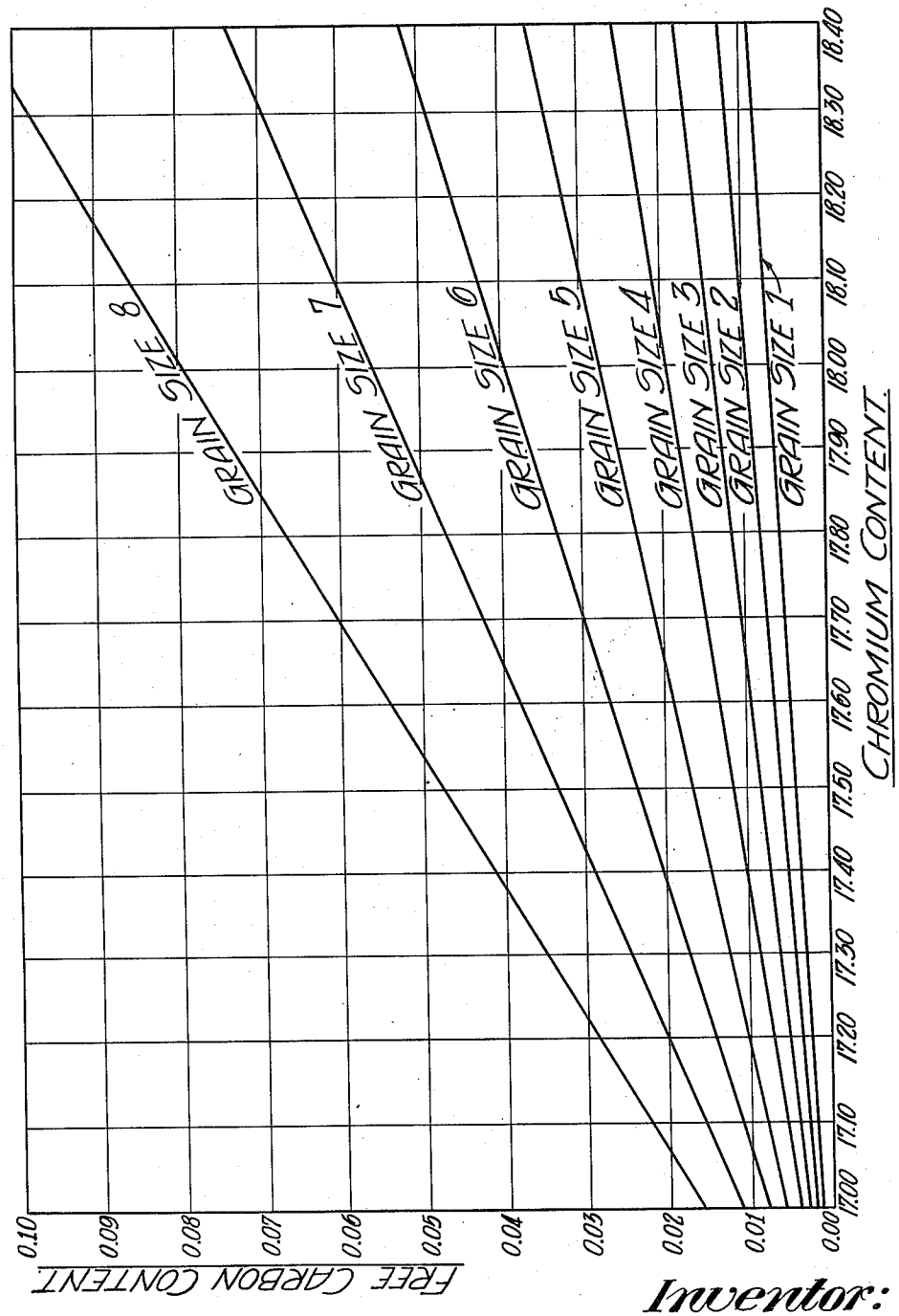
Nov. 21, 1950 F. J. PHILLIPS 2,531,154

PROCESS FOR PRODUCING STAINLESS STEEL IMMUNE TO INTERCRYSTALLINE CORROSION

Filed Nov. 6, 1945 2 Sheets-Sheet 1

FIG. 1.



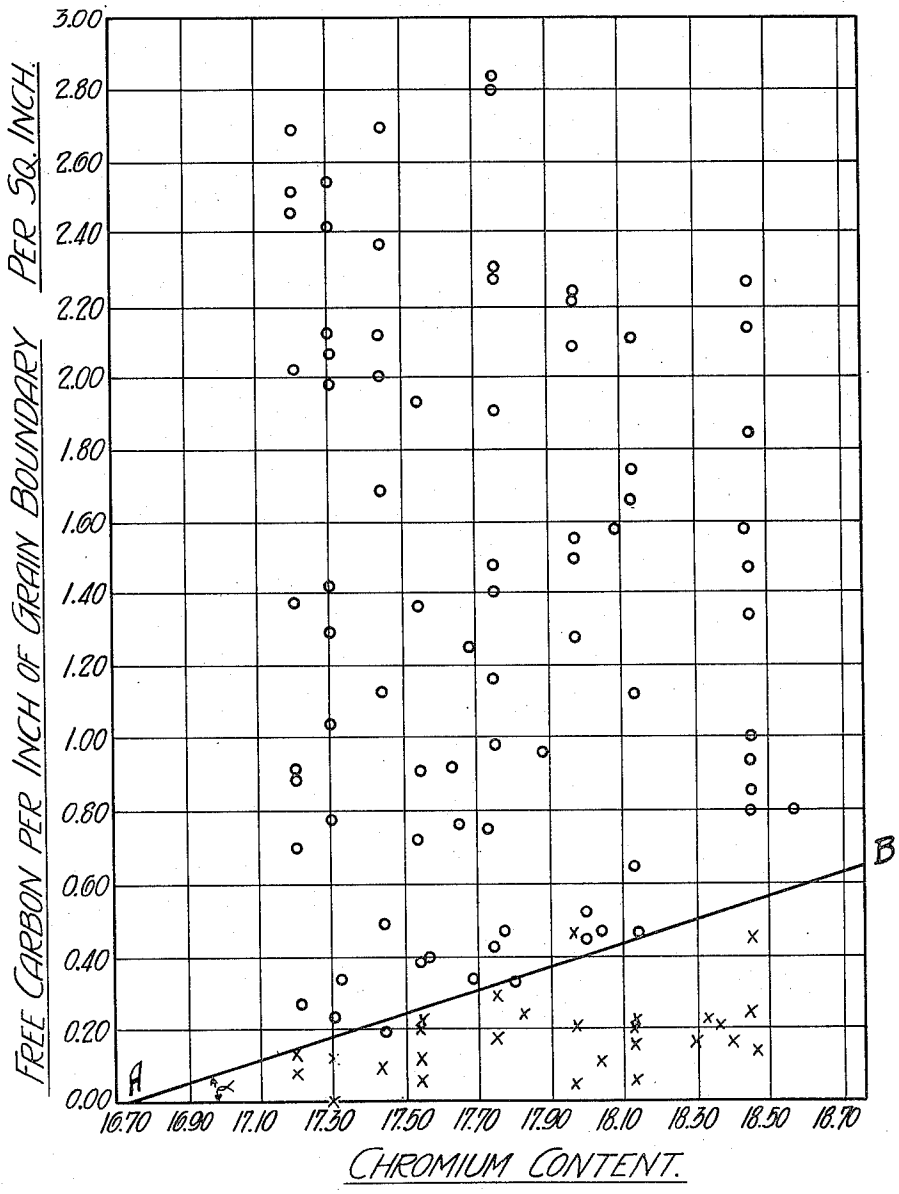
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PROCESS FOR PRODUCING STAINLESS STEEL IMMUNE TO INTERCRYSTALLINE CORROSION

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FIG. 2.



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PROCESS FOR PRODUCING STAINLESS STEEL IMMUNE TO INTERCRYSTALLINE CORROSION

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2 Claims. (Cl. 148—12)

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The present invention has for its object a method for determining the intercrystalline corrodibility of austenitic stainless steels by means other than actual corrosion testing.

A still further object of the present invention is a method for making austenitic stainless steel articles immune to intergranular corrosion under any predetermined set of corrosion factors.

As its further object, the invention is directed to a method for predicting intercrystalline-corrosion behavior of austenitic stainless steels without actual corrosion testing.

Austenitic steels of the type described always carry a certain percentage of carbon. The carbon normally remains in a solid solution in austenite, and is innocuous from the corrosion standpoint. On heating within a specified temperature range, commonly held between 1000 and 1400° F., this carbon combines with chromium, forming chromium carbides substantially insoluble in the ferrous matrix. Chromium carbides then precipitate, principally along the grain boundaries of steel crystals. Said carbides call for a much higher chromium concentration than the one commonly recorded in the alloy, as an average. The formation thereof deprives, therefore, contiguous areas of much of their chromium. Corrosion resistance of steel is generally associated with the chromium content. Lower chromium regions around grain boundaries create areas of reduced resistance. Exposed to corrosive media, these areas tend to dissolve, leading to disintegration of the metal.

Commonly accepted means for preventing precipitation of chromium carbide are associated with the combination of carbon present into more stable carbides than those of chromium. Titanium and columbium have been found to be particularly effective from the standpoint of the stability of their carbides. These elements are alloyed with the steel, and lead to a considerable improvement from the corrosion standpoint. Precipitation of carbides in the 1000–1400° F. range involves substantially chromium carbides alone. This precipitation can eventuate or can be prevented, depending on the nature of carbon compounds extant at the beginning of the sensitizing treatment. When the totality, or substantially predominant proportion of carbon is present as stable titanium or columbium carbides, the possibility of chromium-carbide precipitation is greatly reduced. In the case when prior thermal treatment has been inducive to a solid solution of the elements involved, chromium-carbide precipitation proceeds unimpeded

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independently of the presence of titanium or columbium. Stated otherwise, the respective carbides must be present before sensitizing to assure a satisfactory behavior of steels in question. The presence of a sufficiency of titanium or columbium, as commonly used, cannot be held per se as a warranty for the freedom from intercrystalline corrosion.

All commercial steels of the type described contain, besides iron, carbon, chromium, nickel and titanium or columbium, a plurality of other elements. Certain of these elements have no effect on the ultimate effect of carbide stabilization. Others directly bear on the proportion of carbon remaining free for combination with chromium and acting as a potential menace from the corrosion standpoint. Nitrogen and oxygen occupy a prominent place among the latter. Many authorities hold the combining power of titanium and columbium with nitrogen and oxygen is greater than that recorded in forming corresponding carbides. Titanium and columbium present as nitrides or oxides are eliminated as active phases of the system in the same way as carbides. In this light, a total percentage of titanium or columbium used as a carbide stabilizing agent must be reduced by the proportion of them fixed in nitrides, and oxides.

The present invention is illustrated by the accompanying drawings, wherein:

Figure 1 is a chart showing a series of graphs wherein free carbon content is plotted as a function of chromium content and of grain size of the steels.

Figure 2 shows the distribution of compositions of steels having satisfactory and unsatisfactory corrosion resistance when the behavior of steel after corrosion attack is plotted as a function of the free carbon concentration and the chromium content.

The prior art associates intercrystalline corrosion with the presence of chromium carbide at the grain boundaries. However, in the investigations leading to the present invention, it has been found that the mere presence of the compound at the grain boundaries is insufficient for determining corrosion behavior, and that a critical minimum amount thereof must be present to effect the intercrystalline corrosion, or conversely, to prevent said corrosion under given conditions of corrosive attack applied after an appropriate sensitizing heat treatment.

The aforementioned minimum of carbides issues from the combination of chromium with carbon remaining free in the steel after being

combined with the total available supply of titanium or columbium. This minimum can be determined by subtracting from the total percentage of carbon the amount of carbon held by carbides and cyano-nitrides of titanium or columbium. Similarly, if no stabilizing elements are present, the above minimum can be determined by subtracting from the total percentage of carbon the minimum solid solubility limit of carbon in austenite at room temperature.

Intercrystalline corrosion, as the name implies, deals with phenomena occurring at the grain boundaries. The amount of chromium-carbide precipitation at the grain boundaries must be considered, as precipitation taking place within crystals has no bearing on this type of corrosion other than to lower the amount of chromium carbide precipitated intergranularly. The pronounced mobility of carbon atoms at elevated temperatures permits a tentative assumption of precipitation taking place entirely at the grain boundaries at temperatures in the sensitizing range. A correct representation of the process of chromium-carbide precipitation and subsequent corrosion is obtained, therefore, through reference of the total precipitatable amount of carbon found in a given volume of the metal to the area of grain boundaries present in this volume.

Corrosion resistance of stainless steels of the type described is generally held to be associated with chromium content, higher chromium content causing a greater resistance. Impoverishment of an area of steel by chromium-carbide precipitation might reduce chromium concentration to a dangerous minimum in case of low original chromium content, while a precipitation induced by the same amount of carbon may leave a sufficient chromium concentration in a steel alloyed originally with a higher chromium content. An accurate picture of potential corrosion characteristics can be obtained by relating the amount of carbon precipitated at the grain boundaries to the chromium content of the steel.

A predetermining of corrosion characteristics of stainless austenitic steel requires, therefore: ascertaining the percentage of chromium contained in the metal, determining free carbon content thereof, finding potential free carbon concentration at the grain boundaries, determining carbon-concentration limits inducive to non-corrodibility, and comparing free carbon concentration found in a specimen under investigation with the above limits.

In accordance with the present invention there is determined the chromium content of steel by following generally available methods of quantitative chemical analysis. Also, there is ascertained the percentage of free carbon by conventional methods of analysis, but preferably the total percentage of carbon is determined by a combustion method. Then there is determined the amount of carbon tied up by carbon stabilizing elements, principally in titanium and columbium carbides, through a direct determination of these carbides, the difference between total carbon and the carbon in the carbides being free carbon. Analytical methods used are not a part of the present invention.

The carbon concentration at the boundaries is determined, in accordance with the present invention, by dividing the total free carbon content, as determined above, by the area of the grain boundaries. It may be considered that the grain of any specimen of steel is sufficiently uniform to hold a planar section through it as representative of the three-dimensional relations actually extant. In this light, the area of a specimen can be substituted, for the purpose concerned, for its volume, and the length of the grain boundaries for their area. Equally valid results are obtained by substituting any desired unit area for the total surface examined, and measuring the length of boundaries of the grains contained in this unit area.

In place of actual measurements of grain boundaries length, it is preferred to utilize generalizations laid as the foundation for the A. S. T. M. grain-size chart, to determine by observation under a microscope the grain size number, and to calculate the corresponding length of the grain boundaries by using a suitable formula expressing the length of grain boundaries as a function of the unit of area used and grain size observed.

Several methods for deriving a formula of this character are possible. It has been found convenient to use a formula derived as follows:

Let it be assumed that the grains have uniformly hexagonal shape and same size. The number N of grains per square inch (at 100 diameter magnification) will be:

$$N=2^{n-1}$$

where n is the A. S. T. M. grain size.

Then

$$6a\times\frac{a}{2}\tan 60^\circ\times\frac{1}{2}\times 2^{n-1}=1 \text{ sq. in.}$$

or

$$\frac{3a^2\times 2^{n-1}\tan 60^\circ}{2}=1 \text{ sq. in.}$$

where a is the side of the hexagon.

Hence the perimeter P of the grain will be:

$$P=6a=6\sqrt{\frac{2}{3\times 2^{n-1}\tan 60^\circ}} \text{ inch}$$

The total perimeter A of grains totaling in their area 1 square inch is:

$$A=2^{n-1}\times 6\sqrt{\frac{2}{3\times 2^{n-1}\tan 60^\circ}}\times 10^{-2}$$

$$=\frac{6\times 2^{n-1}\sqrt{\frac{2}{3\times 2^{n-1}\tan 60^\circ}}}{100}$$

Since two grains participate in any grain boundary, the actual length A′ of the grains perimeter is:

$$A'=\frac{A}{2}=\frac{6\times 2^{n-1}\sqrt{\frac{2}{3\times 2^{n-1}\tan 60^\circ}}}{100\times 2}$$

$$=\frac{3\times 2^{n-1}\sqrt{\frac{2}{3\times 2^{n-1}\tan 60^\circ}}}{100}$$

$$=10^{-2}\sqrt{\frac{3\times 2\times 2^{n-1}}{1.732}}$$

$$=10^{-2}\sqrt{3.464\times 2^{n-1}} \text{ inch}$$

The actual methods of deriving the numerical value of the formulas obtained are of minor importance. Said formulas are intended to present the periphery of grains contained in a unit of area expressed in the same units, for example, inches per square inch.

The free carbon content, determined as previously indicated, divided by the length of grain

boundaries in a unit of area, ascertained by calculation through any suitable formula, gives free carbon concentration in per cent per unit length, for example, in per cent per inch per square inch. Selecting a representative number of specimens depicting adequate variations of free carbon and of chromium content, determining boundaries-carbon concentration thereof, sensitizing the metal by proper heat treatment, and subjecting sensitized specimens to actual intercrystalline corrosion testing provide a set of values which supply the basis for predicting corrosion behavior of similar steels.

Figure 2 of the attached drawings presents the distribution of the aforementioned values when the behavior of steel after corrosion attack is plotted as a function of the free carbon concentration and the chromium content. In this figure, circles represent specimens which failed from the corrosion-resistance standpoint, and crosses indicate steels which stood the attack of the corrosive media. A sharp separation between the area comprising satisfactory and that embracing defective specimens is clearly seen here. The separation takes place substantially along the line A—B. When free carbon concentration at grain boundaries is equal to or less than a critical value E, dependent on chromium content of the steel, no intercrystalline corrosion can be produced in the corresponding austenitic steel of the chromium-nickel type.

The above critical value E can be computed from Figure 2. Let P indicate the chromium percentage of the steel. Then the critical value E can be expressed for any point on line A—B as

$$E=(P-16.75)\tan a$$

which gives the maximum percentage of carbon at the grain boundaries permissible for avoiding corrosion.

Actual measurements show value of angle a is substantially 18°. This value is valid in connection with the above given formula for grain periphery computation. Further simplified, the above formula becomes

$$E=0.325\ (P-16.75)$$

Other formulas for grain-periphery determination give different values for the angle a without deviating from the straight-line law of the present invention. A lower or higher chromium concentration than 16.75% used in the present example for deducing a formula for E requires merely replotting of experimental results for determining angle a corresponding to the new chromium content range.

Ascertaining average grain size of a steel according to A. S. T. M. standards, determining the chromium content thereof, computing carbon concentration of the grain boundaries through an appropriate formula, and using a formula for critical value E of carbon concentration similar to that exemplarily shown, permit definite prediction of corrosion characteristics of any steel embraced by the corresponding limits of composition prior to actual corrosion testing.

With a definite range of steel composition, a further simplification of the method is possible. Free carbon concentration is plotted against the chromium content of the steel for each grain size recognized by the A. S. T. M. standards, using the same principles as in plotting Figure 2. Figure 1 of the attached drawings presents the results of this plotting for 18% Cr–8% Ni type stainless steels containing 17.00 to 18.40% chromium content for grain sizes ranging from No. 1 to No. 8 inclusive, of the A. S. T. M. standard grain size chart. The curves of this diagram represent a maximum free carbon content at or under which steels having a given chromium content and grain size remain free from intercrystalline corrosion. The diagram of Figure 1, given as an unlimiting example, eliminates the need for computations and gives at a glance a complete picture of corrosion characteristics of the whole field.

In reducing the present invention to practice, a specimen of the finished article, when heat treatment has been used in the forming operations, or of the original stock, when the effect of heat treatment is substantially absent, is obtained and chromium and free carbon content thereof is determined by any suitable analytical method. A coupon left on the article throughout the manufacturing operations thereof rather than a section of the article is preferably used. A metallographic specimen of the metal suitable for grain-size determination is then prepared and examined under a microscope. The grain size observed is noted, and a diagram similar to that represented in Figure 1 of the drawings is consulted. A point of intersection of chromium content value of the sample, plotted on the abscissa, and that of free carbon content, plotted on the ordinate, is determined and compared with the position of the curve for corresponding grain size. The location of said point of intersection above the curve indicates the tendency of the steel towards intercrystalline corrosion. The position thereof on or below the aforementioned grain size curve is interpreted as indication of steel being substantially free from intercrystalline corrodibility when subjected to corrosive attack.

Potential freedom from intercrystalline corrosion, assured by the application of the above-recited method to structural members ultimately intended for resisting corrosion effects, places in the hands of constructors thereof adequate means for designing and building bodies substantially immune to any desired set of corrosive factors.

Original material is preferably ordered from steel manufacturers in the light of the teachings of the present invention, namely, maintaining a definite relation among free carbon content, chromium percentage of the steel, and the grain size thereof. Either chemical aspects are properly emphasized or attention is called to advantages of smaller grain size which is a function of furnace practice. Cast steel bodies are then reduced to final dimensions following conventional practice, and the smaller reduced bodies, intended for forming operations free from heating at elevated temperatures, are approved for application through the use of the method described, and finally formed into the intended shape. When a heating operation, exemplified by welding, is contemplated, specimens of reduced bodies are subjected thereto, passed for the intended use in the light of teachings of the proposed method, and the bodies manufactured into the final articles with full assurance in respect to the suitability thereof for the purpose intended.

While certain specific methods have been given in a way of illustration, those skilled in the art would readily suggest different variations thereof still fully remaining within the spirit and teach-

ings of the present invention as defined by the appended claims.

I claim:

1. The method of preventing intergranular corrosion in austenitic stainless steels containing at least 16.75% chromium comprising the steps of analyzing the steel for chromium content, analyzing the steel for free carbon content, and treating the steel to produce a maximum grain size such that:

$$E \leqq (P-16.75) \tan 18°$$

wherein E is the maximum free carbon content per inch of grain boundary per square inch of surface, and P is the chromium content.

2. A method of preventing intergranular corrosion in austenitic stainless steels which are alloyed with a metal of the group consisting of titanium and columbium and contain approximately 8 percent nickel, at least 16.75 percent chromium and a small percentage of carbon, comprising analyzing the steel for its chromium content, analyzing the steel for its free carbon

content, and treating the steel to produce a maximum grain size such that:

$$E = (P-16.75) \tan 18°$$

wherein E is the maximum free carbon content per inch of grain boundary per square inch of surface and P is the chromium content.

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