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Copeland et al.

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[54] **PREVENTION OF SURFACE CRACKING DUE TO FORMATION OF COPPER ALLOYS OF TIN AND ANTIMONY DURING REHEATING OF STEEL**

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[52] **U.S. Cl.** **75/125**; 72/365; 72/700

[51] **Int. Cl.**^{2}.................... **C22C 38/08**; C22C 38/16

[58] **Field of Search** ...... 75/125, 129, 123 A; 148/2, 148/3

[56] **References Cited**

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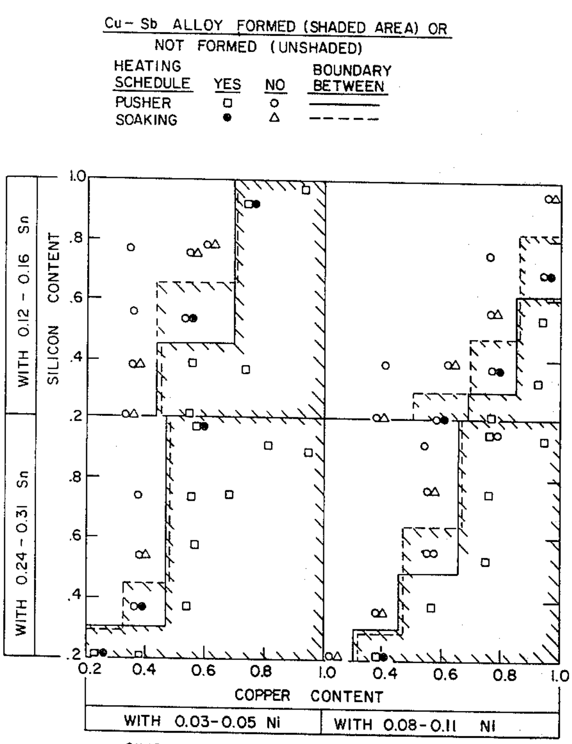
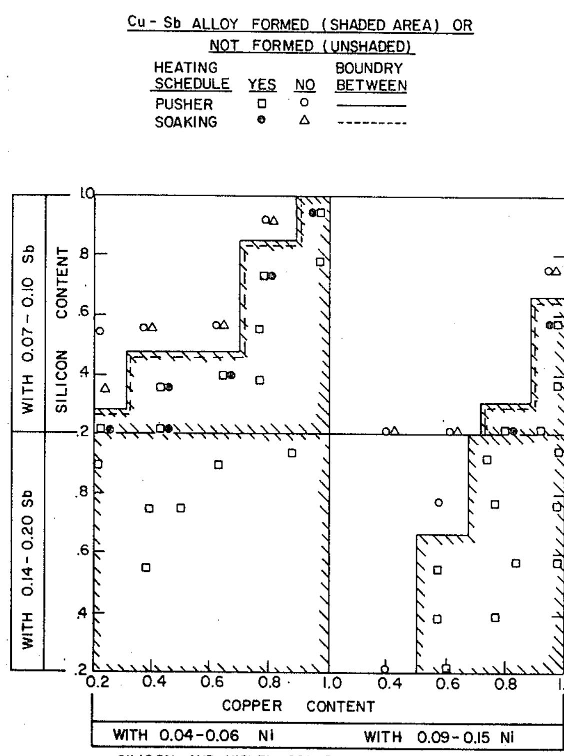
[57] **ABSTRACT**

The surface cracking of steel containing copper and tin and/or antimony during reheating (surface hot shortness) due to the formation of alloys of copper, tin and/or antimony is prevented by adjusting the silicon and nickel content of the steel to an amount necessary to prevent the said alloy formation.

7 Claims, 2 Drawing Figures



SILICON AND NICKEL CONTENTS NECESSARY TO PREVENT- Cu - Sn ALLOY FORMATION ON STEELS CONTAINING COPPER AND TIN.



— SILICON AND NICKEL CONTENTS NECESSARY TO PREVENT Cu - Sb ALLOY FORMATION ON STEELS CONTAINING COPPER AND ANTIMONY.

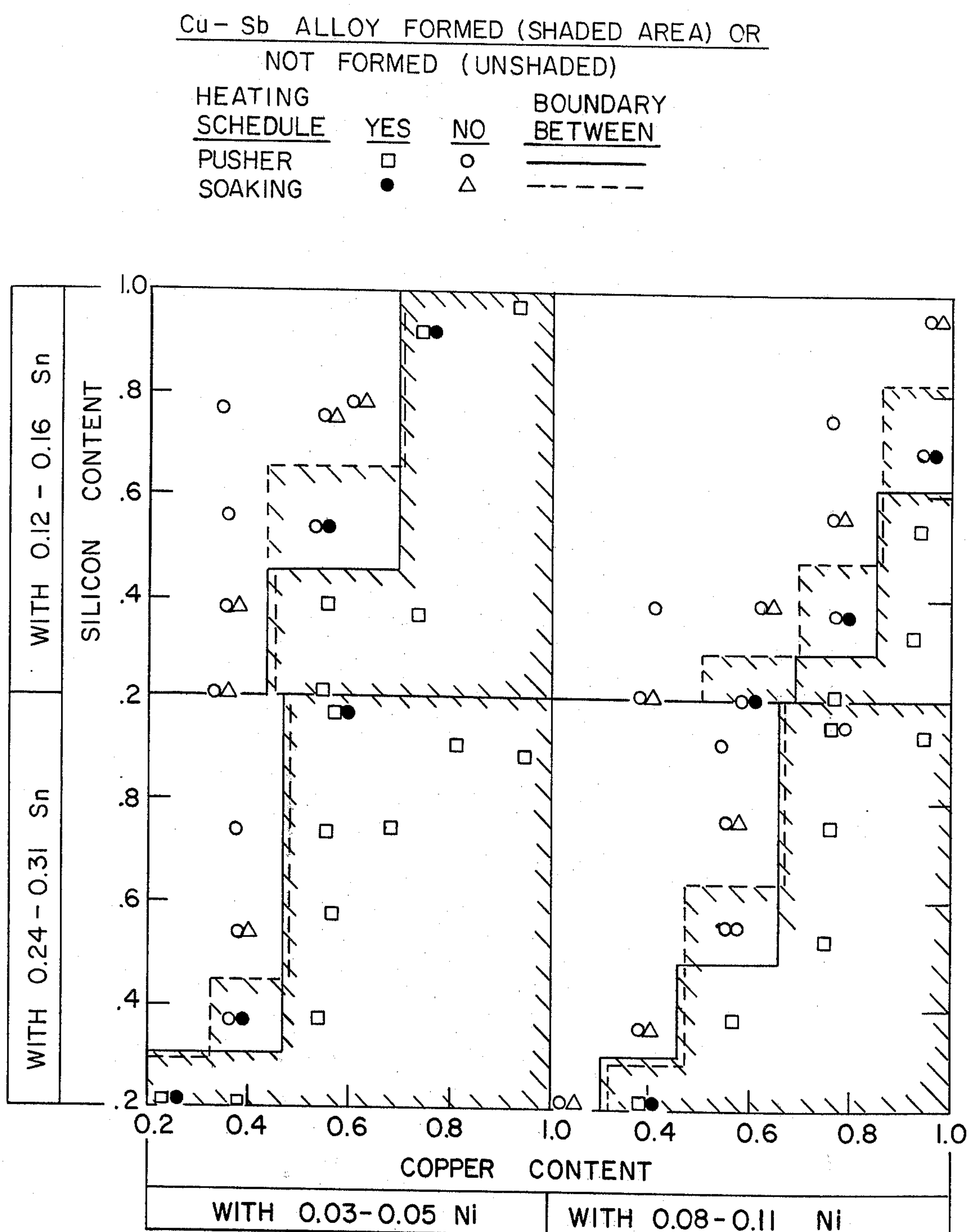


FIG. 1

SILICON AND NICKEL CONTENTS NECESSARY TO PREVENT-Cu-Sn ALLOY FORMATION ON STEELS CONTAINING COPPER AND TIN.

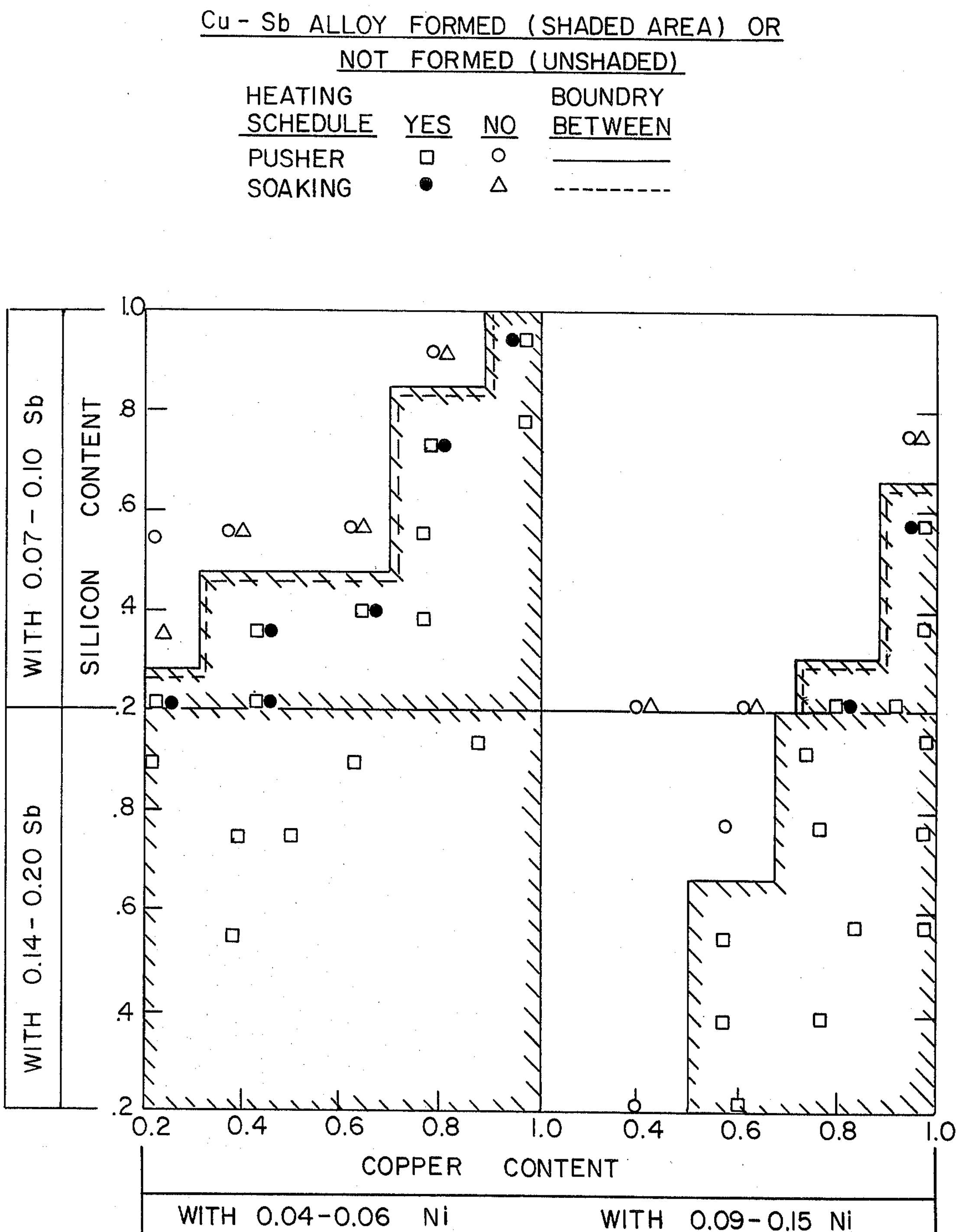


FIG. 2 — SILICON AND NICKEL CONTENTS NECESSARY TO PREVENT Cu - Sb ALLOY FORMATION ON STEELS CONTAINING COPPER AND ANTIMONY.

PREVENTION OF SURFACE CRACKING DUE TO FORMATION OF COPPER ALLOYS OF TIN AND ANTIMONY DURING REHEATING OF STEEL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to steel metallurgy and more particularly to preventing the formation of copper alloys of tin and/or antimony on the surface of steel containing these elements on reheating.

2. Description of the Prior Art

During reheating, several methods are available for preventing copper from forming on the surface of steel containing this element. However, no methods are available, so far as is known, for preventing copper alloys of tin and/or antimony from forming on the surface of steel containing these elements during a reheating operation. The thus formed copper or copper alloy are detrimental because they penetrate the steel austentite grain boundaries during hot rolling. These penetrations weaken the steel surface and cause the formation of deep cracks, especially in the presence of tensile stresses such as occur during hot rolling operations. The alloys make the steel more subject to surface hot shortness (cracking) during hot working than copper alone.

SUMMARY OF THE INVENTION

This invention provides a method for preventing the formation of these detrimental alloys during the reheating of steel containing copper, tin and/or antimony by incorporating nickel and silicon in the steel composition. We have discovered that the presence of nickel and silicon prevents the formation of said alloys on the surface of the steel.

Normally when a steel containing copper, tin, antimony and nickel is reheated in an oxidizing atmosphere, in accord with the usual practice, these elements concentrate at the steel surface. Copper alloys of tin or antimony, or both, form on the surface when the copper present exceeds solubility of copper in iron. In the presence of copper, tin and antimony are more detrimental than copper alone as they lower the solubility of copper in iron and thus promote the formation of greater amounts of copper alloy on the steel surface.

In contrast to antimony and tin, nickel has been found to slightly increase the solubility of copper in iron. Silicon results in the formation of fayalite (Fe_2SiO_4) on the steel surface which reduces the formation of copper on the surface. It was found that the addition of up to 1% silicon and 0.08 to 0.15% of nickel to a steel containing copper, tin and antimony resulted in a marked inhibiting effect on the production of copper alloys of tin and antimony on the surface during reheating. Parenthetically, in the compositions recited, all percentages in the specification and claims are by weight.

OBJECTS OF THE INVENTION

It is an object of this invention to prevent the formation of copper alloys of tin and/or antimony on the surface of steel containing these elements during reheating.

It is a further object of this invention to prevent the formation of such alloys by adjusting the silicon and nickel content of the steel composition.

It is a further object of this invention to prevent the formation of copper alloys of tin and/or antimony on the surface of a steel containing these elements during a reheating by incorporating in said steel silicon and nickel, the amounts of the above elements other than Fe, C and Mn being: Cu, up to 1%, Si, up to 1.0%, Sb, up to 0.20%; Sn, up to 0.31%; and Ni, from 0.03 to 0.15%.

It is a further object of this invention to use less desirable grades of scrap iron and steel containing copper and tin or antimony by adjusting the molten scrap composition to include percentages of nickel and silicon, operative to prevent copper, tin and/or antimony alloy formation during reheating, and forming into a shape, and subjecting it to reheating.

It is a further object to conduct the heat treatment in an oxidizing atmosphere in a hot combustion gas containing about 2% by voluume of oxygen at temperatures of from about 1250°C. to about 1300°C.

It is a further object to conduct the reheating in an oxidizing gas showing a movement of at least one foot per second through the heating zone.

Further objects will become apparent from the following description of the invention and from the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1 and 2 are graphs showing the silicon and nickel content necessary to prevent the copper-tin and copper-antimony alloy formation, respectively, on steels.

BRIEF DESCRIPTION OF PREFERRED EMBODIMENTS

It was found that the beneficial properties of molten fayalite (Fe_2SiO_4) formed from the silicon present in the steel was due to its penetration through the scale grain boundaries to the scale surface. Establishment of local iron-fayalite-oxygen electrolyte cells in the scale promoted the formation of iron-rich iron-copper alloys instead of copper-rich, copper- iron alloys. Since an oxygen potential at the scale surface is required, the free excess oxygen content of the reheating furnace must be regulated to assure a sufficient concentration. It was found that an excess free oxygen content of 2 vol. percent of a burning natural gas combustion atmosphere was generally satisfactory, Liquid petroleum products or other hydrocarbon materials may be substituted for natural gas, if desired. A uniform heating rate was found to be desirable.

The beneficial properties of fayalite in preventing the formation of copper on the surface of steel was found to extend to the prevention of the formation of copper alloys of tin or antimony as well. The following examples show the effects of this presence of Si and Ni in preventing the formation of copper alloys of tin or antimony.

EXAMPLE 1

Steels containing (all figures in weight percent) 0.2C, 0.45Mn, up to 1.0% Cu and Si, 0.03 to 0.06 Ni, and 0.15 or 0.30 Sn, and 0.10 or 0.20 Sb, the balance Fe, were made by a melting step, cooled, and reheated at generally uniform rates to 1300°C. in a burning natural gas atmosphere containing 2 vol. percent excess oxygen. A velocity of at least 1 foot per second of the heating gas through the furnace was maintained.

The reheating was carried out in two types of furnaces. One was a pusher (continuous-type furnace having a **2** hour reheating schedule of from **375°** ± 20°C. to **1310°** ± 10°C. This is represented in the graphs of FIGS. **1** and **2** by solid lines. The other type was a soaking pit furnace having a **8** hour schedule from **820°** ± 20° to **1310°** ± 10°C. This is represented by a dotted line.

The formation or lack of formation of copper-tin and copper-antimony alloys was noted at various alloy compositions and the results are tabulated in the graphs of FIGS. **1** and **2** (lefthand column). Alloy formaton occurs in the cross-hatched regions. It is apparent that for steels containing **0.03** to **0.06**% Ni that the larger the copper and tin or antimony content of the steel, the greater the amount of silicon necessary to prevent copper alloy formation. Copper alloys were not prevented from forming on steels containing **0.12** to **0.16**% Sn and more than about **0.7** Cu or steels with **0.24** – 0.31% Sn and more than about **0.5** Cu. For the antimony steels, copper alloys were not prevented by up to **1**% Si from forming on steels containing **0.14** to **0.20**% Sb at any copper content.

EXAMPLE 2

The nickel content of the steels was increased to **0.08** to **0.15**% and the heating tests of Example **1** were repeated. Larger nickel contents were investigated as copper alloy formation could not be prevented in Example **1** by **0.03** to **0.06**% Ni and up to **1**% Si on many steel compositions containing up to **1**% Cu. The amount of silicon required to prevent copper-tin or copper-antimony formation with the higher nickel content is given in the righthand columns of FIGS. **1** and **2**, respectively. By comparing the left and righthand columns of the Figures, it is apparent that much less silicon is necessary to prevent copper alloy formation on steels containing **0.09** to **0.15**% Ni than on those containing **0.03** – 0.06% Ni. Moreover, the amount of silicon required to prevent copper alloy formation on steels containing **0.4**% or less copper content and **0.12** – 0.16% Sn or **0.07** – 0.10% Sb is similar to the amount used in many commercial steels, **0.2** to **0.4** % Si.

Steels containing larger nickel contents, up to **0.50**%, were likewise investigated. The results with such higher nickel content steels were no better generally than with steels containing **0.08** to **0.11**% Ni.

When both tin and antimony are present in a steel with **0.08** – 0.15% Ni, the combined total percent of tin and antimony generally should not exceed **0.10**% for steel containing up to **1**% Cu. The combined total should not exceed **0.20**% for steels with up to **0.5**% Cu. Reheating of steels containing copper contents greater than **0.5**% Cu and tin and antimony combined contents greater than **0.20**% generally should not be considered unless formation of copper alloys is desired.

Without wishing to be bound by any theory, one possible explanation for the beneficial effects of the combination of silicon and nickel in promoting the formation of iron-rich iron-copper alloys instead of copper-tin or -antimony alloys on the surface of steels containing copper as well as tin or antimony is the following: Iron-rich alloys have been found to form on steel surfaces only when the steel was heated above **1205**°C., which is common in rolling operations. At these temperatures, fayalite melts and penetrates the grain boundaries of the steel. The higher the silicon content, the greater the amount of fayalite produced and concommitantly, the greater penetration of larger amounts fayalite to the scale surface. Under these conditions, iron alloy-fayalite-oxygen electrolytic cells are established in the scale. The iron oxides of the scale and the molten fayalite act as electronic and ionic conductors, respectively. Oxygen ions are transported by the molten fayalite to the steel surface and Fe, Cu, Sn, Sb and Ni ions migrate to the scale surface. The local cell action promotes the formation of iron-rich copper alloys at the steel surface. When Sn or Sb are present in addition to copper, a minimum nickel content of **0.03**% is necessary, with from about **0.08** to **0.15**% as generally desirable. The nickel, which concentrates at the steel surface as the steel scales, increases the solubility of copper at the steel surface and regulates the copper composition of the steel surface to below its solubility in iron.

The process has been described for reducing surface hot shortness of copper steels containing tin or antimony by the addition of silicon and nickel generally and by examples with reference to specific compositions. It will be apparent to those skilled in the art that various modifications of the process and the compositions disclosed may be made without departing from the spirit of the invention.

What is claimed is:

1. In a method of producing steel having resistance to hot shortness due to the formation of copper-tin and copper-antimony alloys on the steel surface during reheating, said steel containing copper in an amount up to about **1**% by weight and a member of the group consisting of tin and antimony, and mixtures thereof, tin and antimony being present in amounts of up to about **0.31**% and up to about **0.20**% respectively, and when both are present, the total not exceeding about **0.10**% for steels containing up to **1**% Cu and not exceeding **0.20**% for steels containing up to **0.5**% Cu, which method includes melting and solidification, the improvement comprising:

in the melting step, adjusting the content of silicon and nickel in the steel to from about **0.2**% to about **1.0**% for the silicon, and from about **0.03**% to about **0.15**% for the nickel, said ranges selected falling within the unshaded portions of the graphs of FIGS. **1** and **2**.

2. The method of claim **1** wherein the steel contains tin in an amount of up to about **0.31**%, the silicon content is from about **0.2**% to about **1.0**%, the nickel content ranges from about **0.03** to about **0.05**%, the copper content ranges from about **0.2** to about **1.0**%, and the amount of silicon and copper falls within the unshaded portion of the lefthand column of FIG. **1**.

3. The method of claim **1** wherein the steel contain tin in an amount of up to **0.31**%, the silicon content is from about **0.2**% to about **1.0**%, the nickel content ranges from about **0.08** to about **0.11**%, the copper content ranges from about **0.2**% to about **1.0**%, and the amount of silicon and copper falls within the unshaded portion of the righthand column of FIG. **1**.

4. The method of claim **1** wherein the steel contains antimony in an amount of up to **0.20**%, the silicon content is from about **0.2**% to about **1.0**%, the copper content is from about **0.2**% to about **1.0**%, the nickel content is from about **0.04** to about **0.06**% and the amounts of silicon and copper falls within the unshaded portion of the lefthand column of FIG. **2**.

5. The method of claim **1** wherein the steel contains antimony in an amount of up to **0.20%**, the silicon content is from about **0.2%** to about **1.0%**, the copper content is from about **0.2%** to about **0.1%**, the nickel content is from about **0.9%** to about **0.15%**, and the amount of silicon and copper falls within the unshaded portion of the righthand column of FIG. **2.**

6. In a method of producing an upgraded steel having reduced surface hot shortness from scrap steel pieces containing in the aggregate copper and a member of the group consisting of tin and antimony and mixtures thereof, which comprises selecting portions of steel scrap to give an overall steel composition containing in addition to Fe, C and Mn up to about **1%** copper, up to about **0.31%** tin, up to about **0.20%** antimony, but when both tin and antimony are present the combined total percentage of these elements is no more than about **0.10%** for steels containing up to **1%** Cu and not exceeding **0.20%** for steels containing up to **0.5%** Cu, the improvement comprising;

melting the selected steel scrap;

adjusting the nickel content to from about **0.03%** to about **0.15%** and adjusting the silicon content from about **0.2%** to about **1.0%**;

the ranges selected falling within the unshaded portions of the graphs of FIGS. **1** and **2.**

7. The method of claim **6** wherein the nickel content is adjusted to from about **0.08** to about **0.15%** and the ranges selected fall within the unshaded portions of the righthand columns of FIGS. **1** and **2.**

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