United States Patent [19]
Gregory et al.

[11] **3,807,991**
[45] **Apr. 30, 1974**

[54] FERRITIC STAINLESS STEEL ALLOY

[75] Inventors: **Eric Gregory**, Bernardsville; **Frederick K. Kies**, Chatham; **Ivan A. Franson**, South Plainfield, all of N.J.

[73] Assignee: **Airco, Inc.**, New York, N.Y.

[22] Filed: **Oct. 29, 1971**

[21] Appl. No.: **193,698**

[52] **U.S. Cl.** .... **75/126 F**, 75/126 J, 75/126 R
[51] **Int. Cl.** **C22c 39/14**
[58] **Field of Search** .... 75/126 C, 126 J, 126 F

[56] **References Cited**

UNITED STATES PATENTS

2,183,715	12/1939	Franks	75/126 C
2,624,671	1/1953	Binder	75/126 J
2,905,577	9/1959	Harris	148/37

Primary Examiner—Hyland Bizot
Attorney, Agent, or Firm—Donald J. Fitzpatrick; Larry R. Cassett; H. Hume Mathews

[57] ABSTRACT

A high purity, low interstitial ferritic stainless steel which in the as-welded condition exhibits a combination of improved resistance to intergranular corrosion, good resistance to general corrosion and improved impact resistance. The steel broadly contains by weight from about 20.0 percent to about 35.0 percent chromium, from about 0.75 percent to about 1.20 percent molybdenum, from about 0.10 percent to about 0.30 percent silicon, up to about 0.020 percent phosphorous, up to about 0.020 percent sulfur, up to about 0.0030 percent carbon, from about 0.0050 percent to about 0.0125 percent nitrogen and columbium from about 13 to about 29 times the nitrogen content.

11 Claims, 2 Drawing Figures

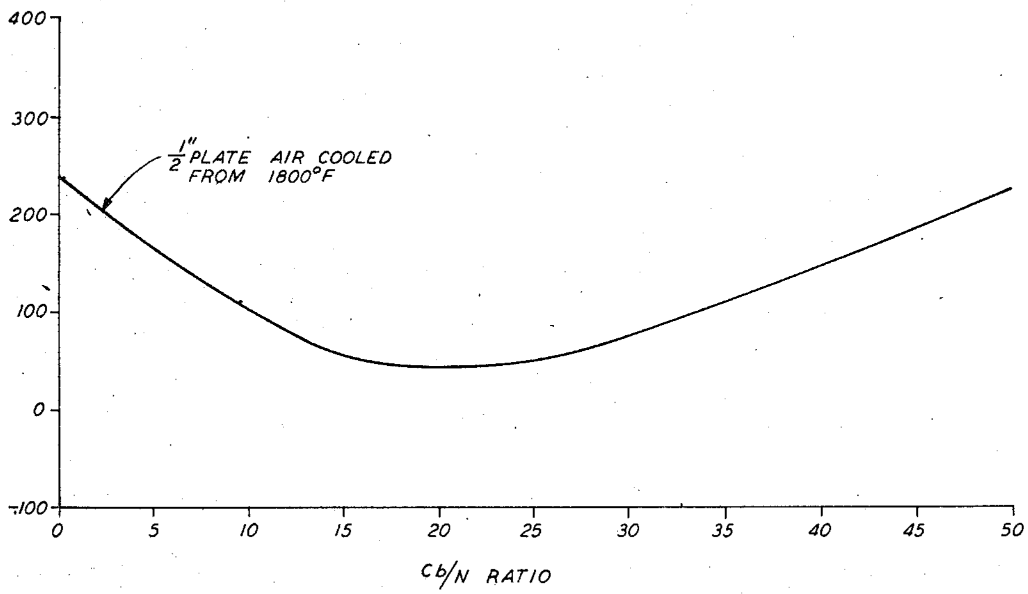


FIG. 1

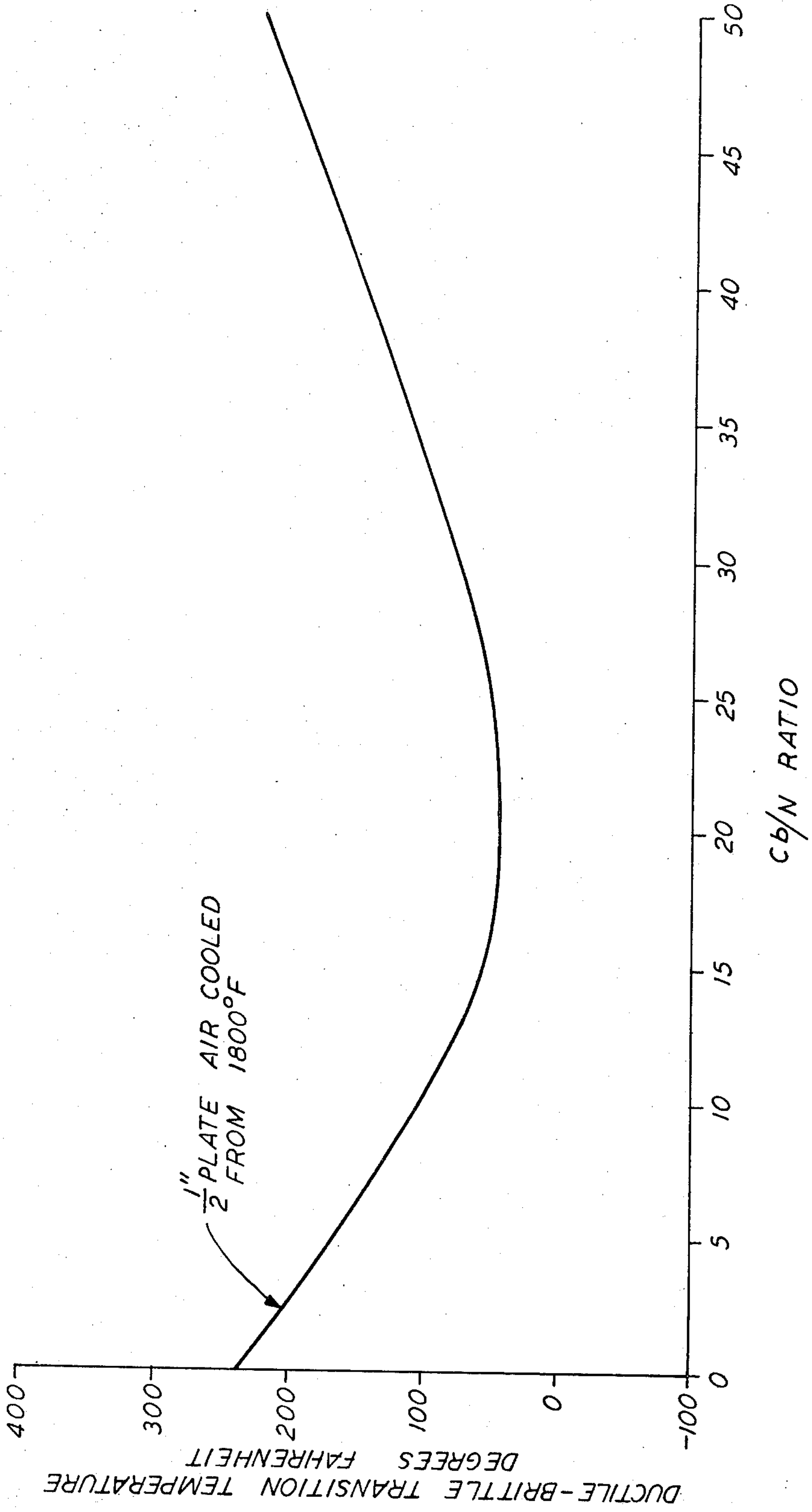
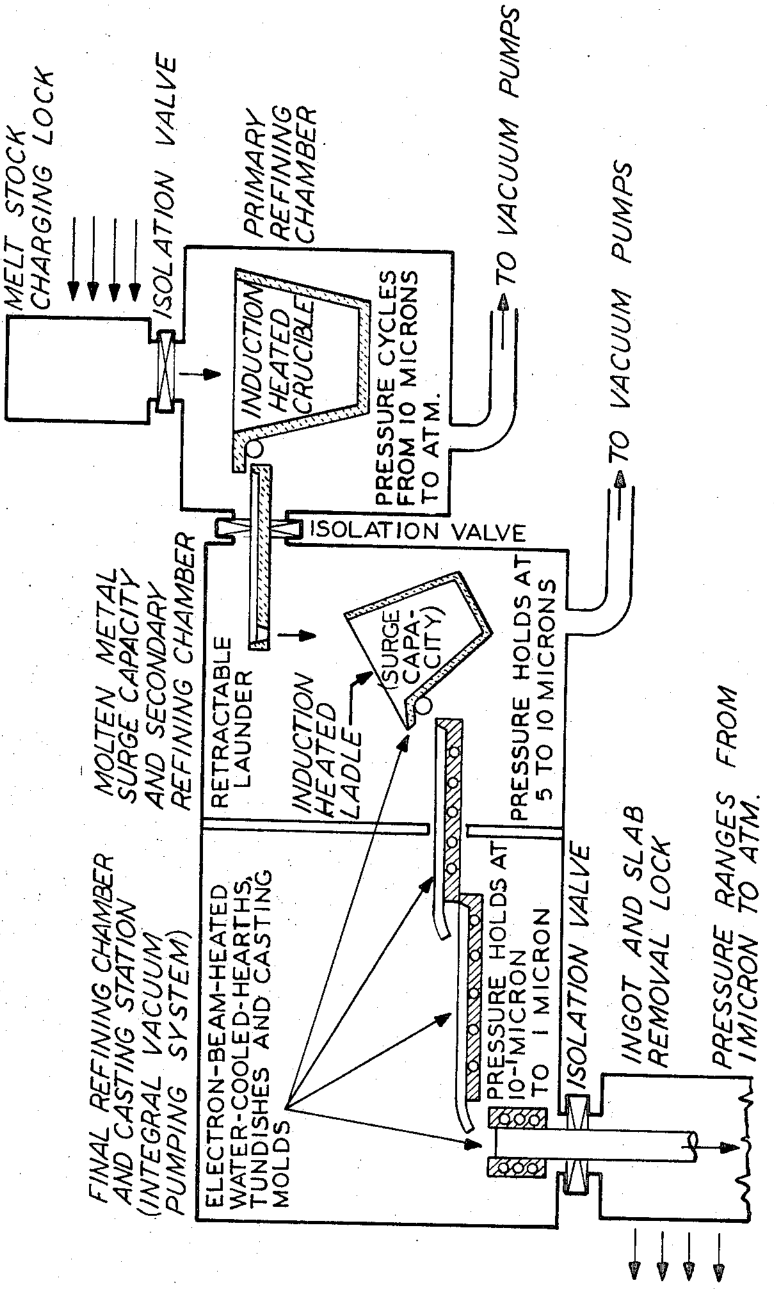

1/2" PLATE AIR COOLED FROM 1800°F
DUCTILE-BRITTLE TRANSITION TEMPERATURE DEGREES FAHRENHEIT
400
300
200
100
0
-100
Cb/N RATIO
0
5
10
15
20
25
30
35
40
45
50

FIG. 2


MELT STOCK CHARGING LOCK
ISOLATION VALVE
PRIMARY REFINING CHAMBER
INDUCTION HEATED CRUCIBLE
PRESSURE CYCLES FROM 10 MICRONS TO ATM.
TO VACUUM PUMPS
ISOLATION VALVE
TO VACUUM PUMPS
MOLTEN METAL SURGE CAPACITY AND SECONDARY REFINING CHAMBER
RETRACTABLE LAUNDER
INDUCTION HEATED LADLE
(SURGE CAPA-CITY)
PRESSURE HOLDS AT 5 TO 10 MICRONS
FINAL REFINING CHAMBER AND CASTING STATION (INTEGRAL VACUUM PUMPING SYSTEM)
ELECTRON-BEAM-HEATED WATER-COOLED-HEARTHS, TUNDISHES AND CASTING MOLDS
PRESSURE HOLDS AT 10^{-1} MICRON TO 1 MICRON
ISOLATION VALVE
INGOT AND SLAB REMOVAL LOCK
PRESSURE RANGES FROM 1 MICRON TO ATM.

FERRITIC STAINLESS STEEL ALLOY

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to iron-chromium alloys and more particularly to high purity and low interstitial content ferritic stainless steels and to a method for producing such alloys.

2. Prior Art

Stainless steel alloys are generally grouped into three broad classes; martensitic, ferritic and austenitic. These classes are established on the basis of the predominating alloy crystal structure at room temperature. The ultimate crystal structure depends upon the alloying elements utilized and their respective proportions. Two of the more important factors which often govern the selection of a stainless steel alloy for a particular application are the desired physical properties and cost. Design engineers strive for optimum physical properties at the lowest cost. Quite naturally the most suitable stainless steel is very often also the most expensive.

There are many industrial applications wherein stainless steels, particularly the austenitic and ferritic types, may be used interchangeably. It is well known that austenitic stainless steels are more expensive than ferritic stainless steels because of the presence of nickel in amounts generally ranging from 6 to 22 percent. However, due to one very significant limitation of ferritic stainless steels, the more expensive austenitic stainless steels are generally selected.

The utility of ferritic stainless steel is usually severely limited because as the chromium concentration is increased toughness at room temperature sharply decreases. Austenitic stainless steel is not so affected. Therefore, although a ferritic stainless steel containing more than 20 percent chromium may exhibit corrosion resistance comparable to a more expensive nickel bearing austenitic stainless steel, the latter steel would generally be selected because it is ductile at room temperature whereas the ferritic steel is brittle.

A further limitation on the utility of ferritic stainless steel is the susceptibility of this steel toward intergranular corrosion. Intergranular corrosion can be minimized by reducing the carbon and/or nitrogen content of the alloy or by stabilizing the composition by employing stabilizers such as titanium or columbium, or by selective heat treatments. Sensitization (to corrosion) involves the intergranular precipitation of chromium carbides, nitrides or carbo-nitrides when the alloy is exposed to elevated temperatures and thereafter slowly cooled. The principal effect is the depletion of chromium in areas adjacent to the grain boundaries. This depletion creates a reduced corrosion resistance in these chromium depleted areas resulting in nonuniform corrosion resistance.

Binder and Franks in U.S. Pat. No. 2,624,671 issued Jan. 3, 1953 recognized the deficiencies of ferritic stainless steels containing 20 to 40 percent chromium. The patentees discovered "that there is a critical relationship in ferritic chromium steels containing 20% to 40% chromium between the toughness of such steels and the sum of their carbon and nitrogen contents." This patent taught that impact strength could be improved in ferritic stainless steels if the carbon and nitrogen are maintained at very low levels. Even though the art has recognized this significant advancement, 20–40 percent chromium ferritic stainless steels have found limited acceptance as a substitute for the more expensive austenitic stainless steels. It is believed that this situation exists because, while the principle taught by Binder and Franks is valid, it is commerically impractical to reduce the carbon and nitrogen contents of a steel having more than about 25 percent chromium sufficiently to provide it with a ductile-to-brittle transition temperature (DBTT) at or below about room temperature. It has been found that this requires nitrogen levels of the order of 50 ppm or less with corresponding low carbon levels.

Although austenitic stainless steels have superior toughness at low temperatures they also have definite deficiencies, including susceptibility to stress corrosion cracking and sensitization. Furthermore, austenitic steels work harden more rapidly than do ferritic stainless steels. To produce austenitic stainless sheet or strip intermediate heat treatments are required during reduction to restore ductility in order to achieve desired thickness. Generally speaking, austenitic stainless steels work harden more rapidly than ferritic stainless steels thereby necessitating intermediate annealing.

It has long been a goal of the steel industry to develop a practical ferritic stainless steel that exhibits satisfactory toughness at room temperature along with full corrosion resistance and resistance to sensitization. Such a steel would be superior in many applications to the austenitic grades now employed because stress corrosion cracking would be eliminated. An additional benefit realized by such a substitution would be less work hardening, thereby eliminating expensive heat treatments that are associated with manufacturing austenitic stainless sheet or strip. The alloy of this invention, a ferritic stainless steel, is a steel that exhibits these desirable characteristics.

SUMMARY OF THE INVENTION

An object of this invention is the provision of a ferritic stainless steel alloy that combines toughness, improved resistance to intergranular corrosion and good resistance to general corrosion.

Another object of this invention is the provision of a low cost ferritic stainless steel alloy that exhibits good wide range corrosion resistance and freedom from corrosion sensitization as well as good impact resistance at room temperature.

Still a further object of this invention is to provide a ferritic stainless steel alloy that is characterized by improved impact resistance, and resistance to intergranular corrosion after heating to an elevated temperature followed by air (slow) cooling.

A further object of this invention is to provide a high chromium nickel free stainless steel that is applicable for weldments fabricated from plate, sheet, strip, pipe or rod and wire products without subsequent heat treatments.

A further object of this invention is to provide a ferritic stainless steel with high purity and a low level of interstitials manufactured from low cost charge materials and scrap.

A further object of this invention is to provide a method for making a ferritic stainless steel having resistance to intergranular corrosion together with toughness.

Referring now particularly to this invention, there is provided a ferritic stainless steel with high purity and a low level of interstitials that may be made by any suitable high purity steel making process. One such process comprises vacuum melting and refining a charge of low cost raw materials and thereafter further refining it by exposing the melt to hard vacuum and high power level electron beams.

The content of this alloy in weight percent can range from about 20.0 percent to about 35.0 percent and preferably from 25.0 percent to 27.5 percent chromium, from about 0.75 percent to 1.20 percent molybdenum, up to about 0.020 percent phosphorous, up to about 0.020 percent sulfur, and from about 0.10 percent to about 0.30 percent silicon. The impact strength is enhanced by limiting the carbon content to not more than about 0.0030 percent (30 parts per million) and the nitrogen content to not more than about 0.0125 percent (125 parts per million). These extremely low levels of carbon and nitrogen can be achieved by vacuum refining. Electron beam refining methods have been found especially useful in the production of alloys of such purity. Essential in the novel alloy is a small but critical columbium content. The columbium content of this alloy ranges from about 13 to about 29 times the nitrogen content.

The advantages of the steel of this invention will be apparent from the following drawings and detailed description in which:

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a graph showing the relationship between the columbium to nitrogen ratio and the ductile-to-brittle transition temperature (DBTT) after air cooling one-half inch plate from 1,800° F.

FIG. **2** is a schematic showing of a steel making process and apparatus suitable for the production of the novel alloy.

DESCRIPTION OF THE PREFERRED EMBODIMENT

It has been discovered that if the chemical composition of a high chromium content ferritic stainless steel is controlled by maintaining the various elements within the ranges as hereinafter set forth, an improved alloy will result. Therefore, in accordance with the present invention there is provided a steel having the following composition, expressed as weight percent.

Carbon	up to 0.0030
Phosphorous	up to 0.020
Sulfur	up to 0.020
Silicon	0.10 to 0.30
Copper+Nickel+Cobalt	up to 0.25
Chromium	20.0 to 35.0 (Broad)
Chromium	25.0 to 27.5 (Preferred)
Molybdenum	0.75 to 1.20
Nitrogen	0.0050 to 0.0125
Columbium	13 to 29 times the nitrogen content
Iron+incidental impurities	Balance

This invention relates to ferritic stainless steels having chromium in the broad range of 20.0 to 35.0 percent and more particularly within the narrow range of 25.0 to 27.5 percent. Within these chromium ranges iron-chromium alloys exhibit a particular high degree of corrosion resistance in highly corrosive media. However, ferritic alloys with chromium contents within these ranges also tend to be brittle, even at temperatures much above room temperature. As previously stated an object of this invention is to provide a ferritic stainless alloy in the 20 to 35 percent chromium range that retains all of the benefits of this amount of chromium while overcoming the problems associated therewith, particularly the problem of embrittlement.

Maintaining the molybdenum content in the range of 0.75 to 1.20 percent improves the corrosion resistance of the alloy in reducing environments. Furthermore, additions of molybdenum within this range enhance the alloys resistance to pitting corrosion. If the steel of this invention has a molybdenum content less than 0.75 percent, corrosion resistance is impaired. Too much molybdenum can be detrimental in that it increases cost and in large amounts can adversely affect the toughness of the alloy. We prefer, in the alloys claimed in this application, to keep molybdenum below about 1.20 percent.

The silicon content should be kept within the range of about 0.10 to 0.30 percent. Silicon, in amounts greater than approximately 0.10 percent, performs the dual function of accelerating oxygen removal during refining and improving the alloy's high temperature oxidation resistance. Silicon in excess of 0.30 percent is not desirable because of solid solution hardening.

The carbon content should be not more than about 30 ppm. This low content is readily achieved by electron beam refining the melt in vacuo. Reducing the carbon content to this level improves toughness by lowering the ductile-to-brittle transition temperature (DBTT), the transition temperature being defined as that temperature at which the amount of energy that can be absorbed on impact without causing fracture very rapidly decreases. Below this temperature the capacity to absorb energy is very low and the behavior of the alloy is said to be brittle. Above the transition temperature the capacity to absorb energy is relatively high and the material is said to be tough. Further, a carbon content below 30 ppm improves the alloy's resistance to intergranular corrosion by reducing the amount of carbon available to form chromium carbides. By preventing the formation of chromium carbides the alloy matrix will not be depleted in chromium if subjected to prolonged heating, and its resistance to intergranular corrosion is retained.

The nitrogen content should be not greater than about 125 ppm. Reducing nitrogen to this level improves toughness as evidenced by the reduced DBTT. Likewise, low levels of nitrogen reduce the alloy's susceptibility to intergranular corrosion. Higher levels of nitrogen can cause chromium to be depleted from the alloy matrix and precipitate at the grain boundries as a chromium nitride in much the same manner as chromium carbides. Reducing the nitrogen content of the alloy minimizes the precipitation of objectionable chromium nitrides. Most important however is the discovery that within the range of 50 ppm to 125 ppm the detrimental effects of nitrogen are neutralized by the small critical addition of columbium contemplated by this invention.

As previously stated the amount of columbium utilized in this alloy is critical. The amount of columbium utilized must be correlated with the nitrogen content of the alloy in a carefully defined critical ratio. Since it is virtually impossible (or at least impractical) to remove all the nitrogen from the alloy, the objects of the invention can be achieved only if residual nitrogen is tied up in such a manner that it cannot impair toughness or resistance to intergranular corrosion. As shown in FIG. 1, the transition temperature is reduced significantly by the addition of columbium in an amount related to the nitrogen content of the alloy. Reduction to about room temperature or below may be achieved when the Cb:N ratio is maintained within the range of about 13 to about 29. In the absence of columbium, even small amounts of nitrogen, e.g., 60 ppm, cause embrittlement. The foregoing small columbium addition makes the air cooled DBTT insensitive to nitrogen variations between about 50 and about 125 ppm. When nitrogen content is less than about 50 ppm the alloy is ductile at room temperature without further modification. 0.05 weight percent columbium significantly and favorably influences the DBTT at all nitrogen levels up to the stated 125 ppm. However the full benefits of the invention are not realized unless the Cb:N ratio is within the stated range of from about 13 to about 29. Excess amounts of columbium adversely affect (raise) the DBTT and the benefits of the invention are lost.

The phosphorous content is preferably kept as low as possible and certainly below 0.020 percent because phosphorous in the alloy acts to elevate the DBTT.

The sulfur content of the steel should be kept to a low level. In any event, the sulfur content should not exceed about 0.020 percent. Large amounts of sulfur tend to form deliterious nonmetallic inclusions.

The nickel, copper and cobalt contents of the steel should likewise be kept low. As impurities in the steel of this invention nickel typically is present in amounts up to 0.10 percent, copper in amounts up to 0.015 percent and cobalt in amounts up to 0.04 percent. The combined amount of these elements should not exceed about 0.25 percent because above that level the alloy's resistance to stress corrosion cracking is adversely affected.

In the foregoing paragraphs there are set forth the general criteria for the novel composition of the present invention. However, as might be expected, there are considerable cumulative and interacting effects of the concentrations of the several elements. For example in addition to nitrogen, the elements carbon and phosphorous appear to clearly influence the toughness of a ferritic stainless steel of a given chromium content. For maximum depression of the air cooled DBTT these elements and nitrogen should be kept on the low side of their respective ranges. If the nitrogen level is toward the high end of the range, carbon and phosphorous must be kept low to assure good DBTT values. It is to be understood that a composition containing the maximum amounts of each of these several elements may not reliably achieve a DBTT of room temperature or less after air cooling from 1,800° F, but such a composition will exhibit significant improvement in this property over a similar material lacking the critical columbium addition.

Illustrating the significance of this invention, there is presented data representing a series of iron-chromium base alloy heats of various analysis. Some of the heats are of a composition that are within the scope of the novel range of this invention. For purposes of comparison, the balance of the heats are outside the novel range of this invention in one or more elemental constituents.

The heats in Group I with a B or C prefix are commerically produced mill production heats. These heats were processed in a manner as hereinafter more fully described. The remaining heats in Groups I, II and III with a MH prefix are laboratory heats remelted from mill heat 2B0005. These heats represent 40 pound melts having closely controlled columbium and nitrogen contents and were produced in a laboratory vacuum induction furnace. The resulting ingots were conditioned by grinding and were subsequently hammer forged into one-half inch by 4 inches cross-section plate after soaking at 2,100° F for 2 hours. Since these heats were processed from a base heat containing .10 percent nickel and .020 percent copper, it is reasonable to assume that the resulting laboratory heats would contain approximately the same elemental amounts. For this reason the laboratory heats were not analyzed for these elements. The nickel and copper content of Heat MH-160 is higher than the other experimental heats because of a contaminated crucible.

GROUP I

The compositions of the steels in this group do not contain the essential critical columbium addition. Furthermore, the molybdenum content in one heat ex-

TABLE I

Heat No.			Percent by Weight						Cb/N	P P M	
	Cr	Mo	P	Si	S	Ni	Cu	Cb		C	N
Group I											
2B0005 (3)	26.4	.95	.018	.17	.012	.10	.020	0		20	99
MH-22 (4)	27.0	1.03	.012	.24	.007	.11	x	0		20	75
2B0123 (3)	25.3	1.31	.011	.21	.012	.09	.012	0		10	101
Group II											
MH-158 (4)	26.8	1.07	.017	.12	.015	(1)	(2)	.05	5	20	105
MH-156 (4)	26.4	1.07	.017	.12	.014	(1)	(2)	.38	34	17	113
MH-152 (4)	26.5	1.08	.017	.15	.013	(1)	(2)	.41	44	>10	94
MH-151 (4)	25.7	1.09	.017	.12	.010	(1)	(2)	.33	47	18	70
MH-144 (4)	26.5	.93	.012	.20	.010	(1)	(2)	.30	35	15	86
MH-148 (4)	26.6	.99	.011	.19	.008	(1)	(2)	.37	56	12	66
Group III											
MH-142 (4)	28.0	1.08	.012	.19	.008	(1)	(2)	.10	21	11	48
MH-25 (4)	25.9	1.06	.011	.21	.007	(1)	(2)	.10	15	24	66
MH-146 (4)	26.9	.96	.011	.19	.010	(1)	(2)	.18	22	13	83
MH-149 (4)	26.4	1.09	.017	.19	.012	(1)	(2)	.19	21	23	91
MH-160 (4)	26.3	1.06	x	.25	.014	—	—	.12	13	22	95
MH-161 (4)	26.9	.83	x	.11	.013	(1)	(2)	.20	21	12	96
Group IV											
MH-143	34.0	1.07	.006	.18	.006	x	x	.11	61	13	18

1. Ni approximately .10
2. Cu approximately .02
3. Mill production heat
4. Laboratory heat, remelted from mill production heat 2B0005
x - Not determined

ceeds somewhat the upper limit established for that element.

GROUP II

The compositions of the steels in this group are generally within the novel range of this invention except for the constituent columbium. The columbium contents of the steels in this group are outside the critical ratio of 13 to 29 times the nitrogen content.

GROUP III

The compositions of the steels in this group are all within the novel range of this invention and contain the correct critical amounts of columbium.

GROUP IV

The composition of this heat contains a chromium content on the high side of the broad range. The columbium content exceeds the critical amount required for effective reduction of the DBTT. This experimental heat was prepared from electrolytic chromium, vacuum remelted and high purity iron, vacuum refined.

Evaluating the physical properties of an alloy in order to predict performance can be accomplished by various recognized and accepted test procedures. The individual test employed should approximate the ultimate alloy application. For example, static testing, such as tensile testing, wherein a load is applied slowly, is employed when ductility and a reproducible measure of strength is desired. Dynamic testing, such as impact testing wherein loading is applied suddenly such as by a blow from a hammer or pendulum, is employed where a measure of toughness is desired. Another form of testing is service testing wherein a specific property such as corrosion resistance can be evaluated.

Tensile testing has revealed that the tensile properties of the alloys of Groups I, II and III and the comparable AISI grade, type 446 are essentially equal. This type of test failed to reveal any significant difference that might be used to predict actual service performance.

Another technique used to predict service performance is to measure an alloy's toughness. A widely accepted test used for measuring toughness is the Charpy V-Notch Impact Test. In this test a specimen containing a carefully machined notch is employed. The specimen, supported at both ends as a beam, is broken by a single blow of a swinging pendulum. The amount of energy absorbed in deforming and breaking the specimen determines the impact value. Specific details of this test are described in ASTM specification E 23–66, Part 31, 1971.

Impact test results of the alloy according to this invention and alloys outside the novel range of this invention are set forth in Table II.

It should be noted that accuracy of impact testing is subject to variation because of the following factors, notch geometry, temperature and equipment calibration. Notch geometry is controlled by proper location of the notch and accurate machining. It is essential that identical notches be located and machined in all specimens. The effect of temperature in notchedbar testing cannot be overlooked. This includes laboratory temperature and temperature of the specimen. Finally, the impact testing equipment must be correctly calibrated and maintained within standard calibration requirements. There are numerous other factors that might effect impact testing accuracy, such as placement of the specimen in the tester, specimen machine finish, etc., however, the three reasons set out above are the most important. Even by carefully controlling all these factors transition temperatures tend to show a variation or scatter of approximately plus or minus 25° F. This fact must be considered when the test data appearing in the following table is reviewed:

TABLE II

Heat No.	Ductile to Brittle Transition Temperature, °F	
	Water Quench	Air Cooled
1800°F		
Group I		
2B0005	−20	250
MH-22	−10	212
2B0123	100	x
Group II		
MH-158	x	175
MH-156	x	300
MH-152	x	250
MH-151	x	250
MH-144	70	100
MH-148	x	300
Group III		
MH-142	x	50
MH-25	−10	90
MH-146	−20	50
MH-149	x	50
MH-160	x	45
MH-161	x	25
Group IV		
MH-143	x	100

x - Not determined

Typical mechanical properties for an alloy of the present invention are as follows:

TABLE III

	Yield Strength (psi)	U.T.S. (psi)	% Elongation (1")	% Red in Area
MH 146	49,000	70,000	40	81

A most significant quality exhibited by the alloy of this invention is the DBTT after exposure to an elevated temperature and followed by air cooling. This is particularly significant in the production of hot rolled products and in the fabrication of weldments. In both applications the alloy is heated to an elevated temperature, worked in some manner and then air cooled.

In the production of plate, a slab approximately 6 to 12 inches thick, approximately 38 inches wide and of a length sufficient to produce the finished plate length is utilized. The slab is heated in a slab reheating furnace to approximately 2,150° F and rolled in a series of passes on a plate-rolling mill to a final thickness of 3/16 inch to 3 inches. After the plate dimensions are achieved on the rolling mill, the plate is transferred to a cooling bed or heat treated and cooled to an ambient temperature. Ideally the finished plate should then be suited for processing into a desired product, such as heat-exchanger tubes, pipes, and vessels for corrosive media. It is essential that steel processed in such a manner have a low DBTT independent of cooling rate to permit fabrication without brittle fracture and to avoid brittle fracture in the fabricated product, even if it is not given a final heat treatment. The alloy of this invention can be rolled into a plate of desired thickness in a manner as hereinbefore described, heat treated and then fabricated (including welding) into a finished product without final heat treatments.

The improved toughness in the air-cooled condition of the alloy of this invention is shown in Table II. Although all the steels in Table II had very low carbon and nitrogen levels, as advocated by Binder and Franks in U.S. Pat. No. 2,624,671 in order to achieve good impact properties, the DBTT is not depressed to room temperature unless the invention disclosed and claimed herein is employed (Group III). Without the present invention the impact properties are comparable to air-melted type 446 stainless (a ferritic stainless steel containing 23.0 to 27.0 percent Cr).

Impact tests performed on the alloy of this invention revealed an interesting phenomenon, namely that transverse and longitudinal impact strengths are equal. Steels produced by conventional steel making practices are characterized by transverse impact strength levels substantially less than longitudinal impact strength levels. This difference in strength level is usually attributed to the orientation of non-metallic inclusions. When an alloy in the form of an ingot is converted to a bloom and finally to a plate or strip globular inclusions that formed during solidification are elongated into stringers. These stringer inclusions are orientated in the plane of rolling, i.e., the longitudinal direction. In a transverse specimen these stringers act as stress risers because they lie parallel to the direction of impact and thereby tend to reduce the specimen's ability to withstand sudden loading.

The steel of this invention is inherently clean and free from non-metallic inclusions. Therefore, transverse specimens are free from this internal weakness. This results in essentially similar impact properties in both longitudinal and transverse directions. Uniform impact properties in both directions is also a desirable fabricating characteristic.

Service tests performed on the alloy are used to evaluate corrosion resistance. The alloy has outstanding general corrosion resistance in many environments and superior resistance to sensitization. It is well known in the art that conventional ferritic stainless steels are subject to severe intergranular attack. ASTM specifications A-262-70 outlines a series of test for evaluating resistance to intergranular corrosion. A particularly severe test, the ferric sulfate — sulfuric acid test, was used to evaluate the alloy of this invention. In this test a specimen is subjected to boiling ferric sulfate — 50 percent sulfuric acid for 120 hours. In this test conventional AISI type 446 fails to show any significant resistance to intergranular corrosion. The resistance to intergranular attack for certain of the alloys of Table I, measured after exposure to boiling ferric sulfate — 50 percent sulfuric acid for 120 hours follows:

TABLE IV

Heat No.	Sensitization Conditions	Corrosion Rate Microns per Year
Group I		
2B0005	1800°F/1 hr./Air Cool	479
MH-22	do.	704
Group II		
MH-158	do.	312
MH-156	do.	321
Group III		
MH-149	do.	343
MH-160	do.	355

The alloys of Group II and Group III exhibit greater resistance to intergranular corrosion than the alloys of Group I. This is attributed to the columbium addition in the Groups II and III alloys. As previously noted, interstitial levels measured in parts-per-million can still impair intergranular corrosion resistance. The small addition of columbium acts to tie up any nitrogen or carbon dissolved in the matrix thereby preventing the precipitation of chromium carbides or nitrides at the grain boundries upon cooling. Preventing precipitation of these carbides or nitrides at the grain boundries insures a uniform distribution of chromium throughout the matrix, thereby eliminating the possibility of intergranular corrosion.

The steel of this invention may be refined commercially in an electron-beam-heated cold-hearth furnace such as the furnace schematically illustrated in FIG. 2.

In FIG. 2 the main refining chamber (A) houses the coreless induction-melting furnace (B). A bulk charger and isolation valve (C) are mounted on the furnace lid for charging the melt stock, including some alloy additives, without exposing the furnace to ambient atmosphere.

An isolation valve (D) separates the main refining chamber from the holding furnace and secondary refining chamber (F) and final refining chamber (G). Molten metal in the main induction furnace is teemed by means of a retractable, refractorylined launder (E), through valve D to the induction-heated holding furnace (H). The holding furnace provides the surge capacity needed for the continuous feeding of molten metal to the electron-beam-heated hearth and continuous casting stations.

The hearth (I) is, in fact, a series of hearths arranged in cascade-fashion to prevent back-mixing.

The final hearth transfers the metal to a water-cooled copper tundish (J), which conducts it to a casting mold (K).

In the above described process the required columbium addition is preferably made after the refining has progressed to the point at which the final nitrogen level can be predicted. A critical amount of columbium is added so as to provide a Cb:N ratio of 13 to 29 in the final composition. Columbium may be added in the form of ferro-columbium. Columbium in this form has a lower melting point that pure columbium and, therefore, dissolves into the melt more rapidly. It is preferred in the above described process, to add the columbium prior to the passage of the alloy down the electron beam refining hearths. This produces a more homogeneous product.

It will be evident that as a result of this invention it has been made possible to provide a ferritic stainless steel alloy that combines toughness, improved resistance to intergranular corrosion and good resistance to general corrosion. It is to be understood that the invention is not limited to the particular embodiments disclosed, but may be used in other ways without departure from its spirit as defined by the following claims.

We claim:

1. A ferritic stainless steel characterized by its toughness and high resistance to intergranular corrosion consisting by weight percent essentially of:

chromium from about 20.0 percent to about 35.0 percent, molybdenum from about 0.75 percent to about 1.20 percent, silicon from about 0.10 percent to about 0.30 percent, phosphorous up to about 0.020 percent, sulfur up to about 0.020 percent, carbon up to about 0.0030 percent, nitrogen from about 0.0050 percent to about 0.0125 percent, columbium from about 13 to about 29 times the nitrogen content, and the remainder substantially all iron.

2. A ferritic stainless steel as defined in claim **1** wherein the chromium content is about 25.0 percent to about 27.5 percent.

3. A ferritic stainless steel as defined in claim **1** in which the total of nickel, copper and cobalt, present as impurities, does not exceed about 0.25 percent.

4. A ferritic stainless steel product having the composition defined in claim **1** and having a DBTT below room temperature after air cooling from 1,800° F.

5. A hot rolled ferritic stainless steel product characterized by its combined toughness and corrosion resistance and characterized further by exhibiting impact strength in the transverse direction substantially equal to the impact strength in the longitudinal direction, said product consisting by weight percent essentially of:

chromium from about 20.0 percent to about 35.0 percent, molybdenum from about 0.75 percent to about 1.20 percent, silicon from about 0.10 percent to about 0.30 percent, phosphorous up to about 0.020 percent, sulfur up to about 0.020 percent, carbon up to about 0.0030 percent, nitrogen from about 0.0050 percent to about 0.0125 percent, columbium from about 13 to about 29 times the nitrogen content, and the remainder substantially all iron.

6. A ferritic stainless steel product as defined in claim **5** wherein the chromium content is about 25.0 percent to about 27.5 percent.

7. A single phase ferritic alloy free of nickel and characterized by high resistance to corrosion, good weldability, and toughness, said alloy consisting essentially of Fe containing by weight 25 to 27.5 percent chromium, 0.75 to 1.20 percent molybdenum, 0.10 to 0.30 percent silicon, and containing as impurities not more than 30 ppm carbon, from about 50 ppm to about 125 ppm nitrogen, not more than 200 ppm sulfur, and not more than 200 ppm phosphorous, and further containing, as an essential element, columbium in an amount of at least 0.05 percent by weight and not more than about 29 times the nitrogen content of the alloy.

8. A ferritic stainless steel consisting, by weight percent, essentially of carbon up to about 0.0030 percent, phosphorous up to about 0.020 percent, sulfur up to about 0.020 percent, silcon from about 0.10 percent to about 0.30 percent, chromium from about 20.0 percent to about 35.0 percent, molybdenum from about 0.75 percent to about 1.2 percent, nitrogen from about 0.0050 percent to about 0.0125 percent, columbium from about 13 to about 29 times the nitrogen content, and the remainder substantially all iron, said steel being ductile in the water quenched condition to less than 0° F and having substantially equivalent transverse and longitudinal impact strength levels, and having an intergranular corrosion rate of less than 400 microns per year.

9. A ferritic stainless steel as defined in claim **8** wherein the chromium content is about 25.0 to 27.5 percent.

10. A ferritic stainless steel as defined in claim **8** in which the total of nickel, copper and cobalt, present as impurities, does not exceed about 0.25 percent.

11. A ferritic stainless steel as defined in claim **9** wherein the DBTT in the air-cooled state after annealing at 1,800° F is below room temperature.

* * * * *