

April 6, 1971

H. W. HAYDEN, JR., ET AL
STAINLESS STEEL HAVING IMPROVED CORROSION AND
FATIGUE RESISTANCE

3,574,002

Filed Aug. 6, 1968

6 Sheets-Sheet 1

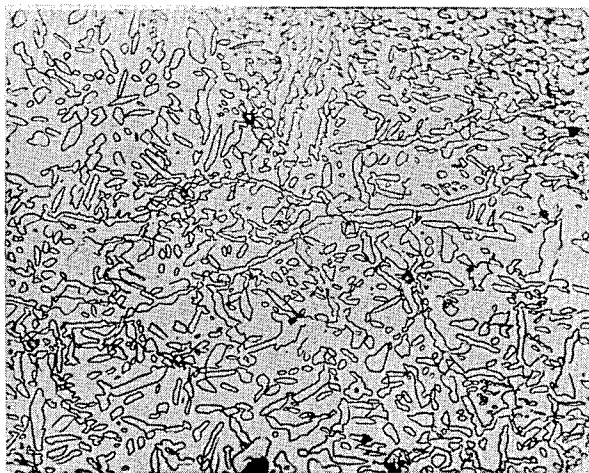


FIG. 1A

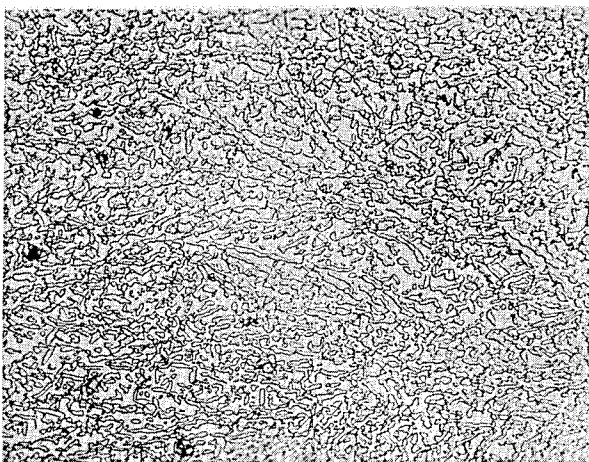


FIG. 1B

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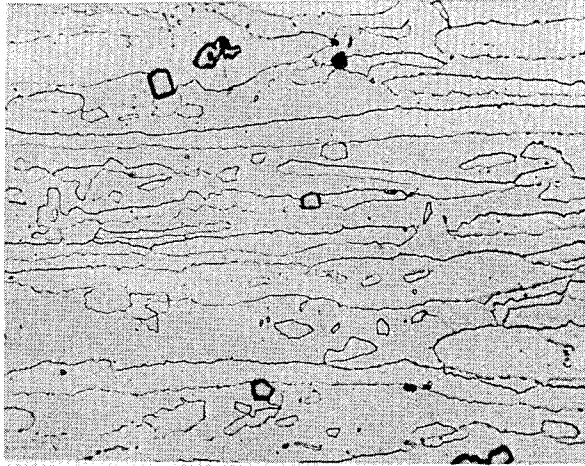


FIG. 2A

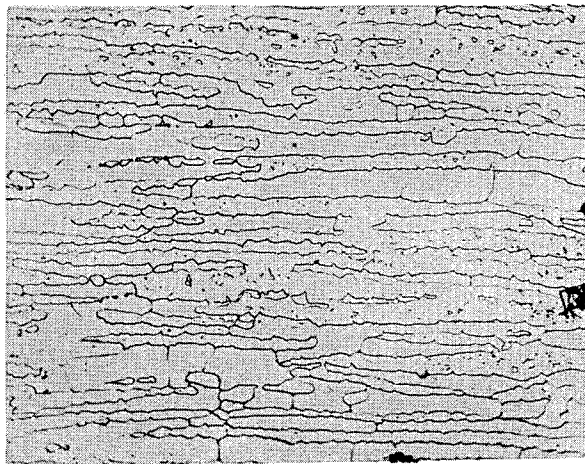


FIG. 2B

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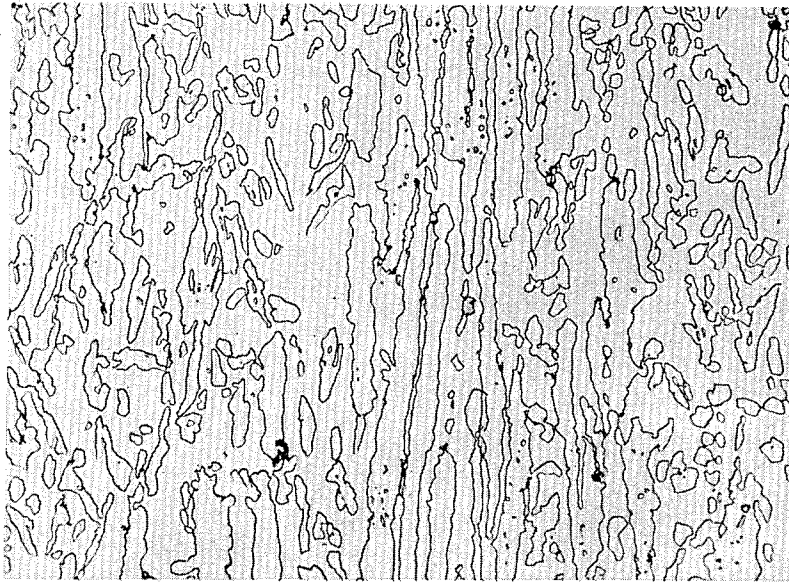


FIG. 2C

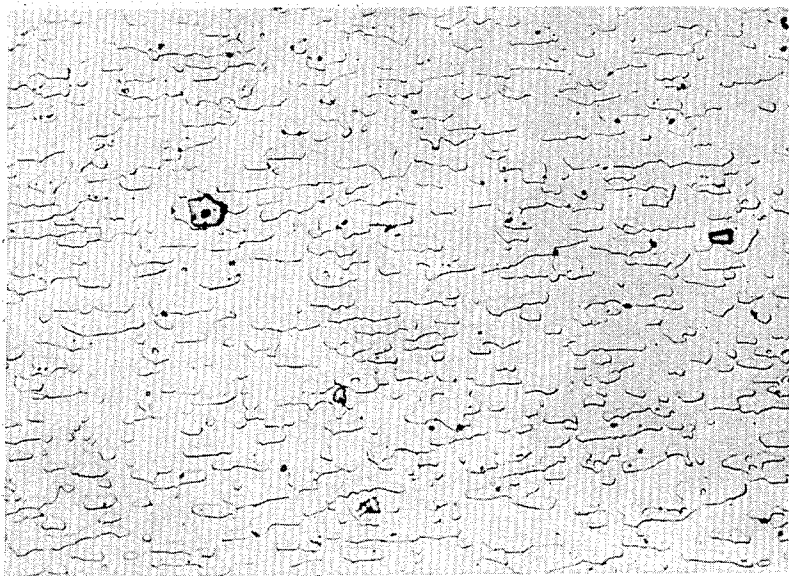


FIG. 2D

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6 Sheets-Sheet 4

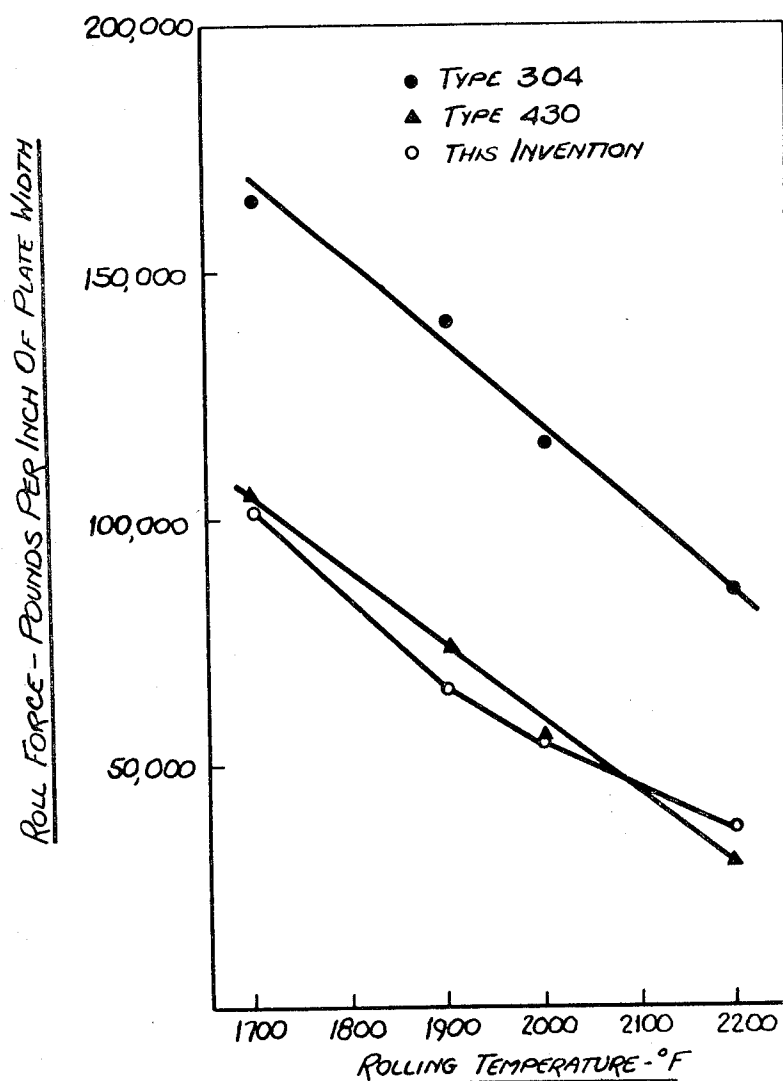


FIG. 3

ROLLING FORCES FOR REDUCTIONS FROM
1 INCH TO 1/2 INCH PLATE THICKNESS
FOR SEVERAL STAINLESS STEELS.

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6 Sheets-Sheet 5

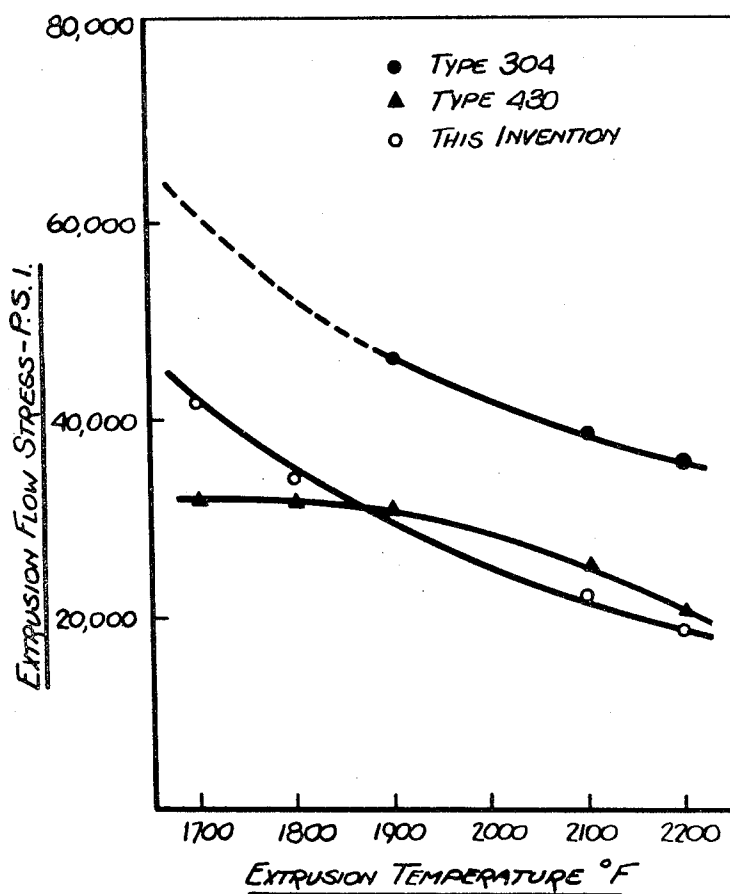


FIG. 4

EXTRUSION FROM
3.45" TO 0.875" ROUND FOR VARIOUS
STAINLESS STEELS.

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6 Sheets-Sheet 6

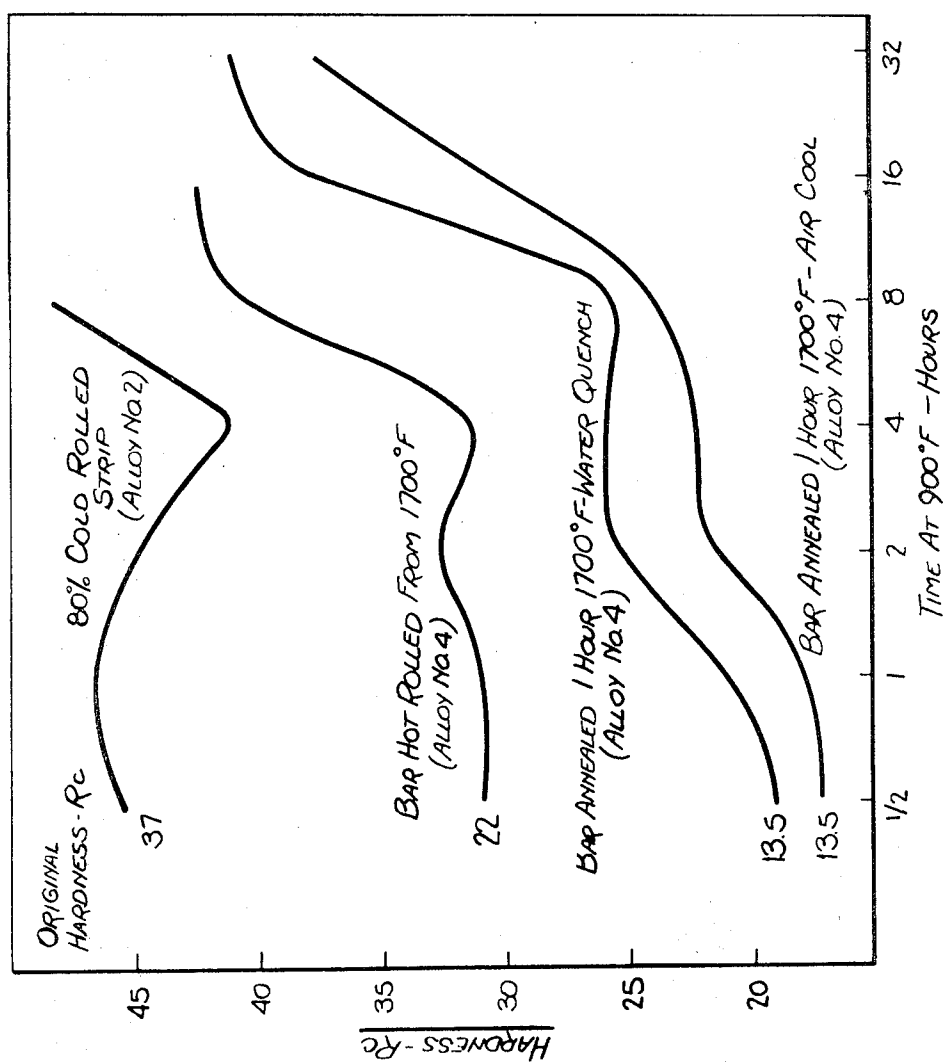


FIG. 5

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STAINLESS STEEL HAVING IMPROVED CORROSION AND FATIGUE RESISTANCE

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Continuation-in-part of application Ser. No. 638,519, May 15, 1967, which is a continuation-in-part of application Ser. No. 559,185, June 21, 1966. This application Aug. 1, 1968, Ser. No. 749,409

Int. Cl. C22c 39/14, 39/20

U.S. Cl. 148—37

19 Claims

ABSTRACT OF THE DISCLOSURE

Directed especially to readily workable stainless steels having a duplex, e.g., austenite-ferrite, microstructure containing about 18% to about 35%, e.g., about 26%, chromium, about 2% to about 12%, e.g., about 6.5%, nickel, up to about 1.5%, e.g., about 0.2%, titanium, up to about 1% vanadium, not more than about 0.08%, e.g., up to about 0.05%, carbon and the balance substantially iron.

The present application is a continuation-in-part of our copending U.S. applications Ser. No. 559,185 filed June 21, 1966 now abandoned, and Ser. No. 638,519 filed May 15, 1967 now abandoned.

The present invention is directed to improvements in stainless steels and like alloys.

Existing grades of austenitic stainless steels such as Type 304 are stiff during hot working which requires high working loads and many reheats to fabricate them. When fabricated they exhibit relatively low strength and fatigue resistance and they are subject to pitting and stress-corrosion failure, particularly when exposed above or in solutions containing chlorides. The other type of existing grade of stainless steel, which is not one of the "hardenable" grades, is the ferritic grade, such as Type 430. This type generally shows intermediate strength, better fatigue resistance than the austenitic grade, but poor resistance to pitting corrosion and poor resistance to stress corrosion in environs such as a bubbling hydrogen sulfide (H₂S) solution.

While each of the many kinds of steels in these two general grades has many very satisfactory applications, each also has severe limitations which jeopardize its wide safe usage. In contrast to these existing steels, special steels within the present invention embody the best combinations of attributes of both ferritic and austenitic grades, and not the worst combination as one skilled in alloy development may have grown to expect. At the same time, special steels within the invention offer higher strength and fatigue resistance and the solution to the widely publicized poor workability of two-phase austenite-ferrite steels. Specific quantitative illustrations of each of these comparisons are included among the examples herein.

This invention pertains to improvements in alloy steels and other alloys having above the recrystallization temperature a stable essentially two-phase structure, one of which phases is of increased solubility at higher temperatures than the other, to methods for improving the plasticity and other properties of such alloys by novel processing procedures in accordance with the invention, to wrought alloy steels and other alloys so processed, and to novel steel compositions susceptible to improvement by such processing.

One method according to the invention for improving the elevated temperature plasticity and other properties of such alloys comprises, heating to temperature sufficiently above the recrystallization temperature to dissolve a substantial portion or all of said more soluble phase, plastically deforming said alloy, heating, either by reheating or by intermediate isothermal treatment, said plastically deformed alloy at a temperature in the two-phase temperature region above the recrystallization temperature to precipitate said dissolved phase, to produce in said alloy a fine grained, two-phase microstructure having high plasticity at said heating temperature. Alternatively, the alloy may be cooled from the aforesaid solution treating temperature and cold worked and thereupon heated to a temperature above its recrystallization temperature but within the two-phase temperature region, thereby to impart to the alloy by recrystallization and precipitation, a fine grained, two-phase microstructure having high plasticity at said heating temperature. It is found that precipitation of said dissolved phase keys or blocks grain growth at the precipitating temperature and contributes to the production and maintenance of fine duplex structures at said temperature. With proper processing, the alloy will have imparted thereto at temperatures above said recrystallization temperature but within the two-phase region, a short-time tensile elongation of above 150% or 200% to 1,000%.

Various modifications of the aforesaid process may be employed to the same end, all of which, however, include as essential steps (1) solution treating the wrought alloy at temperature sufficiently high to dissolve at least a substantial portion of the more soluble phase, and (2) precipitating said dissolved phase at some lower temperature usually above that of recrystallization, accompanied by or subsequent to plastic deformation in the amount of at least 20% reduction, e.g., 40% or 50% or more, in any cross-sectional area either hot or cold such as to produce an ultra fine grained structure, usually essentially a two-phase structure which may also have small amounts of other phases.

The novel methods of the invention are especially applicable to improving the properties of duplex stainless steels of the relatively low-nickel, high-chromium types, to which the invention is particularly directed. These methods impart to the said stainless steels, a duplex, ferrite-austenite microstructure at temperatures above the M_s temperature having a small interparticle spacing between austenite (face-centered cubic) particles in at least one direction, in which austenite is the phase which, upon heating, dissolves to a substantial extent or entirely in the second phase, to wit, in the ferrite (body-centered cubic), and which during processing is caused to come out of solution as a fine grained precipitate in a fine grained ferrite matrix.

The invention particularly contemplates processing by the methods of the invention, stainless steels containing about 18% to 35% chromium, about 2% to 12% nickel, up to about 1.5% titanium, up to about 1% vanadium, not more than about 0.08% carbon, and the balance substantially iron. Optional additions in the steels include: manganese up to 1%, silicon up to 1%, cobalt up to about 2%, molybdenum up to about 3% at the expense of chromium and copper up to about 2% or 2.5%, provided silicon and manganese do not exceed 0.4% and 0.3%, respectively, when copper is 2% or more.

In order to assure proper proportions between austenite (or martensite) and ferrite in the structure of the processed steels, the percentage content of chromium and of molybdenum (if any is present) should be such that the total content thereof does not substantially exceed 3.5 times the percentage of nickel plus 11%, but equals or

exceeds 1.17 times the percentage of nickel plus 13.3%. Steels within the aforementioned compositional ranges when processed as described hereinbefore are characterized, at temperatures above the M_s temperature, by a duplex (essentially two-phase) ferrite-austenite micro-structure, having only a small interparticle spacing between austenite particles when measured in the shortest direction, e.g., the direction perpendicular to a worked surface. Such steels when so processed are characterized by exceptionally high hot ductility as measured in the short-time tensile test at temperatures of the order of about 1600° F. to 1800° F. and are amenable to processing at the aforementioned temperatures by forming methods wherein only exceptionally small loads are required to achieve large deformations. Furthermore, the steels may be readily hot worked as by rolling or extrusion by conventional means at temperatures within the aforementioned temperature range and even lower. When the alloy steels are hot rolled and extruded by usual means, the forces required to deform the steels are comparable to those required for plastically deforming ferritic steels such as Type 430 and considerably less than those required for austenitic stainless steels such as Type 304. The steels are also readily cold workable.

Within the aforementioned stainless steel compositional ranges, we have discovered an especially advantageous range of special compositions for wrought steels which are characterized, when processed as described hereinbefore to provide there in a ferrite-austenite micro-structure having a controlled spacing between austenite particles, by a unique combination of highly useful properties in addition to the aforementioned enhanced elevated temperature plasticity, namely, a combination of exceptional room temperature strength, ductility, toughness, fatigue resistance, corrosion resistance, and good workability by plastic deformation both hot and cold into rod, plate, sheet, strip, wire and other mill or finished products. This especially advantageous compositional range for the special wrought stainless steels of the invention comprises about 23% to 35% chromium, about 4.5% to 12% nickel, not more than about 0.08% carbon, up to about 1.5% titanium, up to about 1% vanadium, up to about 2% cobalt, and up to about 2% or 2.5% copper. In these highly advantageous steels of the invention, the chromium and nickel contents are highly important. Thus, the chromium content is at least about 23% and the nickel content is at least about 4.5% because of decreased toughness (as measured by the standard Charpy V-notch test) in alloys having lower contents of nickel and/or chromium. The chromium content preferably does not exceed about 35% to avoid serious commercial disadvantages such as poor ingot surface, oxide scums in air melting, high cost and the possibility of encountering undesirable embrittlement during exposure to mill heating cycles.

For imparting high resistance to stress corrosion cracking in chloride media, e.g., sodium chloride solutions and vapors, magnesium chloride, ferric chloride, calcium chloride, etc., chromium should exceed about 24% in the special steels. It is usually unnecessary to employ chromium contents exceeding about 28% or 30% while realizing the substantial advantages characterizing the special steel compositions. Advantageously, nickel is at least 5.2% to avoid spontaneous occurrence of martensite on cooling the wrought steel from an elevated temperature, e.g., about 1700° F., and to provide material having a duplex structure comprising ferrite and austenite at room temperature. Steel compositions having lesser amounts of chromium and nickel contain martensite. Excellent results are achieved in the special steels of the invention when the contents of chromium and any molybdenum are related to nickel such that, firstly, the total percentage content thereof does not exceed about 3.5 times the percent of nickel present plus 11%, and, secondly, the said total chromium and any molybdenum content equals or

exceeds 1.17 times the percent of nickel present plus 13.3%. Nickel and chromium (and molybdenum if present) are related in the special steels as aforesaid because at lesser nickel contents than those in accordance with the first relation, the steels have unsatisfactory toughness whereas at greater nickel contents than those in accordance with the second relation, the steels have unsatisfactory strength. Generally satisfactory steels processed to have fine grained duplex ferrite-austenite structures in accordance with the invention contain about 5.2% to about 8% nickel, e.g., about 6% to about 7% nickel, and about 24% to about 28% chromium, e.g., about 25% to about 27% chromium, with minor amounts of other elements as described herein and the balance essentially iron.

In the steels of the invention, control of carbon content is highly important, and carbon should not exceed about 0.08%. It has been found that hot working difficulties are caused by the formation of a brittle cellular carbide phase, believed to be $Cr_{23}C_6$, at the interfaces between austenite and ferrite grains. Difficulties in hot working, which are particularly evident in the case of flat-rolled products, are eliminated by controlling the carbon content so that it does not exceed about 0.03% or by the use of a strong carbide-forming element, preferably titanium, in the steel when carbon exceeds about 0.03%. Formation of interphase grain boundary chromium carbide can thus be prevented and ready hot workability conferred even in large ingot sizes. Preferably, carbon does not exceed about 0.05%. Titanium is employed in amounts at least four times the carbon in excess of 0.03% up to about 1.5%. Titanium adversely affects toughness and, for this reason, should not exceed about 0.3% or about 0.4% when carbon is about 0.08%, with proportionally greater amounts of titanium being acceptable at lower carbon levels down to about 0.03%. Generally, titanium need not exceed 0.7%. Vanadium may be employed as a carbide former in amounts up to about 1% in place of titanium, with the total content of vanadium and titanium not exceeding about 1.5%. Preferably, the vanadium content is not more than about 0.5%, e.g., up to about 0.25%, with the vanadium, like titanium, being at least four times the quantity (percent carbon minus 0.03%). Vanadium-containing steels appear to develop lower strengths than do similar titanium-containing steels. Carbon control as described hereinbefore permits latitude in rolling start temperatures, i.e., permits rolling at start temperatures over a wide range of about 1700° F. to about 2200° F. or 2300° F. Certain steels which are not fully balanced with respect to carbon and, e.g. titanium, can be successfully hot worked at high start temperatures, e.g., 2300° F. or 2350° F., provided the soaking temperature is sufficient to dissolve substantially all austenite or substantially all chromium carbide. An all-ferrite structure at the rolling start temperature is readily hot-workable. Silicon and manganese appear to affect toughness unfavorably, and when copper is present in amounts of about 2% or 2.5%, silicon and manganese should not exceed 0.4% and 0.3%, respectively, or the steel will crack when hot rolled in the conventional manner. Treating agents such as magnesium, zirconium, aluminum, cerium, boron, hafnium, etc., may be employed in amounts up to 1%. Molybdenum may be included in amounts up to about 3%. Preferably, the sum of chromium and molybdenum does not exceed 26% to avoid the formation of brittle phases due to the presence of molybdenum in hot worked or cold worked steels during mill heating cycles in the temperature range of about 900° F. to about 1800° F. Such brittle phases, possibly sigma phase, can prevent successful cold working of molybdenum-containing steels unless a quench from a temperature higher than 1800° F. is employed. Columbium may also be employed as a carbide former in amounts up to 1% but this element adversely affects toughness and ductility. Combinations of columbium and molybdenum are specially detrimental to cold

workability, possibly because of the formation of brittle phases such as sigma phase. Phosphorus, nitrogen and sulfur should be kept as low as possible consistent with good steel-making practice. Nitrogen, which may be present in air melted steels, can combine with carbide-forming elements such as titanium, and this factor must be taken into account in determining the amount of available carbide former, e.g., titanium, required to fix carbon in the steels as will be apparent to those skilled in the art. When the carbon content exceeds about 0.03%, the content of titanium and/or vanadium should be four times the sum of carbon in excess of 0.03% plus the nitrogen content. If columbium is used as a carbide former, the columbium should be eight times the sum of carbon in excess of 0.03% plus the nitrogen content. Vacuum melted steels are essentially devoid of nitrogen, i.e., contain not more than about 0.005% nitrogen.

In the hot worked condition, the special compositions of the new steel, i.e., those containing at least 23% chromium and 4.5% nickel, exhibit exceptional combinations of room temperature tensile strength (90 to 125 thousands of pounds per square inch (k.s.i.)); 0.2% offset yield strength (60 to 80 k.s.i.); ductility (25% to 45% elongation); toughness (Charpy V-notch impact energy up to 75 foot-pounds and higher) and fatigue (an endurance limit of, for example, 78 k.s.i. at 10^8 cycles). Cold working, for example, by rolling or wire drawing is easily accomplished and produces material having tensile strengths up to 350 k.s.i. or more in 0.010" diameter wire and up to 187 k.s.i. or more in 0.050" thick sheet.

The special compositions of the steel are also age hardenable to high hardness levels on the order of 45 to 50 Rockwell C, and, hence, to correspondingly high strength levels with retention of useful ductility.

In the accompanying drawing:

FIGS. 1a and 1b are photomicrographs taken at 750 diameters, illustrating typical duplex, ferrite-austenite structures in a wrought steel of the invention having the highly advantageous composition, which was solution treated in the single phase (ferrite) region prior to breakdown from the ingot stage, the steel being processed as explained hereinafter.

FIGS. 2a and 2b are photomicrographs taken at 750 diameters illustrating duplex, ferrite-austenite structures of another wrought steel which was subjected to a heating the duplex (ferrite-austenite) region prior to breakdown from the ingot stage as explained hereinafter.

FIGS. 2c and 2d are photomicrographs taken at 750 diameters depicting duplex, ferrite-austenite structures of other wrought steels having compositions within the invention in the hot-rolled, annealed condition, the material depicted in FIG. 2d having been solution treated to dissolve substantially all the austenite prior to breakdown from the ingot stage and the material depicted in FIG. 2c having been solution treated in the duplex phase region to dissolve a substantial proportion of the austenite prior to breakdown from the ingot stage.

FIG. 3 is a graphical showing of the relation between rolling force and rolling temperature for the steels of the invention as compared to some prior art steels.

FIG. 4 is a graphical showing of extrusion flow stress versus extrusion temperature for extruding steels according to the present invention as compared to some prior art steels.

FIG. 5 shows the aging response of special steels according to the invention in terms of aging time versus aging hardness.

Steel compositions according to the invention may be quantity-produced in any of the usual industrial types of furnaces. Vacuum or air melting and conventional and continuous casting procedures may be employed to produce ingots. Vacuum melting is a preferred technique for preparing the alloys since this technique permits the

production of steels without deoxidizing additions of silicon and manganese and enables control to low levels of elements such as carbon, oxygen, nitrogen, hydrogen, sulfur, phosphorus, etc. Such elements have a subversive effect upon impact properties. However, air melting techniques can be successfully employed to produce steels having excellent properties even at carbon levels on the order of 0.05% when the special control of carbon and a suitable carbide former such as titanium or vanadium as taught herein is employed. The economic disadvantages flowing from the use of vacuum melting the new stainless steel alloys described herein can thus be overcome. Initial breakdown operations may be carried out by heating the ingots to temperatures on the order of 2200° F. or higher and the steel rolled, forged or extruded thence into mill products finishing preferably at about 1700° F. or below. The hot worked material can be subjected to the special processing described hereinbefore to establish therein the controlled grain structure at any point in the mill processing program. The compositions of typical heats of the special steels of the invention produced as above, in addition to iron, are set forth in the following Table I.

TABLE I

	Percent					
	C	Cr	Ni	Ti	Al	Other
Alloy Number:						
1-----	0.02	30	6	0.6	0.05	
2-----	0.02	25	6	0.6	0.05	
3-----	0.009	25.5	6.05	0.59	0.029	
4-----	0.008	25.6	5.2	0.63	0.045	
5-----	0.012	25.2	7.0	0.61	0.040	
6-----	0.011	29.4	6.2	0.61	0.042	
7-----	0.009	29.6	7.2	0.62	0.036	
8-----	0.010	29.4	8.9	0.60	0.037	
9-----	0.007	25.7	8.6	0.56	0.05	
10-----	0.008	25.6	6.1	0.23	0.018	
11-----	0.005	25.5	6.1	<0.10	<0.01	
12-----	0.05	35	10	0.62	-----	
13-----	0.021	25	6	0.6	0.055	
15-----	0.014	25.4	6.1	<0.01	0.021	
16-----	0.02	25.9	6.1	<0.01	0.031	
17-----	0.05	25.5	6.0	0.08	0.036	
18-----	0.046	25.7	6.0	0.17	0.034	
19-----	0.047	25.3	6.0	0.32	0.035	
20-----	0.010	27.4	6.8	0.57	0.05	
21-----	0.013	28.0	7.2	0.59	0.05	
22-----	0.012	29.8	7.6	0.59	0.05	
23-----	0.08	25.9	6.0	0.16	0.029	
24-----	0.07	25.6	5.9	0.32	0.037	
25-----	0.022	23.5	5.2	0.57	0.03	
26-----	0.030	24	5.6	0.58	<0.03	
28-----	0.034	26.0	6.1	0.14	-----	
28-----	0.044	25.8	7.1	0.64	0.04	
29-----	0.043	25.6	8.1	0.53	0.04	
30-----	0.041	25.4	9.0	0.63	0.04	
31-----	0.039	28.2	10.2	0.55	0.04	
32-----	0.013	24.5	5.7	<0.01	0.049	1 Mo.
33-----	0.006	24.0	5.6	<0.01	0.066	2 Mo.
34-----	0.004	23.5	5.7	<0.01	0.067	3 Mo.
35-----	0.056	26.0	7.05	-----	0.03	0.13 V.

The heats tabulated in Table I, except for Alloys Nos. 27 to 31, were vacuum-melted from virgin materials and the silicon and manganese contents thereof, except for Alloy No. 35, were in the range of about 0.01% to about 0.04%. Alloys Nos. 27 to 31 were air-melted. No intentional additions of manganese and silicon were made to Alloy No. 27 and it contained 0.045% nitrogen. Alloys Nos. 28 to 31 and 35 contained about 0.3% to about 0.4% manganese, about 0.45% to about 0.6% silicon, and Alloys Nos. 28 to 31 contained about 0.01% to about 0.02% nitrogen. The vacuum melted heats contained no more than about 0.005% nitrogen.

The basic requirement for producing improved elevated temperature plasticity in the steel is the imparting thereto of a duplex ferrite-austenite (or martensite) structure in which the grain size of each phase is as fine as can possibly be produced and, preferably, such that the spacing (mean free path) between austenite (or martensite) particles (in the smallest dimension) does not exceed 8 microns. This may be accomplished by preparing alloy compositions within the ranges above set forth which are so balanced that the austenite and ferrite phases will co-exist over a temperature range between the recrystalliza-

tion temperature and the austenite solution temperature, and processing as above stated.

Hot tensile test results on heats having compositions according to the invention are presented in Table II below. These tests were conducted on various forms of material as indicated in the table. In each case, the specimen was heated for about 20 minutes at the test temperature before testing was commenced and precipitation of austenite occurred during said heating.

In treating the steels, initial hot reduction has been performed (forging or direct rolling) from a temperature of 2200° F. After the initial breakdown, subsequent hot working, by rolling or extrusion, is performed at temperatures ranging from 2200° F. to 1700° F. In comparing the hot working characteristics of steel compositions according to the invention with those of existing stainless steels, results have shown that the roll forces and extrusion pressures are comparable to those for Type

TABLE II

Prior condition	Test temperature, ° F.	U.T.S., k.s.i. ¹	Percent elongation	Gage length, inches	Strain rate, in./in./min.
Alloy No.:					
1-----	1,600	11.8	300	.75	.266
1-----	1,700	8.4	200	.75	.266
1-----	1,800	5.2	200	.75	.266
2-----	1,600	10.5	433	.75	.266
2-----	1,700	7.6	600	.75	.266
2-----	1,800	5.4	500	.75	.266
1-----	1,600	10.5	160	1.25	.160
1-----	1,700	6.9	208	1.25	.160
2-----	1,600	10.8	304	1.25	.160
2-----	1,700	7.3	304	1.25	.160
12-----	1,800	5.8	460	1.25	.16
D ² -----	1,700	3.1	210	1.25	.16

¹ U.T.S., k.s.i.= Ultimate tensile strength, thousands of pounds per square inch.

² See Table XII for composition.

As illustrated in Table II, prior cold work with accompanying structural refinement enhances the amount of hot superplastic elongation. Furthermore, cold worked samples exhibit comparable tensile strengths to those of non-cold worked samples even though the latter were deformed at a lower strain rate.

An explanation of the effect of prior cold work on the extent of superplastic elongation can be seen in FIGS. 1a and 1b of the drawing. This compares the structures of wrought material containing dissolved austenite which was cold worked prior to hot rolling from 1700° F. (FIG. 1b), to that of similar material which was hot rolled from 1700° F. without a prior cold working step (FIG. 1a). It can be seen that the prior cold worked material has a markedly finer microstructure. The extremely fine microstructures depicted in FIGS. 1a and 1b (mean free paths of 3.8 and 2.4 microns, respectively, between austenite particles) resulted from initially working the alloy there shown (Alloy No. 2) at a temperature at which the alloy was essentially all ferrite (i.e., about 2200° F.) and thereafter heating and hot working in the two-phase ferrite-austenite region therefor. These structures represent particularly preferred conditions in accordance with the invention for providing steels having enhanced mechanical and corrosion properties as well as elevated temperature plasticity. The photomicrographs of FIGS. 2a and 2b depict the structure of Alloy No. 27 in the condition resulting from an initial breakdown of the ingot starting at 2200° F. but in the two-phase region for this alloy and finishing in the two-phase region therefor at about 1700° F., followed by reheating to 1900° F. and hot rolling from that temperature in the two-phase region followed by annealing at 1700° F. for one hour, again in the two-phase region (FIG. 2a). A portion of the material as depicted in FIG. 2a was cold worked 50% and annealed one hour at 1700° F. and the structure thereof is depicted in FIG. 2b. Marked structural refinement is evident in FIG. 2b as compared to FIG. 2a.

430 stainless steel and considerably less than those for Type 304 stainless steel. These results are shown in FIGS. 3 and 4 of the drawing. It is significant that the steel compositions of the invention, which are a mixture of ferritic and austenitic phases, retain the easy hot workability of an all-ferritic alloy (Type 430) rather than being intermediate between this and an all-austenitic alloy (Type 304).

The two-phase stainless steel compositions of the invention having a controlled duplex structure, are capable of withstanding large amounts of cold reduction. Strip material can be cold rolled to at least 80% reduction in thickness without the necessity of an intermediate anneal. Such operations have been performed on material in the as-hot rolled condition as well as on annealed material, e.g., material annealed at 1700° F. prior to the cold reduction step. Also, such steel compositions are extremely amenable to wire drawing.

4" x 4" ingots from Alloys Nos. 1 to 3 and 13 were converted to hot rolled plate and bar form and/or to cold rolled strip. The Alloy No. 13 material was soaked at 2200° F. for one hour and hot forged to a 2" x 3" section. The forged material was reheated to 2200° F. and hot rolled to 1" plate. The resulting plate was reheated to 1700° F. and hot rolled to 5/8" plate in a single pass. The Alloy No. 3 material was soaked at 2200° F. for one hour and hot forged to a 2" x 2" section. The forging was reheated to 1700° F. and hot rolled to 5/8" square. The Alloys No. 1 and No. 2 material was initially soaked at 2200° F. and hot forged to 2" x 2", reheated to 2200° F. and hot rolled to 5/8" square, a portion was again reheated to 1700° F. and hot rolled to 1/4" strip. Portions of the resulting hot rolled strip were cold rolled to 0.050". Mechanical properties determined upon the resulting duplex ferrite-austenite structured material in the wrought forms and after various heat treatments are 75 given in Table III.

TABLE III

Processing	Form of material	Y.S., 0.2% offset, k.s.i.	T.S. k.s.i.	El., percent	R.A., percent	CVN, ft.-lbs.
Alloy No.:						
13.....	1,700° F. hot rolled.... 5/8" plate	86.1	105.8	27.0	61.5	75.5
	transverse.					
	Longitudinal..	86.5	103.6	29.0	68.0	75.5
3.....	do..... 5/8" bar	110.5	120.2	29.0	77.5	
1.....	1,700° F. hot rolled 0.050" strip	173.6	183.0	5.0		
	80% cold red'n.					
2.....	do..... do.....	176.0	185.0	5.5		
1.....	1,700° F. hot rolled do.....	103.6	118.3	19.0	57.0	
	plus 80% cold red'n.					
	plus 1/2 hour 1,700° F.					
2.....	do..... do.....	71.0	106.0	27.0	57.0	
1.....	1,700° F. hot rolled do.....	252.3	256.3	7.0	15.5	
	plus 80% cold red'n.					
	plus 8 hours 900° F.					
2.....	do..... do.....	237.7	243.4	6.0	22.5	

NOTE.—
Y.S.=yield strength.
T.S.=Tensile strength.
El.=elongation.
R.A.=reduction in area.
CVN=charpy V-notch.

As illustrated by the Table III data, the strength and toughness of Alloy No. 13 plate material, which had a structure similar to that of FIG. 1a, are similar (isotropic) in the longitudinal and transverse directions. Furthermore, the as-hot rolled strength is superior to most other stainless steels and was obtained without resorting to a multi-step working and heat treating cycle.

Ingots produced from Alloys Nos. 4 through 11 were hot rolled to plate having a thickness of about 5/8". The ingots, which were about 4" x 4" in cross section, were heated to 2200° F., rolled to about 3" x 3" section and then rolled to one inch plate, with a finishing temperature between about 1800° F. and 1900° F. The plates were reheated to 1700° F. and rerolled to 5/8" thickness in a single pass. In the case of Alloy No. 35, the initial heating was conducted at 2300° F. The resulting material in the as-rolled condition was subjected to tensile and impact testing with the results set forth in the following Tables IV and V. The Charpy V-notch impact data presented in Table V were determined on specimens cut both from the longitudinal and transverse directions in the plate and indicate that substantially isotropic properties were obtained in the as-rolled plate.

TABLE IV

Alloy Number:	Y.S., k.s.i.	T.S., k.s.i.	Elon- gation, percent	Reduction in area, percent
4.....	88	93	18	44
5.....	89	105	27	65
6.....	98	108	20	52
7.....	111	120	20	57
8.....	110	126	22	58
9 ¹	57.3	93.8	38	73
10.....	78	95	28	64
11.....	79	93	27	65
20 ¹	73.4	99.5	30	67.7
21 ¹	76.6	103.2	30	66.5
22 ¹	80	106.3	30	66.5
35 ¹	66.9	101.4	33	64
35 ²	72.2	103.9	29	62

¹ Annealed 1,700° F. for 1 hour, air cooled.
² Annealed 1,500° F. for 1 hour, air cooled.

TABLE V

Alloy Number:	Charpy V-notch	
	Longitu- dinal specimen, foot- pounds	Trans- verse specimen, foot- pounds
4.....	53	57
5.....	64	77
6.....	50	45
7.....	40	40
8.....	44	43
9 ¹		156
10.....	35	35
11.....	50	51
20 ¹		103
21 ¹		90
22 ¹		60
35 ¹		65
35 ²		47.6

¹ Annealed 1,700° F. for 1 hour, air cooled.
² Annealed 1,500° F. for 1 hour, air cooled.

The detrimental effect of columbium upon the impact property of the steel is illustrated in that similarly processed plate from an alloy similar in composition to Alloy No. 4 but containing 0.6% columbium instead of titanium had 31 and 22 foot-pounds in the longitudinal and transverse specimens respectively. Plate specimens of vacuum-melted Alloys Nos. 32, 33 and 34, which were very low in carbon and contained essentially no titanium, in the condition resulting from hot rolling from 1700° F. followed by a one hour anneal at 1700° F. had Charpy V-notch impact values exceeding 190 foot-pounds, with some of the specimens being unbroken. It was found, however, that Alloy No. 34 rapidly formed sigma phase when heated at 1500° F. whereas Alloys Nos. 32 and 33 did not. This result demonstrated that, even under the favorable compositional conditions existing therein, sigma formation was encountered due to the copresence of 23.5% chromium and 3% molybdenum.

Material from Alloys Nos. 4 through 11 was hot rolled to rod having a diameter of about 0.625". The material was annealed at 1700° F. after hot rolling. The hot

rolled, annealed rod, was cold rolled to a diameter of about 0.11" and annealed at 1700° F. for about one-half hour. At this point in the processing, the material had a wrought duplex ferrite-austenite microstructure wherein austenite was dispersed as fine particles with only a small interparticle spacing of austenite. The cold rolled, annealed material was then cold drawn into wire of 0.02" and 0.01" diameter (about 99% cold reduction) without intermediate annealing, and was subjected to tensile testing at each of the aforementioned diameters. The results of the tensile tests are set forth in the following Table VI.

TABLE VI

Alloy Number:	U.T.S., k.s.i., 0.020"	U.T.S., k.s.i., 0.010"
4-----	220	279
5-----	248	308
6-----	205	275
7-----	222	297
8-----	249	306
10-----	242	306
11-----	252	321
32-----	300	346
33-----	343	355
34-----		342

It was found that the fine diameter wire resulting from the aforementioned drastic cold working could be looped and wrapped about its own diameter without breaking and that appreciable reduction in area occurred at the point of failure in the tensile test, indicating that an even greater amount of cold work could be imparted to the material without difficulty. The detrimental effects of columbium upon the properties of severely cold worked material are illustrated by the fact that wire processed from an alloy very similar in composition to Alloy No. 4 but containing 0.6% columbium instead of titanium broke at a tensile strength of 213 k.s.i. at 0.020" diameter and 261 k.s.i. at 0.010" diameter with no indication of yielding prior to breaking.

We have observed that the special duplex ferrite-austenite stainless steel compositions of the invention containing at least 23% chromium, for example, steels containing about 25% chromium, about 6% nickel, and about 0.6% titanium exhibit an aging response at about 900° F. The extent and rate of hardening are highly sensitive to the prior condition of the material. FIG. 5 of the drawing compares the aging of properly processed material after various cold working, hot working or annealing treatments. It can be seen that there are two domains of aging response, the second being greater than the first in each instance. The hardening is accompanied by a reduction in toughness.

A series of R. R. Moore rotating beam fatigue tests was conducted on Alloy No. 3 bar stock hot rolled from 1700° F. An endurance limit (10^8 cycles) was indicated at a stress level of 78.75 k.s.i. On a separate tensile test on identical bar stock, it was determined that the tensile strength of this material was 120 k.s.i. By comparing these two results, it can be seen that the endurance limit of this material is 65.6% of its tensile strength. Furthermore, the ratio of the endurance limit to the tensile strength is higher than that of other stainless steels. It appears that these highly desirable fatigue properties are a concomitant feature resulting from the unique metallurgical structure of the alloys. Existing stainless steels available to the art in the mill annealed condition show considerably lower determined endurance limits which

represent much lower percentages of the ultimate tensile strength.

	10^7 fatigue limit, k.s.i.	Percent U.T.S.
Type 302-----	34	36
Type 304-----	28	33
Type 310-----	35	37
Type 430-----	40	53
Alloy No. 27, 1,700 H.R. plus 1,700° F. anneal-----	1 57	62.5

1.8×10^7 cycles.

The steels of the invention preferably have a substantially if not entirely ferritic structure as solution treated at high temperatures, e.g., about 2200° F., when cooled or quenched to room temperature. The wrought steels processed in accordance with the invention as above described are characterized by a controlled grain structure having interdispersed phases such that the transverse interparticle spacing (mean free path) between austenite particles preferable does not exceed 8 microns in the shortest direction to impart thereto an enhanced elevated temperature plasticity as shown by a short-time tensile ductility of at least about 150% at a strain rate of about 0.16 to about 0.26 inch per inch per minute at temperatures of about 1600° F. to 1800° F. This very fine structure may be achieved by any of the various methods above described. More preferably, the said mean free path between austenite particles does not exceed 8 microns in any direction. For example, ingots of the steel may be heated to temperatures as high as 2200° F. or higher prior to hot working, and hot working may be continued as long as the temperature of the piece undergoing working is within the temperature range down to 1700° F. or lower. If reheating of the partially hot-worked material is needed, the reheating temperature should preferably not exceed about 1800° F. or 1850° F., e.g., 1700° F., in order to facilitate production of the desired finely interspersed grain microstructure. If higher reheating temperatures are employed, the desired fine-grain structure is still obtained by repeating the working process as described hereinbefore. Even more preferably, from the standpoint of corrosion resistance, the desired treatment is one which produces a mean free path between adjacent austenite (or martensite) particles (i.e., the transverse ferrite mean free path) which does not exceed 6 microns or even 3 microns in the shortest direction. In general, the steels are processed to produce the finest possible structure having regard for variations in chemical composition, the amount of hot and/or cold reduction in processing, heating cycles, final section size, etc., in order to secure maximum benefits for the material in service in terms of strength, corrosion resistance, fatigue resistance, impact, etc.

Heating at temperatures exceeding approximately 1900° F. reduces the proportion of austenite in the structure. Exposure of the wrought structure to a temperature within the range of about 1400° F. to 1850° F. causes precipitation of, and an increase in the amount of, the austenite phase, and the finely interspersed structure thus achieved in accordance with the invention contains at least about 20% up to about 80% of austenite (or martensite) and the remainder essentially ferrite.

It is to be pointed out that the ferrite referred to herein is not the stress laden ferrite, i.e., martensite, such as that resulting from the transformation of austenite during cooling from elevated temperatures to room temperature, as is the case with the precipitation hardening grades of stainless steel. Phase equilibrium between austenite and ferrite in the special steel of the invention is established only sluggishly at temperatures below about 1850° F. and is affected by annealing temperature as well as time. A temperature of about 1500° F. or 1600° F. to 1850° F., e.g. about 1700° F., for annealing is generally satisfac-

tory. Annealing times may range between a few minutes and several hours, e.g., up to 4 hours, depending upon the prior thermal and cold working history of the metal being treated.

It is found that upon hot working no difficulties heretofore associated with prior duplex structured stainless steels are encountered. To the contrary, the special steel produced in accordance with the invention hot works readily at working pressures in rolling or extrusion comparable to those of the ferritic types of stainless steel, e.g., AISI Type 430. The alloys containing carbon and titanium in accordance with the present invention are immune to edge cracking, poor surface, and other defects associated with the hot rolling of difficultly-hot workable materials. The surface of plate and other hot rolled flat stock produced from the special steels is excellent. It is found further that hot rolled material produced from the special steel may be cold reduced as by rolling, drawing, etc., in drastic amounts without encountering the difficulties which are associated with the ferritic stainless steels, e.g., AISI Type 430. In cold working, reductions of up to 90% and even more can be applied to the steel without the necessity for intermediate annealing. The material work hardens during cold reduction as by rolling or drawing but is still readily cold workable at a hardness level as high as 35 Rockwell "C." A combination of heating and hot working, cold reduction and further heating and hot working, with said heating and hot working being conducted in the two-phase region, can be employed to provide even more finely interspersed microstructures in the material, i.e., an interparticle spacing between adjacent austenite particles not exceeding 3 microns.

Many of the special steels provided in accordance with the invention are resistant to cracking in a boiling 42% water solution of magnesium chloride. The latter test is exceptionally severe and present standard austenitic stainless steels do not withstand this test. The special material is also resistant to stress corrosion cracking in a 20% sodium chloride solution at 82° C. Resistance to corrosion, including stress corrosion cracking, in such a variety of media as found in the said special steels containing at least 23% chromium was unexpected since it had been previous experience with prior stainless steels that each type would be resistant to the corrosive effects of certain media but would be susceptible to attack in other media.

The special new two-phase stainless steels containing at least about 23% chromium having the specially dispersed ferrite-austenite microstructure have unexpectedly high fatigue and tensile properties combined with unusually high corrosion resistance. Because of their ease of fabrication and relatively low alloy cost, they are relatively cheap. They are useful for the following applications, among others: (a) structural stainless steels at the 80,000 to 100,000 p.s.i. strength level; (b) marine cable at the 300,000 p.s.i. strength level; and (c) rotating and flexural applications requiring high fatigue strength.

The following examples further typify the special steels of the invention with respect to processing procedures, fabrication characteristics, effects on properties of variations in heat treatment, compositions, fabricated forms and corrosion resistance.

EXAMPLE I

Processed material from Alloys Nos. 2, 4, 5 and 11, which were vacuum-melted alloys, was subjected to stress corrosion testing in two different media, namely, a water solution containing, by weight, 0.5% acetic acid, 3.5% sodium chloride, saturated with H₂S at 30° C. and a water solution containing 42% by weight of magnesium chloride at the boiling temperature for the solution. The corrosion test was conducted by bending specimens about 1/8" x 1/2" x 6" long machined from plate hot rolled from 1700° F. and having a ground surface around a mandrel having a

diameter of 1.5 inch into a U having equal and parallel sides. Tension above the yield strength was applied to the U by securing the ends thereof together.

In the condition resulting from hot rolling from 1700° F., no cracking was observed in the boiling magnesium chloride test during the thirty day period or in the hydrogen sulfide medium for 45 days. Alloys Nos. 1 and 2 also resisted cracking upon partial immersion in a solution containing 20% by weight sodium chloride at 82° C. for the 28 day test period. Standard Type 304 stainless steel fails in this test in a few days.

EXAMPLE II

Material from Alloy No. 27, which was an air-melted alloy, was converted into plate one inch thick by hot rolling from 2200° F. at which temperature a substantial amount of austenite was present in the structure of the alloy. Pieces of the one inch plate were hot rolled to 3/8" plate in a single pass after heating individually to temperatures of 2200° F., 1900° F. and 1700° F. Portions of each of these hot rolled plates were annealed at 1700° F. for one hour. Specimens of various plates were subjected to room temperature tensile tests, Charpy V-notch tests, R. R. Moore fatigue tests and the magnesium chloride stress-corrosion test with the results shown in Tables VII and VIII.

TABLE VII

Rolling temperature, ° F.	Y.S. 0.2% offset, k.s.i.	T.S., k.s.i.	Elongation, percent	R.A., percent	CVN, ft.-lbs.	Fatigue limit 10 ⁸ cycles, k.s.i.
2,200° L-----	52.7	89.7	48	67	31	57.5
2,200° T-----	57.5	93.6	40	61	51.7	53.8
1,900° L-----	69.6	97.8	36.0	65.5	51.2	-----
1,900° T-----	75.8	105.9	36	53.5	45.0	-----
1,700° L-----	58.5	92.3	51	66	63.3	-----
1,700° T-----	63.1	95.8	41	60.5	60.7	57.0
1,700° L-----	73.6	100.6	39.0	61.0	55.3	-----
1,700° T-----	79.3	104.6	38.0	56.5	42.5	68
1,700° L-----	54.8	91.2	45.0	69.0	71	-----
1,700° T-----	61.0	97.0	40.0	61.0	65.5	58.2

¹ Annealed at 1,700° F.

NOTE.—L=longitudinal specimens; T=transverse specimens.

The transverse mean free paths between adjacent austenite particles as measured perpendicular to the plate surface, the corrosion results in the boiling magnesium chloride stress-corrosion test and the austenite contents are set forth in the following Table VIII.

TABLE VIII

Condition	Transverse ferrite mean free path, microns	Percent Austenite	MgCl ₂ stress corrosion
Rollled 2,200° F.	25.35	31.6	-----
Rollled 2,200° F. plus 1 hour anneal	-----	-----	-----
1,700° F.	6.70	57.5	Failed.
Rollled 1,900° F.	6.04	61.6	Do.
Rollled 1,900° F. plus 1 hour anneal	-----	-----	-----
1,700° F.	4.05	66.8	Passed.
Rollled 1,700° F.	5.10	59.2	Do.
Rollled 1,700° F. plus 1 hour anneal	-----	-----	-----
1,700° F.	5.25	56.4	Do.

Alloy 27 material heated at 2300° F. and quenched contained only about 10% austenite, a more suitable situation for the production of a fine structure. Wrought material from Alloys Nos. 1 and 2 as hot rolled, cold rolled and further hot rolled from 1700° F. and having microstructures of the type depicted in FIG. 1b resisted crevice corrosion in aqueous ferric chloride (10% by weight) at room temperature for 72 hours at a level ten times superior to specimens of Type 316 stainless steel.

EXAMPLE III

In order to demonstrate the hot rolling properties of steels within the invention, material from Alloys Nos. 15 to 19, 23 and 24 were subjected to hot rolling tests comprising working ingots about 4" x 4" in cross-section

by heating the ingots to 2200° F. and rolling to plate approximately one inch thick. The one inch hot rolled plates were then reheated to 1700° F. and hot rolled in a single pass to plate ½" thick. In a first group of heats, four alloys of comparable composition but containing, respectively, 0.084% carbon with less than 0.01% titanium (Alloy A), 0.14% carbon with less than 0.01% titanium (Alloy B), 0.046% carbon with less than 0.01% titanium (Alloy AA), and 0.056% carbon and 0.04% titanium (Alloy BB) were included. In a second group of heats, material from a comparable heat containing 0.078% carbon and 0.65% titanium (Alloy C) was also included. The resulting ½" plate stock was thereafter annealed for one hour at 1700° F. and Charpy V-notch impact specimens were machined therefrom in the transverse direction. The results of the observations of hot rolling and of the Charpy V-notch impact testing are set forth in the following Table IX. During the single pass rolling from 1700° F., observations of the rolling mill load were made and the results of these observations are also set forth in Table IX. The results of tensile tests conducted upon the annealed plate material are set forth in Table X.

TABLE IX

Alloy Number	Hot rolling observation	Charpy V-notch, ft.-lbs.	Rolling load, pounds per inch width
Group I:			
15.....	OK.....	170	98.8
16.....	OK.....	139.5	98.8
AA.....	Edge cracking at 2,200° F.....	73.2	101.2
A.....	Severe edge cracking at 2,200° F.....	62.2	105.9
B.....	Very severe edge cracking at 2,200° F.....	43.2	117.6
BB.....	Edge cracking at 2,200° F.....	72.2	103.5
17.....	OK.....	57.0	101.2
Group II:			
18.....	OK.....	65.7	117.6
19.....	OK.....	48.3	115.3
23.....	OK.....	57.0	124.7
24.....	OK.....	43.0	117.6
C.....	OK.....	21.3	108.2

TABLE X

Alloy Number:	Yield strength 0.2% offset, k.s.i.	Ultimate tensile strength, k.s.i.	Elongation, percent	Reduction in area, percent
Group I:				
15.....	65.9	94.5	35	71.5
16.....	66.2	93.5	32	74.0
AA.....	66.9	94.2	33	64.0
A.....	64.4	95.5	34	60.5
B.....	66.9	98.8	35	58.5
BB.....	64.5	94.8	33	63.5
17.....	68.0	96.6	32	59.0
Group II:				
18.....	67.4	96.4	30	55.0
19.....	67.7	96.4	31	68.0
23.....	65.7	97.4	33	59.0
24.....	69.5	98.6	29	57.0
C.....	73.7	97.0	27	58.0

The data set forth in Table IX demonstrate that carbon exceeding about 0.03% must be controlled, preferably by means of titanium, in order to avoid hot rolling difficulties in flat-rolled products. A similar situation is found when vanadium, or less preferably, columbium, is employed to control carbon. It is to be noted in this connection that in instances wherein edge cracking is encountered poor surface of the hot rolled plate is a concomitant factor. The data also demonstrate that the low-carbon, titanium-free Alloys Nos. 15 and 16 had surprisingly improved impact resistance as compared to titanium-free Alloy AA at 0.046% carbon. It is further to be noted by comparing the Charpy V-notch impact testing results for Alloys Nos. 18, 19, 23, 24 and Alloy C that increasing titanium reduces impact resistance. With relation to Table IX, it was found that the hot working results were such that the thickness of material designated as Group I in Tables IX and X was slightly greater

at the 2200° F. hot rolled stage than that of the group of alloys identified as Group II therein. Consequently, valid comparisons could only be made within each of the groupings, since the Group II material was subjected to greater reduction during rolling from 1700° F. The data in Table IX also demonstrate that high Charpy V-notch impact values are obtained as a result of the 1700° F. anneal.

EXAMPLE IV

Material from Alloys Nos. 28 through 31, all of which were air-melted alloys of increasing nickel content from about 7% to about 10% were converted to plate about ⅝" thick wherein as the last operation the plate was heated to 1700° F. and hot rolled from 1" to ⅝" thick in a single pass. Transverse tensile data and Charpy V-notch impact data were obtained upon the plate in the condition resulting from annealing for one hour at 1700° F. The data are set forth in the following Table XI.

TABLE XI

Alloy No.:	Y.S. 0.2% offset, k.s.i.	T.S., k.s.i.	El., per cent	Reduction in area, percent	Charpy V-notch, ft.-lbs.
28.....	74.9	105.8	34	64.5	56
29.....	60.5	99.2	38	67.5	72.8
30.....	57.6	99.6	38	68.0	77.3
31.....	47	96.2	40	68.5	83.5

The data demonstrate that as the nickel content is increased from about 7% to about 10% the strength decreases and the toughness as indicated by the Charpy V-notch impact value increases. The proportion of austenite in the structure increased with nickel content and all of the alloys were magnetic.

EXAMPLE V

Specimens from Alloys Nos. 13 and 27 in the condition resulting from hot rolling from 2200° F. and either annealed at 1700° F. or again rolled from 1700° F. were subjected to a welding test comprising fusion welding of plate stock using the same alloy as filler wire in a covered electrode, by a gas-tungsten arc welding technique and by a gas metal-arc technique. Fatigue, impact and tensile tests on and visual inspection of the welded specimens, showed them to be characterized by weld soundness and to be satisfactory in all of these respects.

In order further to demonstrate the importance of controlling the composition of the special steels provided in accordance with the invention in the manner set forth hereinbefore, a number of other compositions were prepared by vacuum melting and the chemical compositions thereof are set forth in the following Table XII.

TABLE XII

Alloy No.:	Percent				
	C	Cr	Ni	Ti	Al
A.....	0.084	25.7	6.1	<0.01	0.055
B.....	0.14	25.7	6.0	<0.01	0.036
C.....	0.078	25.6	5.8	0.65	0.035
D.....	0.008	18	2	0.6	0.041
E.....	0.010	18	3	0.6	0.034
F.....	0.014	18	4	0.6	0.036
G.....	0.016	18	5	0.6	0.05
H.....	0.018	19.5	3.6	0.6	0.03
I.....	0.016	20.6	4	0.58	0.03
J.....	0.030	21	4.4	0.62	0.03
K.....	0.019	22.6	4.8	0.6	0.03
L.....	0.007	25	4	0.6	0.03
M.....	0.12	25	6	0.68	0.03
AA.....	0.046	25.7	6.0	<0.01	0.034
BB.....	0.056	25.5	6.1	0.04	0.037

The foregoing alloys were hot rolled to plate ⅝" thick employing the procedure described in Example IV. Charpy V-notch specimens and tensile specimens were prepared from the as-rolled plate and the data set forth in the following Table XIII were obtained thereon.

TABLE XIII

Alloy Number:	Y.S. 0.2% offset, k.s.i.	T.S., k.s.i.	El., percent	R.A., percent	CVN, foot-pounds	
					Longi- tudinal specimen	Trans- verse specimen
A-----	64	96	34	60	-----	62.2
B-----	67	99	35	58	-----	43.2
C-----	74	98	27	58	-----	21.3
D-----	58	69	33	74	7	8
E-----	65	76	30	73	11	13
F-----	88	102	22	70	11	15
H-----	-----	-----	-----	-----	-----	15
I-----	-----	-----	-----	-----	-----	13
J-----	-----	-----	-----	-----	-----	17
K-----	-----	-----	-----	-----	-----	18
L-----	81	86	16	37	16	24

Material from Alloys D, E, F and L was drawn to wire 0.020" and 0.010" in diameter in the same manner as that described in conjunction with Table VI hereinbefore. Tensile results on these wires were as follows:

TABLE XIV

Alloy Number:	Tensile strength, k.s.i.= 0.020" diameter	Tensile strength k.s.i.= 0.010" diameter
D-----	154	202
E-----	226	267
F-----	226	299
L-----	189	261

It will be noted that all of the specimens described in Table XIII exhibited a low impact with the exception of Alloys A and B. However, the latter alloys had poor hot working properties as is set forth in Table IX. Alloys H, I and K failed in 40 hours when subjected to stress corrosion in a water solution containing 0.5% acetic acid and 3.5% sodium chloride saturated with hydrogen sulfide at 30° C., whereas alloys within the special advantageous compositional aspect of the invention survived this corrosion test for the entire test period of 45 days. Alloys J and L failed in 4 hours in boiling magnesium chloride. Whereas Alloy K, containing 22% chromium and 4.8% nickel, had a low impact value of 17.8 foot-pounds (C.V.N.), Alloy No. 25 containing 23% chromium and 5.2% nickel had an impact value of 34.8 foot-pounds. Again, Alloy No. 26 containing 24% chromium and 5.6% nickel had an impact value of 49 foot-pounds. All of the aforementioned Alloys H, I, K, 25 and 26 were processed together and were tested in the form of 5/8" plate in the as-rolled condition. Furthermore, Alloy No. 26 resisted the stress corrosion test in aqueous acetic acid-sodium chloride solution saturated with hydrogen sulfide. It is accordingly to be seen that special alloy compositions described hereinbefore provide an improvement in impact of at least about 100% and are also characterized by a marked improvement in corrosion resistance as compared to similar alloys of lower chromium and nickel contents. Alloy M, containing 0.12% carbon and outside the invention, was subjected to the corrosion tests in boiling magnesium chloride and in the hydrogen sulfide solution as described hereinbefore. This alloy, which contained 0.12% carbon and 0.68% titanium, cracked in two hours in the magnesium chloride test and in 17 hours in the hydrogen sulfide test. The wholly inadequate corrosion behavior of this alloy provides fur-

ther experimental verification of the need to control the carbon and titanium contents of alloys within the special range of compositions of the invention as described hereinbefore. While Alloys D through L set forth in Table XII do not respond to the special compositional requirements of the invention with respect to chromium and nickel as set forth hereinbefore, they, nevertheless, respond to the special processing as also set forth hereinbefore and demonstrate the surprising high temperature plasticity when processed to provide the special grain structure as described hereinbefore.

EXAMPLE VI

In order further to investigate the effects of compositional variations upon the properties of the special steels within the invention, a further series of vacuum-melted heats was produced wherein the levels of carbon, nickel, chromium, manganese, silicon, phosphorus and sulfur were varied. The compositions of 17 alloys produced are set forth in Table XV.

TABLE XV

Alloy Number:	Percent						
	C	Mn	Si	Ni	Cr	Ti	P
36-----	0.044	0.13	0.19	5.9	24.8	0.57	-----
37-----	0.048	0.13	0.19	6.9	25.4	0.59	-----
38-----	0.049	0.34	0.47	6.0	25.3	0.62	-----
39-----	0.043	0.33	0.48	6.9	25.4	0.61	-----
40-----	0.039	0.14	0.19	5.9	25.6	0.17	-----
41-----	0.043	0.14	0.17	7.0	25.3	0.15	-----
42-----	0.048	0.33	0.48	6.0	25.7	0.15	-----
43-----	0.043	0.34	0.47	7.0	25.5	0.16	-----
44-----	0.022	0.29	0.41	6.40	25.0	0.30	-----
45-----	0.020	0.30	0.40	7.20	25.2	0.30	-----
46-----	0.020	0.30	0.42	6.20	25.95	0.29	-----
47-----	0.023	0.30	0.40	7.15	26.03	0.29	-----
48-----	0.021	0.30	0.44	6.20	25.3	0.28	0.006
49-----	0.021	0.29	0.42	6.20	25.2	0.30	0.011
50-----	0.022	0.30	0.40	6.20	25.4	0.29	0.0078
51-----	0.022	0.30	0.45	6.10	25.3	0.29	0.011
52-----	0.025	0.30	0.48	6.10	25.3	0.29	0.006 0.0095

In instances wherein phosphorus and sulfur levels are not reported in Table XV, these elements were very low, i.e., at levels of about 0.001% phosphorus and 0.002% to 0.003% sulfur. In Table XV, the balance of the composition is essentially iron. The nitrogen content of these heats did not exceed about 0.005%.

The ingots were heated to 2200° F., soaked for one hour and rolled to one inch thick plate. The plates were reheated to 1700° F. and rolled in one pass to 5/8" thickness. No hot working difficulties were encountered. Test blanks were cut from each of the plates in the transverse direction and were annealed for one hour at 1700° F.

followed by air cooling. Standard room temperature tensile bars, Charpy V-notch impact specimens and R. R. Moore rotating beam fatigue specimens were then prepared from the annealed blanks and were subjected to testing with the results shown in the following Table XVI.

TABLE XVI

Alloy No.:	Y.S. 0.2% offset, k.s.i.	T.S., k.s.i.	El., percent	R.A., percent	CVN, ft.-lbs.	10 ⁷ cycle fatigue stress, k.s.i.	Volume percent austenite
36.....	73.3	96.2	28.0	65.0	49.2	62.53	44
37.....	67.7	96.8	34.0	67.0	60.2	60.5	48
38.....	74.8	97.2	30.0	65.5	35.8	58.32	40
39.....	73.3	99.4	31.0	66.0	71.2	64.61	44
40.....	69.5	98.0	38.0	66.0	64.8	66.15	49
41.....	67.5	99.0	35.0	71.0	71.3	64.35	55
42.....	72.2	100.2	32.0	60.5	53.3	62.625	38
43.....	65.5	99.6	37.0	67.5	65.2	64.74	53
44.....	71.6	96.8	33.0	72.5	51.7	62.92	40
45.....	59.5	96.6	39.0	70.5	90.7	60.375	45
46.....	74.3	98.2	26.0	67.5	47.7	58.92	31
47.....	70.8	99.2	32.0	69.5	72.2	59.52	53
48.....	69.5	96.8	31.0	67.0	52.5	63.92	-----
49.....	72.3	98.2	28.0	66.0	64.3	61.375	-----
50.....	69.9	97.2	35.0	71.5	65.8	60.75	-----
51.....	71.7	98.4	31.0	68.0	56.2	59.04	-----
52.....	70.5	97.2	31.0	76.0	46.0	63.18	-----

Comparison of the results obtained on Alloys Nos. 36 to 39 with the results obtained on Alloys Nos. 40 to 43 indicated that the higher titanium content of the former group tended to reduce impact and increase yield strength and that this effect of titanium was countered by increasing the nickel. Comparison of the properties obtained on Alloys Nos. 44 to 47 indicated that higher yield strengths and lower impact values were obtained at higher chromium and lower nickel contents. When the yield strength values for Alloys Nos. 36 through 47 are plotted against the austenite contents (in volume percent) found therein a definite band relating yield strength to austenite content was obtained. The band was about 7 k.s.i. wide in yield strength and about 17 volume percent wide in austenite content. Only the result obtained for Alloy No. 45 was found to be inconsistent with the plot in terms of yield strength. Inspection of the microstructure of the Alloy No. 45 specimen showed that the austenite content thereof was present as elongated stringers similar to that shown in FIG. 2a herein. This structure indicated that, during the 2200° F. heating prior to ingot breakdown, an insufficient amount of austenite was dissolved. Micrographic examination of the other alloys in the group of Alloys Nos. 36 through 47 demonstrated that the specimens of Alloys Nos. 36 to 39, 44 and 46 contained precipitated austenite and that the specimens of Alloys Nos. 40 to 43 and 47 contained combinations of undissolved and precipitated austenite. The structures of these alloys were materially finer than was that of Alloy No. 45. FIG. 2c herein was taken from the Alloy No. 43 specimen and is illustrative of this microstructural type. The investigation demonstrated further the importance, from the property standpoint, of dissolving all or substantially all of the austenite at initial hot working temperatures so as to secure as fine a duplex microstructure as possible.

The properties obtained on Alloys Nos. 48 to 52 demonstrated that the variations in sulfur and phosphorus investigated therein did not detrimentally affect the properties obtained.

A review of data set forth in this Example and elsewhere herein indicates that satisfactory steels can be produced when made to the following nominal specification: about 6.5% nickel, about 26% chromium, about 0.05% or 0.06% carbon (max.), about 0.5% silicon (max.), about 0.5% manganese (max.), about 0.025% phosphorus (max.), about 0.025% sulfur (max.), about 0.2% to about 0.35%, e.g., 0.3%, titanium, with the balance essentially iron,

EXAMPLE VII

In order to demonstrate the properties of special steels in accordance with the invention when produced on a larger scale, two 1200 pound air melts were produced in an induction furnace and were cast into 12" x 12" ingots.

The compositions of these melts are set forth in the following Table XVII.

TABLE XVII

Alloy No.	Percent								
	C	Mn	Si	Cr	Ni	Ti	Al	P	S
53.....	0.022	0.48	0.65	25.5	6.05	0.23	0.012	0.014	0.003
54.....	0.022	0.33	0.58	26.9	6.1	0.24	0.017	0.011	0.012

The balance of the composition in each case was iron. Alloy No. 53 contained 73 parts per million (p.p.m.) oxygen, 2.5 p.p.m. hydrogen, and 125 p.p.m. nitrogen while Alloy No. 54 contained 198 p.p.m. oxygen, 4.4 p.p.m. hydrogen, and 189 p.p.m. nitrogen.

The ingots were forged to 6" x 6" section, with the Alloy No. 53 material being heated to 2150° F. and the Alloy No. 54 material being heated to 2300° F. prior to forging. A portion of the Alloy No. 53 material was reheated to 2300° F. and hot rolled to 4" x 1" section. The material was then reheated to 1700° F. and rolled to 4" x 5/8". After an anneal at 1700° F. for one hour, the 5/8" thick material had a yield strength (0.2% offset) when tested in the direction transverse to the rolling direction of 69.5 k.s.i., a tensile strength of 100.2 k.s.i., an elongation of 32%, and a reduction in area of 68%. The material had a room temperature Charpy V-notch value of 67 foot-pounds and a fatigue strength (10⁷ cycles) of 61.2 k.s.i. Identical material was annealed at 2250° F. for 1/2 hour and water quenched, a treatment which produced a coarse grained, all-ferrite structure having a tensile strength of 90.5 k.s.i. This material had a rotating beam fatigue strength between 40 and 45 k.s.i., a value less than one-half the ultimate strength.

Strip material was produced by hot rolling to 5/8" thickness, annealing for one hour at 1700° F., followed by air cooling. This material was cold worked 80%. A portion was reannealed in the same manner and was then subjected to various amounts of cold work (from 10% to 40% reduction in thickness) and the cold worked

strip products were subjected to various heat treatment as set forth in the following Table XVIII.

TABLE XVIII

Cold reduction	Con- dition	Y.S. 0.2% offset, k.s.i.	T.S., k.s.i.	Elongation, percent
Percent:				
10-----	A	97.8	110.6	15.0
	B	67.2	97.1	31.0
	C	68.5	97.1	34.0
	D	103.4	134.7	24.0
	E	136.0	152.7	16.0
20-----	A	119.9	130.1	11.0
	B	64.6	95.1	36.0
	C	63.6	93.9	35.0
	D	95.9	134.7	25.0
	E	160.3	170.4	13.0
40-----	A	135.9	144.4	7.0
	B	65.2	94.7	35.0
	C	63.2	92.2	33.0
	D	101.3	134.2	25.0
	E	181.6	189.8	10.0
80-----	A	158.9	177.7	6.0
	B	66.3	97.4	36.0
	C	68.0	95.8	35.0
	D	94.9	134.6	24.0
	E	207.3	221.9	4.0

NOTE.—
A=as rolled.
B=annealed 1,600° F., one hour, air cooled.
C=annealed 1,700° F., one hour, air cooled.
D=annealed 1,700° F., one hour, air cooled, aged 16 hours 900° F.
E=aged 16 hours 900° F.

Hot rolled 5/8" diameter bar material from Alloy No. 54 had a room temperature Charpy V-notch impact of 240 foot-pounds after a 1700° F. anneal and, in the same condition, had a Charp V-notch impact of 155 foot-pounds at minum 106° F.

Forged material from Alloy No. 54 was reheated to 1700° F. and hot rolled to 4" x 1" section. The material was again reheated to 1700° F. and hot rolled to 5/8" thick plate and to 0.3" strip. The properties of the plate and strip material are set forth in the following Table XIX after anneals as indicated therein.

TABLE XIX

Annealing temper- ature, ° F.	Y.S. 0.2% offset, k.s.i.	T.S., k.s.i.	El., percent	R.A., percent	Room temper- ature CVN, ft.-lbs.
5/8" plate:					
1,500 ¹ -----	75.3	100.4	30.0	63.0	65.7
1,700 ¹ -----	73.8	99.2	30.0	63.0	66.3
1,800 ¹ -----	69.6	96.8	29.0	58.0	59.7
1,900 ¹ -----	72.0	95.0	29.0	62.0	51.3
0.3" strip:					
1,500 ¹ -----	81.5	108.5	33.0	63.0	-----
1,500 ² -----	73.8	100.5	35.0	64.0	-----
1,700 ¹ -----	75.4	103.2	35.0	58.0	-----
1,700 ² -----	70.7	97.9	36.0	60.0	-----

¹ Air cooled.
² Water quenched.

The material in the 5/8" plate form was found to have an austenite interparticle spacing of 10.4 microns while the 0.3" strip material had an austenite interparticle spacing of 6.85 microns. The structure of the 0.3" strip material taken at 750 diameter is shown in FIG. 2d herein. The austenite is in the precipitated form. The 5/8" plate material had a rotating beam fatigue strength (10⁷ cycles) of 62.75 k.s.i. when annealed at 1500° F. and air cooled.

EXAMPLE VIII

A 300 pound air induction melt was made of an alloy (Alloy No. 55) containing about 0.017% carbon, 0.6% manganese, 0.58% silicon, 6.7% nickel, 26.2% chromium, 0.03% titanium, 0.014% aluminum, 0.01% phosphorus, 0.009% sulfur, about 0.039% nitrogen, balance iron, and cast into a 6" x 6" ingot. The ingot was soaked for two hours at 2300° F. and hot rolled to a 4" x 1 1/2" slab. The slab was then reheated to 1700° F. and hot rolled to 5/8" thick plate. Test coupons were cut from the plate in the

direction transverse to rolling and were annealed for one hour at temperatures from 1500° F. to 1800° F. followed by air cooling or water quenching. Standard tensile and Charpy V-notch impact specimens were prepared from the annealed blanks and the test results obtained thereon are set forth in the following Table XX.

TABLE XX

	Annealing Temperature, ° F.	Y.S. 0.2% off- set, k.s.i.	T.S., k.s.i.	El., percent	R.A., percent	CVN, ft.-lbs.	
						Room Temper- ature	Minus 106° F.
10	1,500 ¹ -----	76.7	107.3	29.0	53.0	43.7	25.6
	1,500 ² -----	75.7	104.2	31.0	62.0	55.3	43.0
15	1,600 ¹ -----	67.6	103.0	31.0	55.5	59.0	38.3
	1,600 ² -----	65.4	97.0	36.0	68.0	70.6	62.0
	1,700 ¹ -----	66.2	100.8	34.0	59.5	74.6	48.7
	1,700 ² -----	64.0	94.7	34.0	65.5	70.0	64.3
	1,800 ¹ -----	67.0	100.0	31.0	65.0	72.3	39.7
	1,800 ² -----	63.5	93.5	33.0	61.0	80.5	60.3

¹ Air Cooled.
² Water quenched.

The results demonstrated further that excellent results are obtained in steels having low levels of carbon and titanium, and that water quenching improved toughness markedly while lowering strength only slightly.

EXAMPLE IX

A 300 pound air induction melt made of an alloy (Alloy No. 56) containing about 0.02% carbon, about 0.54% manganese, about 0.53% silicon, about 26.5% chromium, about 6.7% nickel, about 0.23% titanium, about 0.02% aluminum, about 0.009% phosphorus, about 0.012% sulfur, about 0.0445% nitrogen and the balance essentially iron was produced and cast into 6" x 6" ingots. An ingot was soaked at 230° F. for two hours and hot rolled to 6" x 2" section. The material was reheated to 1700° F. and hot rolled to 6" x 5/8" section, was again reheated to 1700° F. and hot rolled to 6" x 1/8" strip. In the 1700° F. annealed condition, the strip had a 0.2% offset yield strength of 70.7 k.s.i., a tensile strength of 104.7 k.s.i., and an elongation of 30%.

Duplicate U-bend samples of the 1700° F. annealed strip material having a ground surface were subjected to corrosion in various media along with similar material from Alloy No. 54 with the results set forth in the following Table XXI.

TABLE XXI

Test solution and concentration	Tempera- ture, ° C.	Cracking time— days	
		Alloy No. 56	Alloy No. 54
42% MgCl ₂ -----	Boiling	7, 11	1, 1
36% CaCl ₂ -----	Boiling	OK	OK
NaCl vapor, over 3% NaCl solution-----	95	OK	OK
3% NaCl-----	95	OK	OK
NaCl vapor, over 28% NaCl solution-----	95	OK	OK
28% NaCl-----	95	OK	OK

Note: "OK" means no cracks in 30 day duration of test.

The resistance of the alloys to sodium chloride corrosion was marked, since standard Type 304 is susceptible in this medium, particularly when subjected to vapor phase corrosion.

As noted hereinbefore, the special steels provided in accordance with the invention are extremely easy to hot work. However, when copper is included in the steels, attention must be given to the manganese and silicon contents and these contents should not exceed about 0.3% and about 0.4%, when copper is included in amounts of about 2%. Thus, a 32 pound vacuum-melted ingot made of an alloy containing about 0.005% carbon, about 25% chromium, about 5.5% nickel, about 2.1% molybdenum, about 3% copper, about 0.89% manganese, about 0.9% silicon and the balance essentially iron, cracked badly

upon hot rolling to plate form from 2200° F. A similar ingot made of an alloy containing about 0.3% manganese and about 0.4% silicon exhibited less cracking on hot rolling to plate but still some edge cracking in the same experiment. However, a similar ingot made of another alloy containing 2% copper and the lower amounts of manganese and silicon was successfully hot rolled to plate.

The special stainless steels provided in accordance with the invention make available to the art a series of new materials having outstanding hot workability, cold workability, strength, corrosion resistance in a wide variety of media, fatigue resistance and toughness. Because of the good workability both hot and cold which are provided in the material, it can be produced in all of the common mill forms, including tubing, sheet, strip, plate, rod, bar, wire, extruded shapes, etc. No complicated and expensive heat treating cycles are required to provide desired mechanical properties and the material does not undergo any unfavorable changes in properties as a result of being subjected to usual mill processing cycles. The highly favorable combinations of properties and relatively low cost afforded by the material render it highly useful in structural applications such as covered hopper cars, petroleum tankers, cargo containers, chemical equipment, van trailers, light poles, highway bridges, load bearing members in buildings, mullions, railway cars and engines, sour oil well equipment including tubing and fish lines therefor, wire rope for use in sea water, welding wire for the production of welds and overlays, etc.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A wrought stainless steel having an ultra fine grained microstructure comprising ferrite and a phase from the group consisting of austenite and martensite with the transverse mean free path between particles of the said phase consisting of austenite and martensite in the shortest direction not exceeding eight microns and said steel consisting essentially of about 18% to about 35% chromium, about 2% to about 12% nickel, not more than 0.08% carbon, up to about 1.5% of an element from the group consisting of up to about 1.5% titanium and up to about 1% vanadium, provided that when carbon exceeds 0.03%, the amount from said group is at least about four times the carbon content in excess of 0.03%, up to about 1% manganese, up to about 1% silicon, up to about 3% molybdenum, up to about 2.5% copper, with the contents of chromium and any molybdenum in percent being not in excess of 3.5 times the percentage of nickel plus 11% but being at least equal to 1.17 times the percentage of nickel plus 13.3%, and the content of manganese and silicon not exceeding 0.3% and 0.4%, respectively, when copper is at least 2%, and with the balance essentially iron said steel having at a temperature of about 1700° F. to about 1800° F. a short-time tensile elongation of at least about 150%.

2. A steel according to claim 1 containing not more than about 0.05% carbon, at least about 23% chromium and at least about 4.5% nickel.

3. A steel according to claim 1 containing not more than about 0.03% carbon.

4. A steel according to claim 1 having a transverse ferrite mean free path not exceeding about 6 microns.

5. A steel according to claim 1 wherein the element from said group is titanium.

6. A steel according to claim 1 wherein the element from said group is vanadium.

7. A steel according to claim 2 containing about 5.2% to about 8% nickel.

8. A wrought stainless steel having in the annealed condition an ultra fine grained microstructure comprising ferrite and stable austenite with a transverse mean free path between adjacent austenite particles in at least one direction not exceeding about 8 microns, said steel consisting essentially of about 23% to about 35% chromium, about 5.2% to about 12% nickel, up to about 1.5% titanium, not more than about 0.08% carbon, the carbon percentage being related to the titanium percentage such that when carbon exceeds 0.03%, titanium is available in amounts at least 4 times the carbon content in excess of 0.03% but such that titanium does not exceed about 0.3% when carbon is as high as 0.08%, up to about 1% manganese, up to about 1% silicon, up to about 2% cobalt, up to about 3% molybdenum, up to about 2.5% copper, with the contents of chromium and any molybdenum in percent being not in excess of 3.5 times the percentage of nickel plus 11% but being at least equal to 1.17 times the percentage of nickel plus 13.3%, with the contents of manganese and silicon not exceeding 0.3% and 0.4%, respectively, when copper is at least 2%, and with the balance being essentially iron, said steel having at a temperature of about 1700° F. to 1800° F. a short-time tensile elongation of at least 150%, and having in the annealed condition tensile and 0.2% offset yield strengths of at least 100,000 and 60,000 pounds per square inch, respectively, a tensile elongation of at least 25% and a Charpy V-notch impact value of at least 35 foot-pounds.

9. A steel according to claim 8 containing not more than about 0.05% carbon.

10. A steel according to claim 8 containing not more than about 0.03% carbon.

11. A steel according to claim 8 having a transverse ferrite mean free path not exceeding about 6 microns.

12. A steel according to claim 8 having a transverse ferrite mean free path not exceeding about 3 microns.

13. A steel according to claim 8 containing at least about 24% but not more than about 28% chromium.

14. A steel according to claim 13 containing about 5.2% to about 8% nickel.

15. A wrought stainless steel having an ultra fine grained microstructure comprising ferrite and a phase from the group consisting of austenite and martensite with the transverse mean free path between particles of the said phase consisting of austenite and martensite in the shortest direction not exceeding eight microns and said steel consisting essentially of about 18% to about 35% chromium, about 2% to about 12% nickel, up to about 1.5% titanium, not more than 0.08% carbon provided that when carbon exceeds 0.03%, titanium is present in amounts at least 4 times the carbon content in excess of 0.03%, up to about 1% manganese, up to about 1% silicon, up to about 3% molybdenum, up to about 2.5% copper, with the contents of chromium and any molybdenum in percent being not in excess of 3.5 times the percentage of nickel plus 11% but being at least equal to 1.17 times the percentage of nickel plus 13.3%, and the content of manganese and silicon not exceeding 0.3% and 0.4%, respectively, when copper is at least 2%, and with the balance essentially iron, said steel having at a temperature of about 1700° F. to 1800° F. a short-time tensile elongation of at least about 150%.

16. A steel according to claim 15 containing not more than about 0.05% carbon, at least about 23% chromium, and at least about 4.5% nickel.

17. A steel according to claim 15 containing not more than about 0.03% carbon.

18. A steel according to claim 15 having a transverse ferrite mean free path not exceeding about 6 microns.

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19. A steel according to claim 15 having a transverse ferrite mean free path not exceeding about 3 microns.

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5 HYLAND BIZOT, Primary Examiner

U.S. Cl. X.R.

75—128

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,574,002

Dated April 6, 1971

Inventor(s) H.W. Hayden, Jr., R.C. Gibson and J.H. Brophy

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 3, line 29, for "there in" read --therein--.

Col. 5, line 21, for "temperautre" read --temperature--.

Line 47, after "ing" insert --in--.

Col. 6, Table I, under "Alloy No." for "28", first occurrence, read --27--.

Col. 7, Table II, for the last Alloy No. under "Prior Condition", for "do" read --as hot worked from 1700°F.--.

Line 59, for "prefered" read --preferred--.

Col. 9, Table III, for Alloy No. 1, first occurrence, and "Processing", before "80%" insert --plus--.

Col. 12, line 22, for "preferable" read --preferably--.

Col. 21, line 33, for "minum" read --minus--.

Col. 22, Table XX, under "T.S., ksi", second number, for "104.2" read --104.3--.

Line 31, for "siilcon" read --silicon--.

Signed and sealed this 25th day of January 1972.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents