 |
| 3-20 | .93 | .21 | .10 | .09 |
| 3-21 | 1.00 | .37 | .07 | .14 |
| 3-22 | .98 | .58 | .07 | .12 |
| 3-23 | .95 | .75 | .07 | .13 |
| CONTAINING $\approx$0.05 Ni | | | | |
| 3-24 | 0.22 | 0.19 | 0.19 | 0.04 |
| 3-25 | .22 | .38 | .14 | .04 |
| 3-26 | .23 | .57 | .14 | .04 |
| 3-27 | .22 | .75 | .17 | .05 |
| 3-28 | .21 | .90 | .17 | .04 |
| 3-29 | .40 | .55 | .14 | .06 |
| 3-30 | .40 | .75 | .14 | .05 |
| 3-31 | .65 | .90 | .14 | .03 |
| 3-32 | .88 | .94 | .18 | .05 |
| CONTAINING $\approx$0.10 Ni | | | | |
| 3-33 | 0.40 | 0.18 | 0.20 | 0.11 |
| 3-34 | .60 | .20 | .19 | .13 |
| 3-35 | .58 | .39 | .19 | .11 |
| 3-36 | .59 | .55 | .17 | .10 |
| 3-37 | .58 | .76 | .18 | .12 |
| 3-38 | .78 | .39 | .19 | .14 |
| 3-39 | .85 | .57 | .22 | .13 |
| 3-40 | .77 | .76 | .19 | .13 |
| 3-41 | .75 | .91 | .14 | .13 |
| 3-42 | 1.02 | .57 | .20 | .15 |
| 3-43 | 1.00 | .75 | .20 | .13 |
| 3-44 | 1.02 | .94 | .20 | .13 |

TABLE A-4. - Content of series IV steels containing ≈0.10 As

| Steel No. | Cu | Si | As | Ni |
|---|---|---|---|---|
| CONTAINING ≈0.05 Ni | | | | |
| 4-1 | 0.22 | 0.20 | 0.13 | 0.05 |
| 4-2 | .20 | .41 | .10 | .05 |
| 4-3 | .39 | .20 | .10 | .04 |
| 4-4 | .42 | .33 | .08 | .05 |
| 4-5 | .57 | .21 | .08 | .05 |
| 4-6 | .60 | .39 | .09 | .04 |
| 4-7 | .64 | .55 | .10 | .05 |
| 4-8 | .74 | .18 | .08 | .05 |
| 4-9 | .75 | .37 | .08 | .06 |
| 4-10 | .74 | .56 | .11 | .04 |
| 4-11 | .72 | .82 | .10 | .04 |
| 4-12 | 1.00 | .18 | .10 | .06 |
| 4-13 | 1.05 | .38 | .10 | .06 |
| 4-14 | .98 | .57 | .11 | .05 |
| CONTAINING ≈0.10 Ni | | | | |
| 4-15 | 0.20 | 0.20 | 0.14 | 0.10 |
| 4-16 | .19 | .41 | .11 | .11 |
| 4-17 | .44 | .41 | .09 | .11 |
| 4-18 | .61 | .18 | .11 | .09 |
| 4-19 | .62 | .39 | .10 | .10 |
| 4-20 | .65 | .56 | .09 | .09 |
| 4-21 | .75 | .20 | .10 | .10 |
| 4-22 | .75 | .38 | .11 | .10 |
| 4-23 | .75 | .58 | .10 | .09 |
| 4-24 | 1.05 | .18 | .09 | .11 |
| 4-25 | 1.07 | .37 | .10 | .10 |
| 4-26 | .96 | .58 | .11 | .10 |
| 4-27 | .96 | .77 | .10 | .11 |
| 4-28 | 1.00 | .95 | .09 | .11 |

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