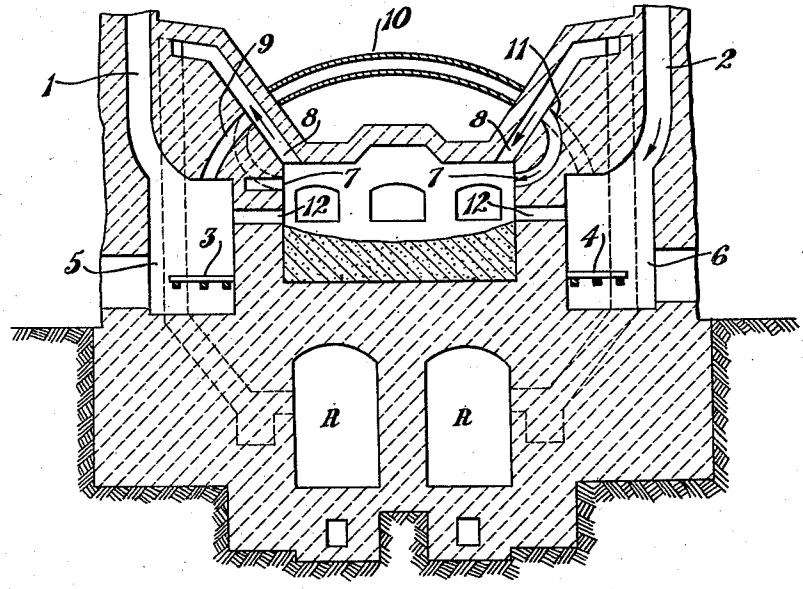
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METHOD OF MAKING STAINLESS STEEL

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METHOD OF MAKING STAINLESS STEEL

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The invention relates to an improved method of making stainless iron and steel, and more particularly to a novel method of producing stainless steel in an open hearth furnace; and this application is a continuation in part of the common subject matter in our copending application Serial No. 142,411, filed May 13, 1937, entitled Method of making stainless steel.

A very high percentage of present day stainless steel is made in the electric furnace, because with known processes, the extremely high refining temperatures and close control over furnace atmospheres required cannot be satisfactorily obtained in the ordinary open hearth practice.

Stainless steel contains a high percentage of chromium, which may be 12 to 27%, and a low percentage of carbon, preferably approximately 0.10% or under. The refining of high chrome steels requires higher temperatures than ordinary steel because high chrome steels are relatively thick and sluggish, but chromium is easily oxidized and has a marked affinity for carbon at those temperatures.

In the ordinary open hearth, the atmospheric conditions are strongly oxidizing. Consequently with high chrome steels the tendency of the chromium to become oxidized and pass into the slag on the metal bath is greatly increased, and as a result steels containing more than about 8% chromium cannot be successfully made in the conventional open hearth furnace.

Since the furnace atmosphere of the electric furnace can be controlled to a considerable extent, stainless steels can be made relatively satisfactorily in the electric furnace by superheating the metal bath before each addition of ferro-chrome.

However, electric furnace practice is expensive, and there is always a great tendency of increasing the carbon content of the metal bath due to dispersion of carbon from the electrodes. This tendency greatly limits the proportion of stainless scrap which may be used in the charge.

Accordingly, it is a general object of the present invention to provide an improved method of making low carbon high chromium stainless steel of high quality in an open hearth furnace.

Another object is to provide an improved method of making high quality stainless steel more economically than the electric furnace product.

A further object is to provide an improved method of making high chromium steel having a lower carbon content than can satisfactorily and consistently be made in electric furnace practice.

Another object is to provide an improved method of making stainless steel which permits a greatly increased proportion of scrap in the furnace charge.

Another object is to provide an improved method of making stainless steel which permits increased flexibility in varying the materials charged.

A still further object is to provide an improved method of making stainless steel in an open hearth, and which produces a uniform product giving a high yield of the alloying metal.

And finally, it is an object of the present invention to provide an improved method of making stainless steel in an open hearth furnace, which includes providing a neutral protective blanket on the bath, and providing an atmosphere in the furnace immediately above the blanket which is neutral or non-oxidizing or reducing with respect to the protective blanket, to the extent that it will not oxidize FeO in the blanket so as to produce Fe_2O_3 in the blanket, and to the extent that it will not oxidize silicon so as to produce SiO_2 in the blanket by a reaction between the blanket forming materials and the atmosphere; and which blanket is substantially neutral or substantially non-oxidizing with respect to the chromium in the bath.

These and other objects are accomplished by the improvements, methods, and order of method steps comprising the present invention, which may be stated in more general terms as comprising a novel method of making stainless steel in an open hearth including forming a neutral protective blanket on the metal bath before adding the alloying element, and continuously maintaining a substantially non-oxidizing atmosphere in the furnace immediately above the metal protective blanket. This non-oxidizing atmosphere may be either neutral or reducing.

Thus, the terms "non-oxidizing atmosphere," "neutral atmosphere" or "reducing atmosphere," when used herein and in the appended claims with respect to the furnace atmosphere immediately above the protective blanket, mean an atmosphere which is non-oxidizing, neutral or reducing, to the extent that it will not oxidize FeO in the blanket so as to produce Fe_2O_3 in the blanket; and to the extent that no SiO_2 forming reaction will occur between the silicon in the blanket forming materials and the furnace atmosphere; and to the extent that there will be

no appreciable chromium oxide forming reaction between the blanket and the bath.

These distinctions are made, because, while SiO_2 is present in the blanket as hereinafter described, the SiO_2 present in the blanket is produced by other reactions and not by a reaction between the blanket forming materials and the furnace atmosphere.

These distinctions are also made, because, while chromium oxides may be formed during the melting period, the same is produced by other reactions and not by any appreciable reaction between the blanket and the furnace atmosphere immediately thereabove.

The present improved method has been carried out commercially to produce high quality stainless steel having the required high chromium content and low carbon content, and we are able to use an open hearth furnace having either a neutral or a basic lining, although a basic lining including magnesite, is generally preferred. The following description of our invention is by way of example, and it is understood that the improved method may be applied to the making of similar high chromium, low carbon alloys of iron and steel containing additional alloying elements such as manganese, tungsten, vanadium, molybdenum, columbium, boron, zirconium and titanium.

The figure in the accompanying drawing is a diagrammatic cross sectional view of an open hearth furnace in which our improved method may be successfully practiced.

The furnace shown in approximately 3½ ton capacity, although the invention may be practiced in a larger furnace if desired. The furnace is preferably operated on a schedule of three heats every twenty-four hours, during which about seven hours is required from the time charging is started until a heat is tapped.

Although the furnace diagrammatically shown in the accompanying drawing is hereinafter described as being a coal fired furnace, the practice of the improved method is not limited to the use of a coal fired furnace, because the method can be carried out in an oil fired furnace, or a natural or artificial gas fired furnace such as is disclosed in the copending application of William D. Bradford, Serial No. 148,756, filed June 17, 1937 matured in Patent No. 2,137,892, dated November 22, 1938.

In operating the furnace shown in the drawing, after a heat is tapped, the furnace is brought up to required temperature, preferably by charging soft coal alternately through the hoppers 1 and 2 onto grates 3 and 4 located in gas producing chambers 5 and 6 respectively.

Obviously, the coal burning gas producers may be supplemented or replaced, as previously stated, by natural or artificial gas burners, or oil burners if desired.

At each end of the furnace there are smoke gas ports 7 which introduce the volatile gases generated from both chambers 5 and 6. Air ports 8 are located above the gas ports 7 for introducing air for combustion downwardly at a sharp angle to the hearth to insure combustion.

The air for combustion is preheated in the customary checker regenerators indicated at R, located below the furnace hearth, and adapted to be alternately connected with the air ports 8 according to usual open hearth practice.

While one producer is on air, the other is shut off and the coal simply cokes, the volatile matter therefrom being transferred to the opposite gas port 7. In the drawing, producer 6 is shown as being on air and producer 5 is shut off, the volatile matter or smoke gases from producer 5 being transferred through passage 9, pipe 10 and passage 11 to discharge from the opposite gas port 7 where it mixes with the volatile matter from producer 6. The coal bed in producer 6 is kept high enough so that the air coming through the grates is drawn directly into the furnace through the lower producer ports 12 after passing through the lower part of the fuel bed. This stream of non-oxidizing gas enters immediately above the metal bath and effectively protects the bath from the smoke gases and air above. This non-oxidizing gas is essentially a coke producer gas as distinguished from the volatile gases issuing from the gas ports 7.

After a short interval, say twenty minutes, the furnace is reversed and fired from the opposite side, the volatile matter from the coking coal being transferred through a pipe in the opposite direction to the opposite gas port 7.

By means of this particular arrangement of ports and the small number of openings admitting air to the furnace, the flame and gas conditions in the furnace can be controlled to a considerable extent, and are preferably controlled to maintain a substantially non-oxidizing furnace atmosphere directly above the bath throughout the heat. Otherwise, with an oxidizing flame there is an excess of oxygen which will tend to combine with the chromium present and cause a loss of chromium from the bath before the protective blanket is provided, and which would tend to combine with certain constituents of the protective blanket during or after the formation thereof; and with a smoky atmosphere directly above the bath there is carbon present which tends to enter the bath so as to add to the carbon content of the bath.

At the beginning of a heat, the furnace is brought up to a temperature of about 3000° to 3200° F., after which it is ready for charging.

The body of the initial charge may consist either of carefully selected stainless steel scrap of the approximate analysis of the steel to be made, or it may consist of a good grade of common steel scrap; depending somewhat upon the kind of scrap available and somewhat upon the analysis of the steel to be made, particularly upon the desired carbon content.

In making 18—8 (18% chromium and 8% nickel) stainless steel in the furnace illustrated, using stainless steel scrap having a typical analysis of approximately 17.05% chromium, 9.52% nickel, and 0.10% carbon, about 7500 pounds of the scrap is charged with about 60 pounds of burnt lime, preferably some or all of the lime first, and some ferro-chrome may be added if necessary to increase the chromium content.

The furnace is maintained at a temperature of 3000° to 3200° F., and the charge is melted down in about 4 to 5 hours, the temperature of the metal bath being about 2800° to 3000° F.

If a gas fired furnace is utilized, the gas conditions in the furnace can be controlled as set forth in said copending Bradford application, Serial No. 148,756, to maintain a substantially non-oxidizing furnace atmosphere directly above the bath throughout the heat; and in using a gas fired furnace, a heat may be charged and melted down in a manner similar to that just described.

After a heat has been melted down as just described, a neutral protective blanket is formed on the bath. This blanket may be formed by add-

ing certain materials, three examples of which are given as follows:

Example 1

	Pounds
Ferro-silicon (75% Si, 25% Fe)	40
Burnt lime (CaO)	25
Barium carbonate ($BaCO_3$)	25
Fluorspar (CaF_2)	10
Chrome ore (Cr_2O_3 and FeO)	65

Example 2

	Pounds
Calcium silicon	50
Burnt lime	20
Strontium carbonate	25
Chrome ore	65

Example 3

	Pounds
Ferro-silicon	40
Burnt lime	25
Barium carbonate	25
Sodium carbonate	10
Chrome ore	65

These blanket forming materials, together with certain ingredients of the melt, form what is termed herein a neutral protective blanket on the metal bath in approximately thirty minutes, and this neutral protective blanket is the same when formed, whether the furnace lining be basic or acid. The neutral protective blanket might be termed a neutral slag in the sense that it forms a fluid layer covering the metal bath; but the same is not a slag in the usual sense of that word, because it does not remove sulphur or phosphorus or any other impurities from the metal bath.

The function of the neutral protective blanket over the metal bath is to prevent oxidation, especially of the chromium therein, and especially at and after the time when an analysis determination is made and at and after the time when additions are made to obtain the desired analysis; and to throw chromium in chromium oxides which may have formed on the bath during the melting down period, back into the bath.

After the neutral protective blanket has been formed on the metal bath, a sample is taken from the bath and analyzed in order to determine how much chromium and how much nickel are needed to obtain the desired specification or analysis, after which the necessary amount of chromium is added in the form of ferro-chrome, together with the necessary amount of nickel, and a small amount of ferro-manganese if necessary, to increase the manganese content.

An analysis of the important alloying elements is shown below, determined from a typical sample of the metal bath taken after the neutral protective blanket was formed by the addition of materials in accordance with Example 1, as follows:

	Per cent
Chromium	16.77
Nickel	9.56
Carbon	0.10
Manganese	0.20

In this particular case, after the determination was made, 200 pounds of ferro-chrome was added about one hour before tapping and 20 pounds of ferro-manganese was added about ten minutes before tapping in order to obtain the desired specification or analysis of the metal when tapped.

The heat is tapped into a ladle when ready, after the additions have been made as just described; and the heats are usually ready for tapping in approximately seven hours from the beginning of the charging. Sufficient ferro-silicon may be added if necessary to bring the silicon content up to the desired specification. A typical analysis of the principal alloying elements in the steel as tapped, is as follows:

	Per cent
Chromium	18.23
Nickel	9.32
Carbon	0.10
Manganese	0.30

In the example given, the weight of the tapped steel was 7200 pounds, constituting a yield of 93%, although average yields range from 93 to 97%.

The neutral protective blanket

The formation of the neutral protective blanket from the additions given in Example 1 results from reactions occurring between the materials added and certain reactions which may occur between those materials and any of the oxides of chromium and iron which may have formed on the bath during the melting down period.

Silicon or ferro-silicon, as such, do not constitute a part of the protective blanket when formed, but the silicon is oxidized to SiO_2 by the reduction of the oxides of chromium and iron included in the chrome ore added and those which may have formed on the bath during the melting down period.

In other words, the function of the silicon in the ferro-silicon added, is to provide a de-oxidizing agent. This deoxidizing agent, in reducing the oxides of chromium and iron to chromium metal and to iron, forms SiO_2; and the surplus or remaining FeO and SiO_2 form a low melting point and fluid ingredient of the neutral protective blanket. Thus, chromium which may have formed chromium oxides on the bath during the melting down period is thrown back into the bath, so that the protective blanket when formed contains SiO_2, FeO and for equilibrium purposes, may contain a small amount of chromium oxides. However, more chromium oxides are contained in the chrome ore added than is present in the neutral protective blanket when formed.

The protective blanket, in being neutral, is stable or inert after being formed by its own reactions so that it does not thereafter react with the bath or the furnace atmosphere.

Likewise, the protective blanket contains oxidized constituents, or constituents which cannot be oxidized by a reaction with the neutral furnace atmosphere; and the character of the blanket is such that pure metals are thrown back into the bath by the formation of the blanket and thereafter retained in the bath after the blanket is formed.

A certain amount of FeO resulting in the protective blanket when formed, is necessary, in order to assist in maintaining fluidity in the blanket and to prevent silicon from going into the bath. Thus, the protective blanket prevents chromium from being lost from the bath or picked up in the blanket and adequately covers or protects the bath by reason of its fluidity.

It is necessary, in making the additions to form the neutral protective blanket that the same contain chrome ore, which chrome ore is a material containing reducible iron and chromium compounds, or some other similarly cheap chromium and iron containing material or materials in order that the blanket results in being neutral,

stable or inert when formed. That is to say, the materials for supplying the oxides of iron, chromium and silicon constituents in the stable or inert neutral blanket are the blanket forming materials added. On the other hand, certain prior art electric furnace stainless steel making practices which include merely the addition of lime and ferro-silicon for slag forming purposes, pick up Fe and Cr from the bath in order to satisfy the slag when ferro-chrome additions are made to bring up the chrome content of the bath.

The burnt lime in the blanket forming materials is believed to react with the SiO_2 derived from the ferro-silicon to form the usual silicates. Barium or strontium or sodium carbonates are believed to react with the other blanket forming materials to lower the melting point of the blanket and maintain it more fluid and the barium or strontium or sodium carbonates apparently speed up the reaction between the iron and chromium oxides and ferro-silicon. The fluorspar apparently tends to make the blanket more homogeneous.

The improved method may also be used in making stainless steel from plain carbon steel scrap and pig iron. Thus, an initial charge including plain carbon steel scrap and pig iron instead of stainless steel scrap may be made, and for instance when it is desired to produce 17% chromium stainless steel with a carbon content as low as 0.05% or 0.06%, the furnace is brought up to heat and the initial charge may consist of approximately 5000 pounds, two-thirds being low carbon common scrap and one-third pig iron, together with about 300 pounds of burnt lime.

The charge is melted down as before in about four to five hours, some iron ore being added as necessary to maintain an oxidizing slag and reduce the carbon to 0.05% or less. Next, a sample is taken from the metal bath and analyzed to determine the carbon, sulphur and phosphorus content of the bath. When these are found to be satisfactory, the next step is to pull off or remove the oxidizing slag which has been formed during the melting down step.

The neutral protective blanket forming materials are then added, as previously described in connection with the manufacture of stainless steel from stainless steel scrap in an open hearth furnace, to form a neutral protective blanket on the carbon steel scrap and pig iron melt. However, the proportions of the neutral blanket forming material additions given in Example 1 for instance, are changed so that about 125 pounds of chrome ore is added rather than 65 pounds.

After the neutral protective blanket has been formed, approximately 1700 pounds of ferro-chrome (70% chrome) is added to bring the chromium content of the tapped steel up to 17%.

When stainless steel scrap is used in the initial charge, by carefully selecting low carbo- scrap, substantially all of the charge is made up of stainless steel scrap. In making stainless steel of the same specification in an electric furnace, the amount of stainless steel scrap in the initial charge is ordinarily limited to about 50%, because of the pick up of carbon from the ele- trodes.

Stainless steel made by our improved method contains a relatively small amount of insolubles or non-metallic inclusions, because the metal bath is substantially quiescent throughout. In the electric furnace, the application of heat by the electrodes necessarily caused agitation of the bath, which results in some dispersion of slag into the metal.

The present improved method is equally successful in making 27% chromium down to 12% chromium stainless steels and stainless steels as low as 0.05% to 0.06% carbon can be produced. It is extremely difficult, however, to make stainless steel having such a low carbon content in the electric furnace because of the ever present tendency of pick up of carbon from the electrodes.

Items in the cost per ton of metal in making high quality stainless steel in the electric furnace are approximately $6.00 for electric current, $1.00 for electrode consumption, $.50 for water, making a total of $7.50, plus a high refractory cost.

Corresponding items in the cost per ton of metal in making high quality stainless steel according to the present improved method in an open hearth furnace are materially lower fuel costs and a low refractory cost. Thus, the present improvements show marked savings in the cost of making stainless steel.

Having now described the features of the invention, the details of the necessary or desirable steps of the same, and the advantages and results obtained by use of the invention; the new and useful methods, steps, treatments and reasonable mechanical equivalents thereof obvious to those skilled in the art are set forth in the appended claims.

We claim:

1. In the manufacture of high chromium, low carbon stainless steel alloys in a heated open hearth furnace, the method which includes charging materials on the furnace hearth and treating the same to form a low carbon ferrous metal bath; forming a neutral, stable, inert, fluid protective blanket on the metal bath by the interaction of added materials including silicon, burnt lime, and reducible iron and chromium compounds, which blanket when formed contains silica and oxides of iron and chromium derived from the materials added for thereafter preventing oxidation of and chromium loss from the bath; adding ferro-chrome to the metal bath after the neutral blanket has been formed; and continuously maintaining a heated non-oxidizing atmosphere immediately above the blanket.

2. In the manufacture of high chromium, low carbon stainless steel alloys in a heated open hearth furnace, the method which includes charging low carbon ferrous scrap on the furnace hearth and heating the same to form a metal bath; maintaining the heating atmosphere non-oxidizing immediately above the bath; forming a neutral, stable, inert, fluid protective blanket on the metal bath by the interaction of added materials including silicon, burnt lime, and reducible iron and chromium compounds, which blanket when formed contains silica and oxides of iron and chromium derived from the materials added for thereafter preventing oxidation of and chromium loss from the bath; adding ferro-chrome to the metal bath after the neutral blanket has been formed; and continuously maintaining the heated non-oxidizing atmosphere immediately above the blanket.

3. In the manufacture of high chromium, low carbon stainless steel alloys in a heated open hearth furnace, the method which includes charging low carbon stainless steel scrap on the furnace hearth and heating the same to form a metal bath; maintaining the heating atmosphere non-oxidizing immediately above the bath;

forming a neutral, stable, inert, fluid protective blanket on the metal bath by the interaction of added materials including silicon, burnt lime, and reducible iron and chromium compounds, which blanket when formed contains silica and oxides of iron and chromium derived from the materials added for thereafter preventing oxidation of and chromium loss from the bath; and continuously maintaining the heated non-oxidizing atmosphere immediately above the blanket.

4. In the manufacture of high chromium, low carbon stainless steel alloys in a heated open hearth furnace, the method which includes charging ferrous scrap on the furnace hearth and heating the same to form a metal bath; adding iron ore to reduce excess carbon by oxidation; removing the oxidizing slag; forming a neutral, stable, inert, fluid protective blanket on the metal bath by the interaction of added materials including silicon, burnt lime, and reducible iron and chromium compounds, which blanket when formed contains silica and oxides of iron and chromium derived from the materials added for thereafter preventing oxidation of and chromium loss from the bath; adding ferro-chrome to the metal bath after the neutral blanket has been formed; and continuously maintaining a heated non-oxidizing atmosphere immediately above the blanket.

5. In the manufacture of high chromium, low carbon stainless steel alloys in a heated open hearth furnace, the method which includes charging materials on the furnace hearth and treating the same to form a low carbon ferrous metal bath; forming a neutral, stable, inert, fluid protective blanket on the metal bath by the interaction of added materials including silicon, burnt lime, and reducible iron and chromium compounds, which blanket when formed contains silica and oxides of iron and chromium derived from the materials added for thereafter preventing oxidation of and chromium loss from the bath; reducing chromium oxides to chromium during the formation of said blanket; adding ferro-chrome to the metal bath after the neutral blanket has been formed; and continuously maintaining a heated neutral atmosphere immediately above the blanket.

6. In the manufacture of high chromium, low carbon stainless steel alloys in a heated open hearth furnace, the method which includes charging materials on the furnace hearth and treating the same to form a low carbon ferrous metal bath; forming a neutral, stable, inert, fluid protective blanket on the metal bath by the interaction of added materials including ferro-silicon, burnt lime, barium carbonate, and chrome ore, which blanket when formed contains silica and oxides of iron and chromium derived from the materials added for thereafter preventing oxidation of and chromium loss from the bath; adding ferro-chrome to the metal bath after the neutral blanket has been formed; and continuously maintaining a heated non-oxidizing atmosphere immediately above the blanket.

7. In the manufacture of high chromium, low carbon stainless steel alloys in a heated open hearth furnace, the method which includes charging low carbon ferrous scrap on the furnace hearth and heating the same to form a metal bath; maintaining the heating atmosphere non-oxidizing immediately above the bath; forming a neutral, stable, inert, fluid protective blanket on the metal bath by the interaction of added materials including ferro-silicon, burnt lime, barium carbonate, and chrome ore, which blanket when formed contains silica and oxides of iron and chromium derived from the materials added for thereafter preventing oxidation of and chromium loss from the bath; adding ferro-chrome to the metal bath after the neutral blanket has been formed; and continuously maintaining the heated non-oxidizing atmosphere immediately above the blanket.

8. In the manufacture of high chromium, low carbon stainless steel alloys in a heated open hearth furnace, the method which includes charging low carbon stainless steel scrap on the furnace hearth and heating the same to form a metal bath; maintaining the heating atmosphere non-oxidizing immediately above the bath; forming a neutral, stable, inert, fluid protective blanket on the metal bath by the interaction of added materials including ferro-silicon, burnt lime, barium carbonate, and chrome ore, which blanket when formed contains silica and oxides of iron and chromium derived from the materials added for thereafter preventing oxidation of and chromium loss from the bath; and continuously maintaining the heated non-oxidizing atmosphere immediately above the blanket.

9. In the manufacture of high chromium, low carbon stainless steel alloys in a heated open hearth furnace, the method which includes charging ferrous scrap on the furnace hearth and heating the same to form a metal bath; reducing excess carbon by oxidation; removing the oxidizing slag; forming a neutral, stable, inert, fluid protective blanket on the metal bath by the interaction of added materials including ferro-silicon, burnt lime, barium carbonate, and chrome ore, which blanket when formed contains silica and oxides of iron and chromium derived from the materials added for thereafter preventing oxidation of and chromium loss from the bath; adding ferro-chrome to the metal bath after the neutral blanket has been formed; and continuously maintaining a heated non-oxidizing atmosphere immediately above the blanket.

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