

June 16, 1936.

E. C. BAIN ET AL

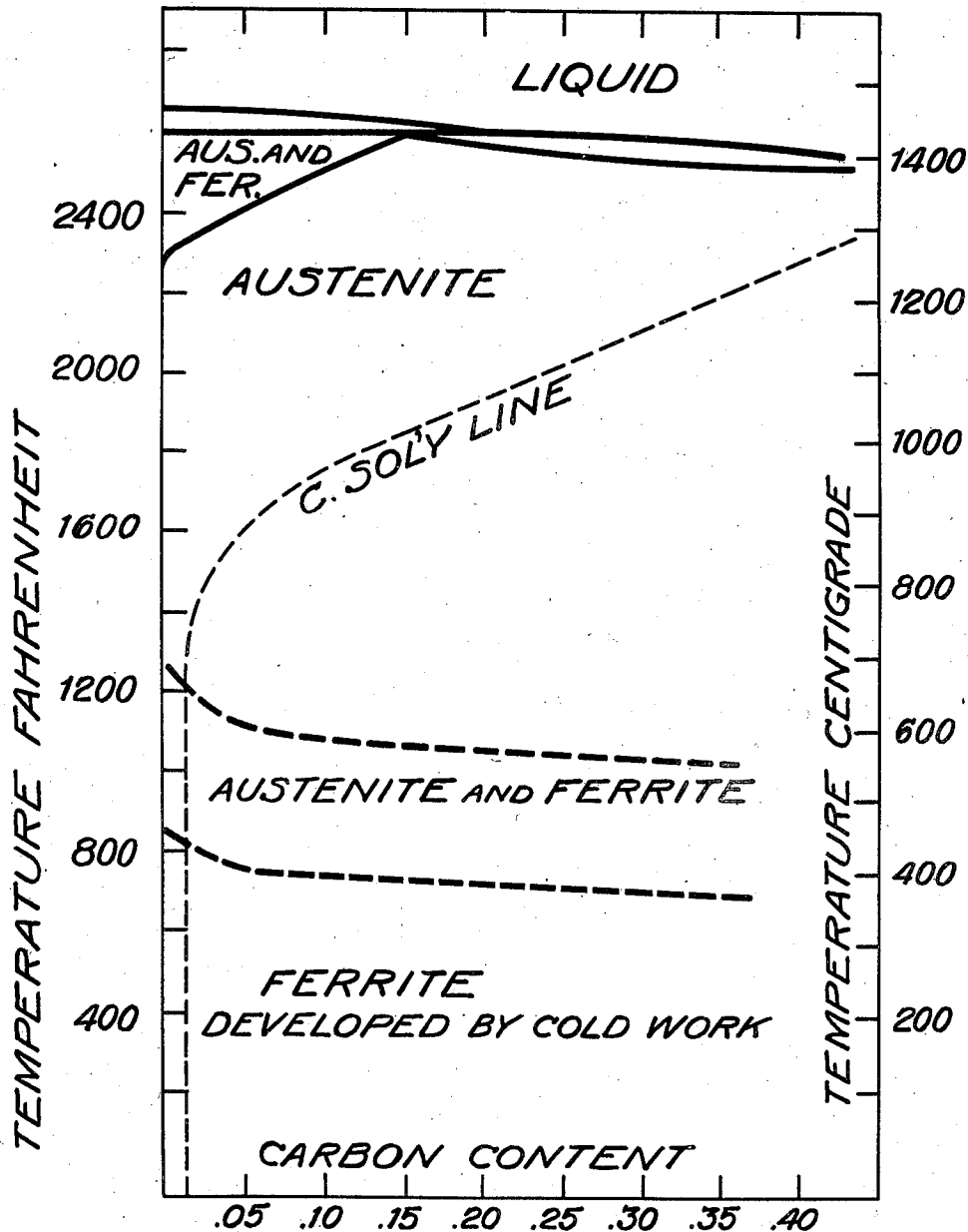
2,044,743

TREATING AUSTENITIC STEEL

Filed May 4, 1935

3 Sheets-Sheet 1

Fig. 1



INVENTORS
EDGAR C. BAIN.
ROBERT H. ABORN.
BY *Wm. H. Ransom*
ATTORNEYS

June 16, 1936.

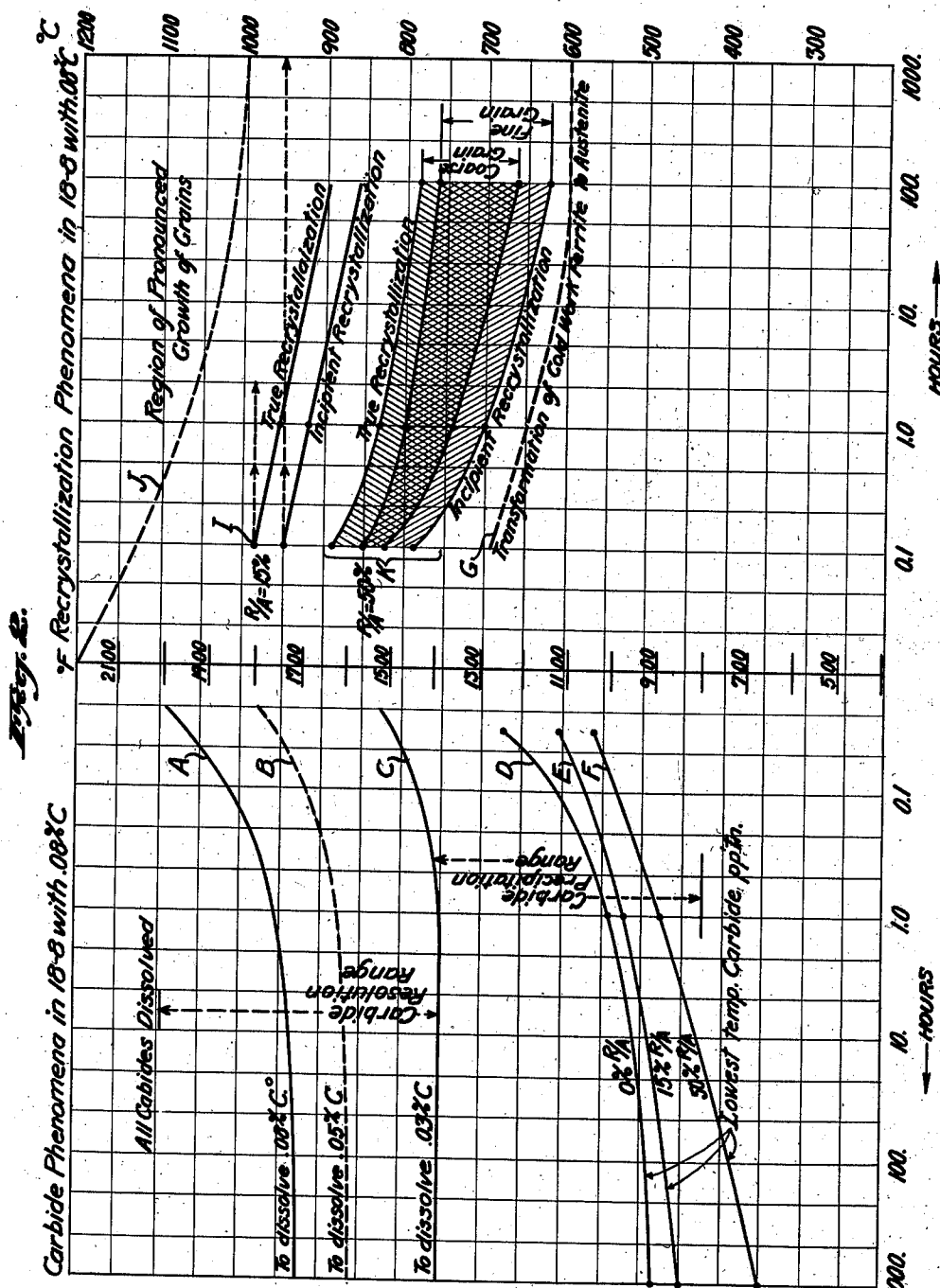
E. C. BAIN ET AL

2,044,743

TREATING AUSTENITIC STEEL

Filed May 4, 1935

3 Sheets-Sheet 2



INVENTORS
EDGAR C. BAIN.
BY ROBERT H. ABORN.
Wain & Barker
ATTORNEYS

June 16, 1936.

E. C. BAIN ET AL
TREATING AUSTENITIC STEEL

2,044,743

Filed May 4, 1935

3 Sheets-Sheet 3

Fig. 3.

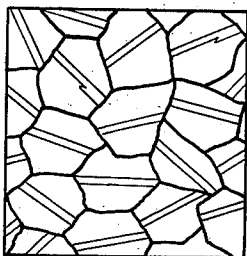


Fig. 4.

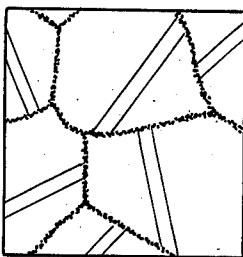


Fig. 5.

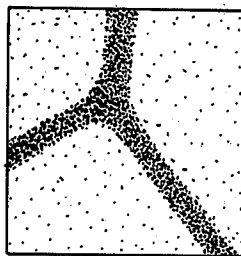


Fig. 6.

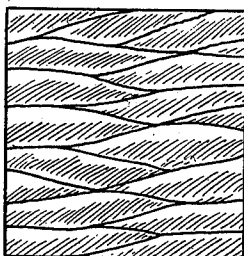


Fig. 7.



Fig. 8.

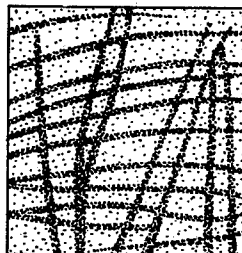


Fig. 9.

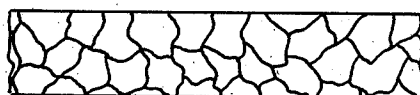
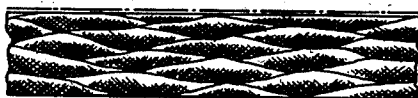


Fig. 10.



INVENTORS
EDGAR C. BAIN.
ROBERT H. ABORN.
BY *Mama & Hauber*
ATTORNEYS

UNITED STATES PATENT OFFICE

2,044,743

TREATING AUSTENITIC STEEL

Edgar C. Bain and Robert H. Aborn, Short Hills,
N. J., assignors to United States Steel Corpo-
ration, New York, N. Y., a corporation of New
Jersey

Application May 4, 1935, Serial No. 19,865

4 Claims. (Cl. 148—12)

This invention relates to iron and steel alloys and more particularly to those alloys containing carbon, chromium and nickel in such relative proportions as to produce what is known in the art as stainless steel of the austenitic type. A familiar example of this type of steel is the approximately 18% chromium, 8% nickel alloy known as "18-8" which however may carry either more or less of the alloying elements than indicated. The invention is equally applicable to all such alloys as are austenitic even though the nickel content ranges as widely as from about 6% to about 50% and with chromium between about 10% and 40% with or without various proportions of other auxiliary elements. This application is a continuation in part of our prior application filed February 17, 1931 bearing Ser. No. 516,474.

Heretofore in the art austenitic chromium, nickel and iron alloys have been known. Such alloys, however, have been characterized by a marked loss in corrosion resistance and loss in toughness when subjected to temperatures within the range 800° F. to 1500° F. This loss in corrosion resistance and toughness is attributed to the intergranular precipitation of metal carbide compounds of a chromium-rich type probably based on the compound Cr₄C with more or less of other elements such as iron incorporated therewith.

Heretofore in the art it has been customary to subject such alloys to a relatively high temperature heat-treatment (1800° F. or above) in order to "homogenize" the alloys prior to subjecting the alloy to service use wherein the corrosion resisting properties of the alloy are desired. This homogenizing heat-treatment is for the purpose of converting the alloy structure entirely into austenite. In such an austenite structure all of the carbon and associated metal constituents of the alloy are in solid solution.

Following this heat-treatment the alloy is rapidly cooled to atmospheric temperatures to preserve the austenitic structure, hence retaining the carbon and associated metal constituents in solid solution. Thereafter, when the alloy is heated within the range 800° F. to 1500° F. during its service use the carbon in solid solution tends to separate out as metal carbide compounds along the grain boundaries. The principal carbide compound formed is a chromium-rich carbide. Due to the fact that the diffusion rate of chromium is relatively low as compared to the diffusion rate of carbon, the separation of chromium-rich carbide at the grain boundary

at first results in a marked depletion of the chromium content of each grain in the region immediately adjacent the grain boundary irrespective of the temperature of heating. A very prolonged time interval of heat-treatment is required after the carbide is precipitated to replace this chromium by diffusion of chromium thereto from the areas more remote from the carbide precipitation area. If the alloy is cooled very slowly, instead of rapidly from the homogenizing temperature mentioned above, carbide precipitation may occur while the metal is in the range 1500 to 800° F.

If during or after a more brief time interval of heating the alloy is also subjected to corrosive fluids and gases especially under pressure conditions, corrosion of the alloy along the grain boundaries in the chromium-depleted areas will rapidly occur, which in many cases is sufficient to proceed throughout the cross-section of the alloy with resultant loss in strength and failure of the alloy. This limits the useful application in many fields wherein it is desired to be employed.

In iron, chromium, nickel austenitic alloys the corrosion resisting properties of the alloy are imparted primarily by the chromium. It is estimated that the minimum chromium content to obtain marked corrosion resistance is approximately 10 to 12%. In these alloys it may readily be seen that it would require but relatively small carbide precipitation along the grain boundaries to lower the chromium content in the area immediately adjacent the said boundary to below that necessary to maintain corrosion resistance in this area, as for each atomic weight of carbon as much as four atomic weights of chromium may be precipitated. For this reason, in the past it has been essential to limit the carbon content of these alloys to a relatively low figure, e. g., .10% or below. Where the carbon content is higher than .10% the amount of metal carbides precipitated intergranularly is frequently sufficient to cause a marked loss in toughness irrespective of the action of corrosion agents which often is such that the metal may be readily crumbled to pieces.

These circumstances are such as to markedly limit the useful application of these alloys if, as in the case of welding, they are, in any zone, heated in the range of temperatures 800° F. to 1500° F., or if employed at temperatures in this range and the object of this invention is to remove this limitation.

Another object of this invention is to provide a

method of treating these alloys whereby the loss in corrosion resistance and toughness incident to metal carbide precipitation with or without intergranular corrosion is substantially eliminated.

Still another object of this invention is to improve the corrosion resistance and toughness of austenitic stainless steel alloys within, and after exposure to, the temperature range 800° to 1500° F.

Other objects and advantages will become apparent as the invention is more fully disclosed.

In accordance with the above objects we have made an intensive study of the phenomenon of metal carbide precipitation in the said austenitic alloys. As a result of such study we have discovered that slip bands, located within the interior of the austenitic grains of the alloy, are fully as potent loci for metal carbide precipitation as are the grain boundaries themselves, and that by causing metal carbides to precipitate along the slip bands rather than along the grain boundaries and by properly heating the said alloy after the carbides have been precipitated the objects of the present invention thereby may be achieved. Slip bands are formed in a grain when the grain is "cold worked" or mechanically distorted at a cold working temperature.

Since in cold worked austenitic stainless steel the carbides are precipitated along slip bands in a veritable shower within the grains rather than along the grain boundaries, loss of corrosion resistance or toughness incident to such carbide precipitation is not so readily manifested as corrosion is then a general surface reaction rather than an intergranular reaction. Also by shortening the path along which chromium and carbon must diffuse in order to precipitate, the extent of local impoverishment in the area immediately adjacent the place of precipitation thereby is reduced and the time interval required for uniform re-distribution of the remainder of the chromium by diffusion throughout the austenitic matrix thereby is markedly shortened. Moreover by markedly increasing the number of nuclei for carbide precipitation the intensity of chromium impoverishment at any point is thereby decreased.

Slip bands within the metal grains are caused or produced by "cold working". "Cold working" as it is understood in the art means working or mechanically deforming the metal at temperatures below that at which it will "recrystallize". "Recrystallization" is the process of reorganization of mechanically deformed or strained grains into equiaxed or unstrained grains. When a cold worked metal is recrystallized the slip bands within the interior of the grains and the old grain boundaries entirely disappear and a new grain structure dissimilar to the old structure is obtained. It is characteristic that the presence of slip bands in a grain indicate a cold-worked or strain-hardened metal whereas the absence of such slip bands indicates an unworked and unstrain hardened metal. These terms and phenomena are well recognized by those skilled in the art.

It is known, for example, that austenitic alloys of chromium, nickel, iron will cold work at temperatures below about 1550 to 1600° F. depending upon composition and it is also known that when cold worked the temperature at which these alloys will recrystallize depends primarily upon the degree of cold work imparted, the time at temperature and somewhat upon the grain size or physical state of the alloy.

For the purposes of the present invention accordingly it is essential first to obtain a cold-worked or strain-hardened austenitic alloy having a degree of cold work with consequent number of slip bands favorable for the purposes of the present invention and thereafter to heat-treat the same to a temperature, below that at which it will recrystallize, for such a time interval as will effectively cause the major portion of the metal carbide compounds to precipitate along the slip bands and uniformly to re-distribute the remaining chromium throughout the austenitic matrix. Any temperature of heating that will substantially destroy or eliminate the said slip bands by recrystallization is not within the scope of the present invention since thereby some of the advantages would be lost. The precise optimum temperature of heat-treatment accordingly is subject, as one skilled in the art will recognize, to wide variation depending upon the degree of cold working imparted, the time at temperature of heat-treating and the grain size of the metal as well as other factors as will be more fully hereinafter disclosed. After such treatment the alloy may be subjected to the action of many corrosive agents (fluid or gaseous) without the usual intergranular attack or material loss in strength or toughness.

Before further disclosure of the present invention reference should be made to the accompanying drawings wherein:

Fig. 1 is a chart indicating the carbon solubility of a typical austenitic chromium, nickel, iron alloy at various temperatures superposed upon a constitutional diagram of said alloy.

Fig. 2 is a chart correlating the various factors involved which determine the temperature of heat-treating in accordance with the present invention.

Fig. 3 illustrates the microscopic appearance of austenitic alloys in the homogenized condition, the parallel twin bands being characteristic of such alloys.

Fig. 4 illustrates with moderate degree of magnification the microscopic appearance of the alloy of Fig. 1 after the metal carbide compounds have been precipitated along the grain boundaries by heating within the range 800° F. to 1500° F.

Fig. 5 illustrates at still greater magnification the microscopic appearance of the abnormally large grain boundaries caused by carbide precipitation and the consequent separation of the grains resulting from intergranular attack.

Fig. 6 illustrates the microscopic appearance of cold work or strain hardened austenitic alloys, the hatching appearing in the center of each elongated grain being employed to illustrate the infinite number of slip bands created interiorly by cold deformation.

Fig. 7 illustrates microscopically the appearance of the grains of Fig. 6 after heat-treating the cold worked metal at temperatures favorable for carbide precipitation but unfavorable for recrystallization of the cold worked grains.

Fig. 8 illustrates in greater degree of enlargement the microscopic appearance of the metal of Fig. 7 and shows the criss-cross arrangement of the slip bands within the interior of the cold worked grain upon which the shower of metal carbides precipitate and illustrates the relatively short diffusion paths for the chromium and carbon in reaching the points of chromium depletion next to the carbon particles, as compared to the path indicated in Figs. 3 to 5 inclusive, thereby shortening the time interval of carbide

precipitation and chromium restoration by diffusion into the areas immediately adjacent the point of carbide precipitation.

Figs. 9 and 10 illustrate diagrammatically the comparative internal structure of sheet or tube material comprised of austenitic alloys treated in accordance with prior art practice and treated in accordance with the present invention respectively. In Fig. 9 the grain boundaries provide connecting paths through the metal from surface to surface which when filled with metal carbides provides a vulnerable line of attack for corrosive fluids and gases particularly if under pressure. In Fig. 10 by locating the carbide precipitation throughout the interior of the grain rather than along the grain boundaries the line of attack by corrosive fluids and gases is confined, if it occurs at all, to the surface area of the grains exposed to said fluids and gases and proceeds as a surface deterioration rather than an intergranular deterioration and can thereby be visually noted.

Referring to Fig. 1 of the drawings, we have determined that the solubility of carbon in austenitic alloys of the type herein discussed and more particularly the solubility of carbon in those alloys containing about 18% Cr and 8% Ni is substantially constant, or changes very little, at temperatures below about 1200° F. and approximates .025%, more or less. Above this temperature the solubility of carbon increases, slowly at first, but more rapidly above about 1500° F. At 1500° F. we have estimated the carbon solubility as being about .03%.

It is extremely difficult to manufacture the austenitic alloy with a carbon content much below about .10% or .08%. Accordingly such an alloy when heated to temperatures approximating and below about 1200° F. will ultimately precipitate all carbon in excess of about .025%, at least in the vicinity of the grain boundaries. It is apparent from the chart of Fig. 1 that when the alloy is heated to temperatures approximating 1800° F. the carbon solubility is about .10% and hence with this usual low carbon content of this type of alloy no carbide precipitation will occur, nor, if previously precipitated, will any be able to remain undissolved. The resolution of this precipitated carbide to obtain the equilibrium carbon solubility percentage at any given temperature requires a time interval which decreases with increase in temperature.

In the contemplated use of these alloys the temperatures to which they are subjected seldom exceed about 1500° F. Accordingly, it is highly desirable to render the alloy stable with respect to carbide precipitation at or below this temperature.

We have determined that both the precipitation and re-solution of carbides are essentially time-temperature reactions. The greater the temperature, the less the time interval, and vice versa, to obtain any desired degree of precipitation or solution compatible with the actual solubility.

We have also determined that the time interval of treatment at any given temperature must be prolonged over and above the time required to obtain substantially complete carbide precipitation for a further time interval necessary to obtain a uniform diffusion of the chromium remaining after carbide precipitation throughout the alloy in order to eliminate the loss in corrosion resistance of the alloy due to chromium impoverishment in the areas immediately ad-

jacent to the line of carbide precipitation. This also is a time-temperature reaction as the rate of diffusion of chromium through the austenite increases with increase in temperature and vice versa.

We have further determined that this time interval of heat-treatment and the temperature of heat-treatment to obtain a substantial precipitation of carbides and uniform dispersion of the remaining chromium is markedly affected by the profuseness of the precipitation and hence by the degree of cold working imparted to the alloy prior to heat-treating. In general the higher the degree of cold working the lower the temperature of heat-treatment and the shorter the time interval of treatment at any given temperature to obtain carbide precipitation and uniform re-distribution of the remaining chromium in the austenitic matrix.

The degree of cold working that may be applied to the alloy in accordance with the present invention, accordingly, may vary widely depending upon the mode of cold working, the amount of carbon in solution, the mechanical properties developed, the desired temperature and time of heat-treatment, and in part upon the contemplated service temperatures to which the metal is to be exposed.

In general with alloys containing not over .12% carbon, which is the customary range of carbon content in accordance with present practice, we have determined that the degree of cold working imparted to the alloy may vary from about 5% to 80%, depending upon the particular manner of cold working such as rolling, drawing, forging, etc. and the temperature of cold working. In most cases we have found that 15% to 50% reduction of cross-section by cold deformation produces a satisfactory development of slip planes in alloys containing up to about .12% carbon.

Inasmuch as carbide precipitation may initiate in these alloys at temperatures approximating 800° F. obviously the temperature of cold working should preferably be below 800° F. Still more preferably cold working should be done at atmospheric temperatures and such cold working as is referred to in the specification is to be understood as referring particularly, but not as a limitation, to mechanical deformation at temperatures approximating atmospheric temperatures, or such as result naturally from cold working without intentional heating of the metal.

In Fig. 2 we have graphically illustrated the time-temperature characteristics of metal carbide precipitation and solution (left) and of recrystallization (right) in an austenitic alloy containing 18% Cr and 8% Ni with carbon about .08%. This alloy is characteristic of the stainless austenitic steel alloys included within the scope of the present invention. Referring to this chart, we have illustrated in the left hand section the time-temperature characteristics of carbide precipitation. In the chart the center vertical line sets forth the temperature in degrees F. and the base line in either direction from the center vertical line sets forth time in hours on a logarithmic scale. The right hand vertical line denotes temperature in degrees C.

Curves A, B and C of Fig. 2 indicate the approximate heating temperatures and time intervals at these temperatures necessary to dissolve the indicated proportions of carbon, starting with an alloy in which a large part of the carbon is in the form of carbide particles. Above the tem-

perature of the horizontal portion of curve A the whole of the .08% carbon will always be dissolvable. Obviously after holding this austenitic stainless alloy at the temperatures of the horizontal portion of curves B and C only .05% and .03% carbon respectively will remain in solution. Substantially complete precipitation (probably less than .025% dissolved) would probably ultimately occur at lower temperatures.

Curves D, E and F indicate the temperatures and time intervals at these temperatures required to accomplish a substantial carbide precipitation in the homogenized 18-18 alloys which have been cold worked to the several degrees shown. It may be easily seen by one skilled in the art that the cold working greatly accelerates the rate of carbide precipitation. In the light of this explanation the area below curve C but above curve F is for convenience identified as the "carbide precipitation" range.

Referring to the curves lying to the right of the center line the time-temperature characteristics of recrystallization of these alloys is illustrated. As hereinabove noted before a metal may recrystallize the metal must be strain hardened by cold working or mechanical deformation at a cold working temperature.

We have found that for the purposes of this invention the degree of cold working that is imparted to the austenitic alloy must be such as to increase the surface area for carbide precipitation at least sufficiently to (a) shorten the time interval for carbide precipitation, (b) to reduce the localized area of chromium impoverishment adjacent the points of carbide precipitation, and (c) to shorten the time interval for the remaining chromium to diffuse uniformly through the austenitic matrix.

When an austenitic alloy such as the so-called 18-18 alloy is cold worked or mechanically deformed at a cold working temperature a certain amount of ferrite may be formed along the slip bands. On heating to elevated temperatures this ferrite is the first constituent to be affected. This ferrite, often containing carbide particles after initial heating, transforms into austenite at temperatures ranging from about 1100° F. to 1300° F. depending upon the time interval of heating at any given temperature. This is indicated in the chart of Fig. 2 in curve marked G. This allotropic transformation is not to be confused with recrystallization in this description of our invention.

On heating to more elevated temperatures the temperature at which the cold worked austenitic metal will recrystallize depends upon (a) the degree of cold working imparted, (b) the time interval of heating, (c) upon the particular grain size of the metal, and (d) upon the composition of the alloy.

In the chart of Fig. 2, curves "I" identified as R/A=15% (reduction area=15%) the time-temperature relationship of recrystallization is indicated with 15% reduction in area. When the alloy is heated for 0.1 hour (as indicated at bottom of chart) incipient recrystallization occurs at a little below 1750° F. If the temperature is raised to about 1800° F. for the same time interval (0.1 hour) recrystallization will be complete. If, however, the time interval at 1750° F. is extended to a little over an hour recrystallization will be complete as indicated by horizontal dotted line (a). The same result will be obtained at lower temperatures with still longer time intervals of heating. At 100 hours heating

incipient recrystallization may be observed at a temperature approximating 1600° F. but complete recrystallization will not occur until a temperature of about 1650° F is maintained for the same prolonged time interval.

With a reduction in area (R/A) of 50% the temperature of recrystallization for any given time interval is lower than with a 15% reduction in area, as indicated in the group of curves identified by the letter "K" on the chart of Fig. 2. In this group of curves we have also indicated the effect of coarse and fine grain structures, showing that the finer grain structure with the same degree of cold working recrystallizes at a lower temperature than coarser grain structures.

The group of curves "K" show that with a time interval of heating of about 0.1 hour incipient recrystallization of a fine grained austenitic alloy, having a degree of cold work approximating 50%, occurs in the neighborhood of 1450° F. and at 10 hours heating in the neighborhood of 1200° F., while complete recrystallization is obtained at temperatures approximating 1550° F. and 1450° F. respectively. With coarse grained metal under the same conditions the temperatures of heating for incipient and complete recrystallization respectively are materially higher, approximating 1500° F. and 1650° F. respectively for 0.1 hour of heating and approximating 1300° F. and 1500° F. respectively for 10 hours of heating.

Upon recrystallization the old cold worked grain structure of the alloy entirely disappears and an entirely new and dissimilar pattern appears. This new pattern is free from any evidence of cold working such as the presence of slip bands and is subject to change by reason of grain growth which involves the phenomenon of adjacent grains merging to form larger grains. This latter effect is a time-temperature reaction as indicated by curve identified by letter "J".

From the above description of curves I, K, G and J, it is believed apparent that the temperature of heat-treating the cold worked alloy in accordance with the present invention to obtain precipitation of the carbides without substantial recrystallization of the cold worked structure may be widely varied depending upon the degree of cold working imparted, the time interval of heat-treating and in part upon the grain size of the cold worked alloy.

It is apparent to one skilled in the art that the present invention in order to be economically practical must employ a time interval of heat-treating that is reasonable in view of operating costs. Curves D, E and F indicate the lowest temperatures of treating at any given time interval to obtain carbide precipitation. Curve C indicates the maximum temperatures at any given time interval of treating to obtain precipitation of carbon in excess of about .03%.

In between these temperatures at any given economically practical time interval, for example 10 hours, the temperature of heat-treating must be selected with any given alloy to which any given degree of cold working has been imparted, to accomplish the purposes of the present invention, namely, (a) a substantial precipitation of the metal carbide compounds above the carbon solubility, of about .025-.030%, (b) uniform distribution of the remaining chromium throughout the austenitic matrix, and (c) without sub-

stantial recrystallization of the cold worked metal.

By the term "substantial recrystallization" is meant the recrystallization of the major portion of the cold worked grains. As may be noted from the charts of Fig. 2, at temperatures short of complete recrystallization, incipient recrystallization may occur. Within the scope of this invention incipient recrystallization may occur to some extent as long as "substantial recrystallization" of the cold worked metal is not obtained. The extent of incipient recrystallization permissible depends in part upon the carbon content and in part upon the degree of cold work imparted. With relatively low carbon and with relatively high degrees of cold working the amount of incipient recrystallization permissible may be higher.

As the rate of carbide precipitation and the rate of chromium diffusion increase with increase in temperature, it is to be clearly observed that the maximum temperature of heat-treatment to perform purposes (a) and (b) above is limited only by the temperature of recrystallization.

This can be determined readily by one skilled in the art from a knowledge of the degree of cold working imparted given any arbitrary economically practical time interval of treating.

This can be noted from the following tabulated results:

In this connection, however, the cross-sectional area and mass of the alloy to be heated must be considered in actual furnace schedules. Relatively small articles and articles of relatively small cross-section may be readily heated to elevated temperatures for relatively short time intervals. But as the mass and cross-section of the article increases longer time intervals are required to obtain uniform temperatures throughout the mass of the article.

Accordingly, in the practical application of the present invention to austenitic alloys the size, shape and configuration of the article also control the choice of time-temperature heating combinations to obtain optimum precipitation of the carbide and chromium redistribution without substantial recrystallization of the cold worked austenitic structure. For purposes of brevity the redistribution of chromium is herein identified as "desensitizing". When the carbide is so precipitated as to induce local chromium depletion the alloy is "sensitized" towards corroding reagents.

About 16 hours for heat-treating to obtain carbon precipitation and chromium re-distribution (desensitizing) has been found economically practical, although for special purposes the treating may be as long as 100 hours or as short as 1 hour.

The best and most economically practical tem-

Degree of cold work (R/A)**

Type of material	R/A 5 to 10%	Result *	R/A 15 to 20%	Result*	R/A 35 to 50%	Result *
Sheet and strip stock 18-8 (.08 C)			15% 4 hrs. 1470° F... (C) 16 hrs. 1380° F... (B) 100 hrs. 1290° F... (A)		50% 1 hr. 1425° F... (B) 4 hrs. 1380° F... (A) 16 hrs. 1290° F... (A)	
Wire and rod stock 18-8 (.05 C)			15% 16 hrs. 1200° F... (B)		30% 16 hrs. 1200° F... (A)	
18-8 (.14 C)			20% 4 hrs. 1380° F... (C)		35% 4 hrs. 1380° F... (C)	
Tubing 18-8 (.07 C)	5% 16 hrs. 1200° F... (C)		15% 16 hrs. 1200° F... (C) 16 hrs. 1350° F... (A)			

**R/A=reduction in cross-sectional area.

*Result:

A=Excellent (fully de-sensitized).

B=Good (substantially de-sensitized).

C=Fair (in major part de-sensitized).

From these results and a large number of other tests we have determined that with tubes and the like articles the minimum degree of cold work should approximate 5% and may be as high as 50 to 70%. With wire, strip, sheet and bar materials the minimum should approximate 15% but the reduction may be as high as 50% to 80%.

For example, with respect only to avoiding substantial recrystallization in the alloy composition of the chart of Fig. 2, the maximum temperature of heating at 10 hours approximates 1600° F. with a reduction in area of 15%; with a reduction in area of 50% the maximum temperature of heat-treating approximates 1300° F. When the arbitrary time interval of heat-treating is set at 1 hour, the maximum temperature of heat-treating for 15% reduction in area material is approximately but under 1700° F. and for 50% reduction in area material is approximately 1400° F. However, we have found that re-solution of carbon imposes a limiting maximum temperature of about 1500° F. for the best results.

perature range for treating appears to be between 1200° F. to 1400° F. as in this range the rates of carbide precipitation and chromium diffusion appear most favorable for the purposes of the present invention and the time interval most flexible for general commercial application. At lower temperatures these rates are markedly slower and the required time interval of treating accordingly longer.

The most effective degree of cold working for heat-treatment of sheet, strip, plate, wire and bar products, within this temperature range appears to be between 35% and 60%. The effect of higher degrees of cold working is to shorten the time interval of heating within this specified range which for some purposes may be desirable. For tubes and similar drawn articles the optimum degree of cold working for this temperature range appears to range from 15% upwards; for other articles from 35% upwards, although the cross-sectional area and mass of the article may vary this appreciably. The degree of cold working in those articles of relatively small thickness or diameter may well be sufficient to extend sub-

stantially uniformly throughout the cross-section of the article. In relatively thick sectioned articles the degree of cold work need only be sufficient to immunize the article for a moderately extended distance inwardly from the surface.

By the practice of the present invention we are enabled to condition the austenitic iron, chromium, nickel alloys so that within the so-called "damaging range" the deleterious effects of carbide precipitation are substantially eliminated and these alloys may be employed in contact with corrosive gases and vapors at service temperatures within this so-called "damaging" range as well as thereafter at atmospheric temperatures. The alloys moreover are in such physical condition that they may be welded together without substantial loss in strength or corrosion resistance in the area adjacent to the weld. Tubes made of this alloy treated in accordance with the present invention are adapted for use at elevated temperatures under pressure without the immediate danger of failure as has heretofore been experienced. After treatment in accordance with the present invention the alloys are adapted to use at all temperatures up to about 1500° F. whereas alloys not so treated cannot be used at temperatures above about 800° F. with complete assurance.

Having broadly and specifically described the present invention and indicated the extent to which the broad idea may be modified commercially to apply the same, it is apparent that the present invention is adapted to wide use and modification without departing from the nature and scope thereof as may be included within the following claims:

What we claim is:

1. The method of treating austenitic iron-nickel-chromium steel alloys to render them resistant to corrosion in the temperature range 800° F. to 1500° F. and at all temperatures below 800° F. after heating in said range, which comprises cold working the steel and then heat-treating the steel to temperatures not in excess of 1500° F. but below the temperature of complete recrystallization for a time interval at least sufficient to effect a precipitation of substantially all of the carbon in excess of the solubility limit at the temperature of heating and at least sufficient to effect substantially uniform redistribution of the chromium throughout the said steel.

2. The method of treating austenitic iron-nickel-chromium steel alloys containing between 6-50% Ni and 10-40% Cr, to render them resistant to corrosion in the temperature range 800° F. to 1500° F. and at all temperatures below 800° F. after heating in said range, which comprises cold working the steel and then heat-treating the steel to temperatures not in excess of 1500° F. but below the temperature of complete recrystallization for a time interval at least sufficient to effect a precipitation of substantially all of the carbon in excess of the solubility limit at the temperature of heating and at least sufficient to effect substantially uniform re-distribution of the chromium throughout the said steel.

3. The method of treating austenitic iron-nickel-chromium steel alloys containing chromium at least 10% and nickel between 6-50% in such an amount as to impart to the composition a substantially stable austenitic structure, to render them resistant to corrosion in the temperature range 800° F. to 1500° F. and at all temperatures below 800° F. after heating in said range, which comprises cold working the steel and then heat-treating the steel to temperatures not in excess of 1500° F. but below the temperature of complete recrystallization for a time interval at least sufficient to effect a precipitation of substantially all of the carbon in excess of the solubility limit at the temperature of heating and at least sufficient to effect substantially uniform redistribution of the chromium throughout the said steel.

4. The method of treating austenitic iron-nickel-chromium steel alloys containing nickel approximately 8% and chromium approximately 18%, to render them resistant to corrosion in the temperature range 800° F. to 1500° F. and at all temperatures below 800° F. after heating in said range, which comprises cold working the steel and then heat-treating the steel to temperatures not in excess of 1500° F. but below the temperature of complete recrystallization for a time interval at least sufficient to effect a precipitation of substantially all of the carbon in excess of the solubility limit at the temperature of heating and at least sufficient to effect substantially uniform re-distribution of the chromium throughout the said steel.

EDGAR C. BAIN.
ROBERT H. ABORN.