Oct. 27, 1964 A. KASAK ETAL 3,154,412

HEAT-RESISTANT HIGH-STRENGTH STAINLESS STEEL

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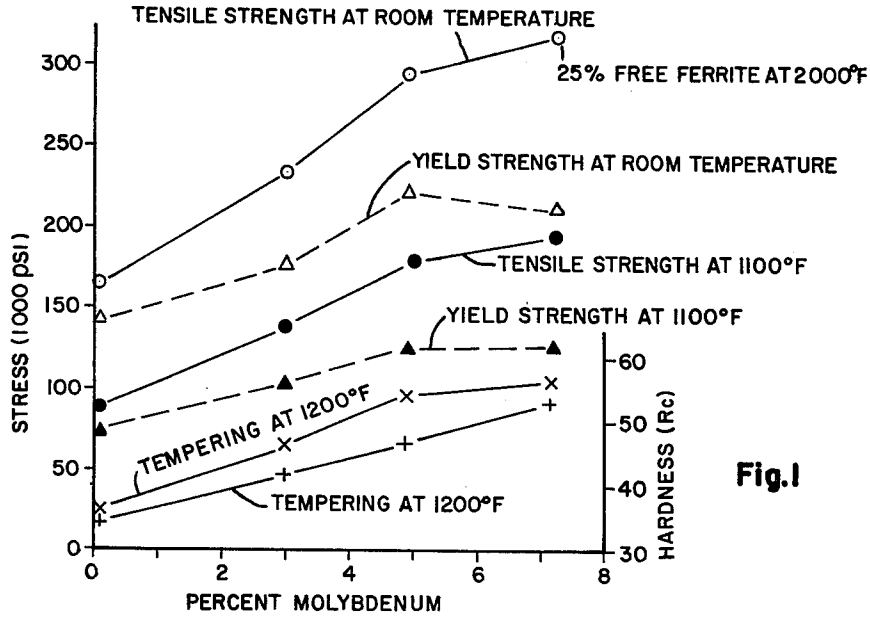


Fig.1

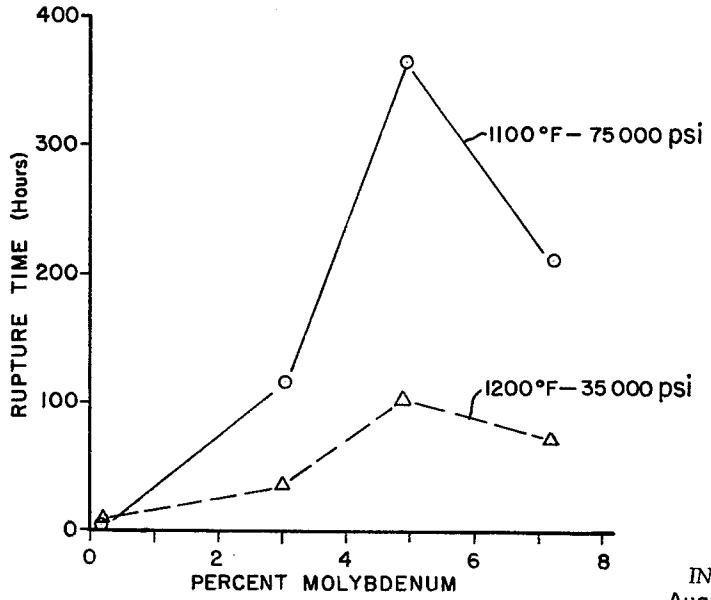
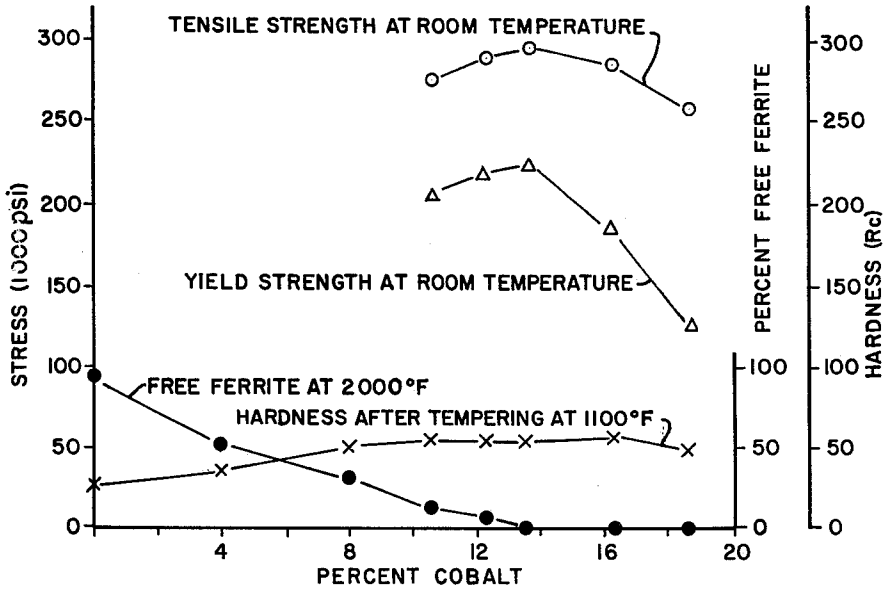


Fig.2

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Fig.3


TENSILE STRENGTH AT ROOM TEMPERATURE
YIELD STRENGTH AT ROOM TEMPERATURE
FREE FERRITE AT 2000°F
HARDNESS AFTER TEMPERING AT 1100°F
STRESS (1000psi)
PERCENT FREE FERRITE
HARDNESS (Rc)
300
250
200
150
100
50
0
4
8
12
16
20
PERCENT COBALT

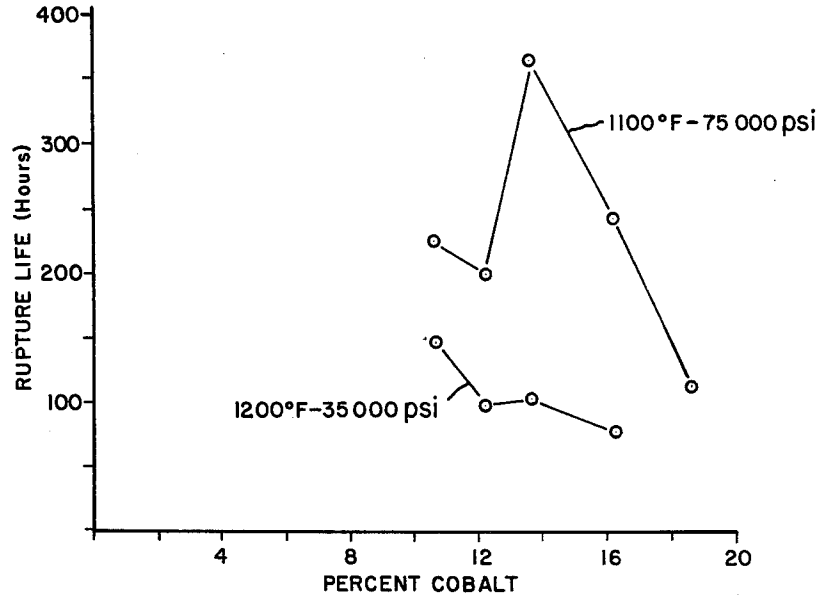

1100°F-75 000 psi
1200°F-35 000 psi
RUPTURE LIFE (Hours)
400
300
200
100
4
8
12
16
20
PERCENT COBALT

Fig.4

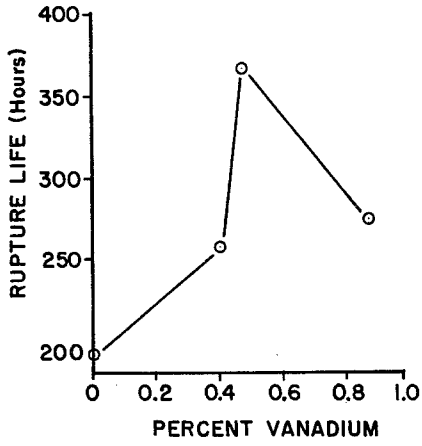

400
350
300
250
200
RUPTURE LIFE (Hours)
0
0.2
0.4
0.6
0.8
1.0
PERCENT VANADIUM

Fig.5

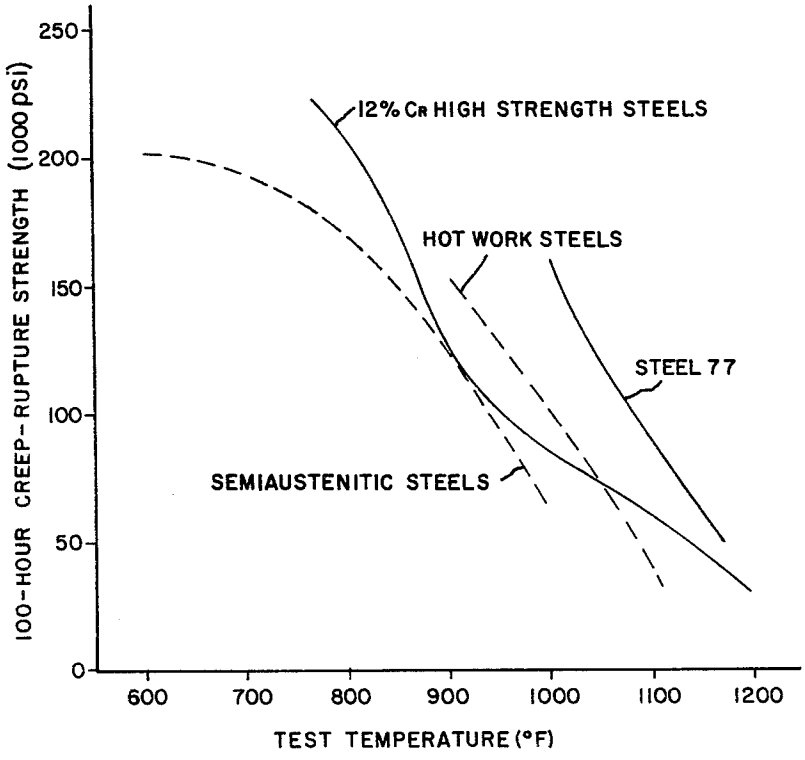
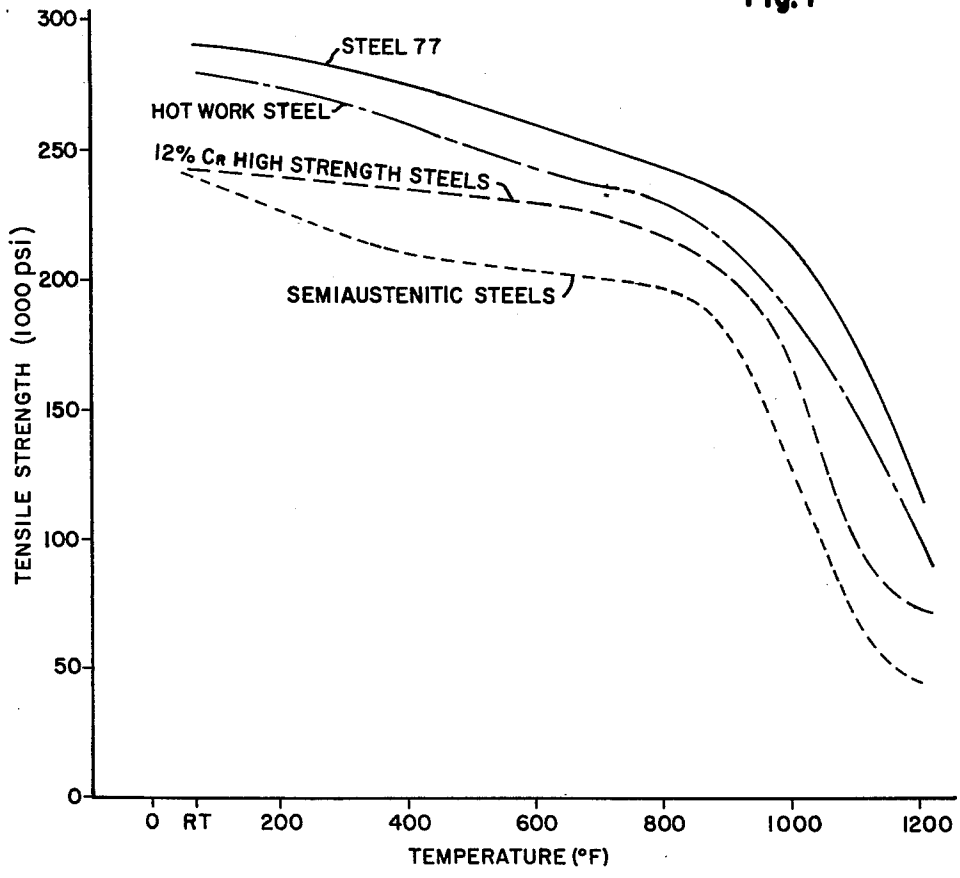

250
200
150
100
50
0
100-HOUR CREEP-RUPTURE STRENGTH (1000 PSI)
12% Cr HIGH STRENGTH STEELS
HOT WORK STEELS
STEEL 77
SEMIAUSTENITIC STEELS
600
700
800
900
1000
1100
1200
TEST TEMPERATURE (°F)

Fig.6

HEAT-RESISTANT HIGH-STRENGTH STAINLESS STEEL

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Fig. 7



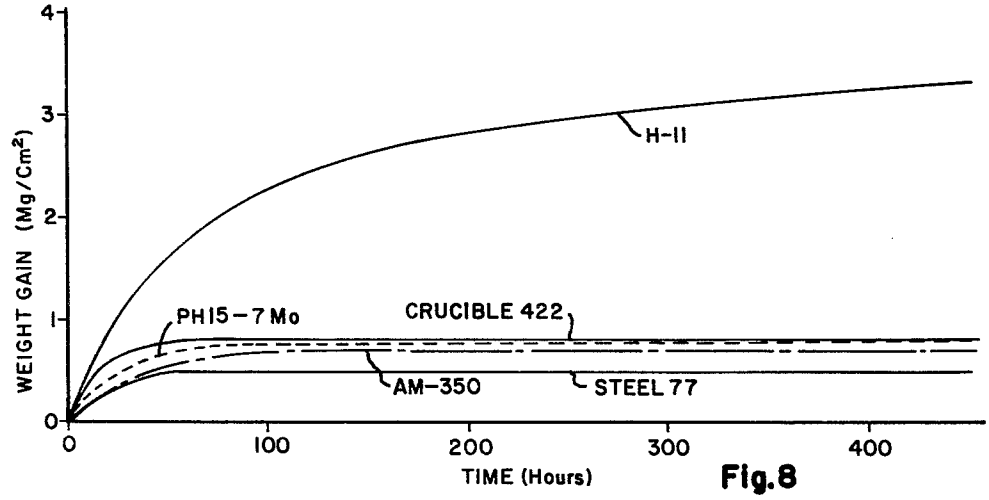


Fig. 8

United States Patent Office 3,154,412 Patented Oct. 27, 1964

3,154,412 HEAT-RESISTANT HIGH-STRENGTH STAINLESS STEEL

August Kasak, Bridgeville, and Edward J. Dulis and Vijay K. Chandhok, Pittsburgh, Pa., assignors to Crucible Steel Company of America, Pittsburgh, Pa., a corporation of New Jersey

Filed Oct. 5, 1961, Ser. No. 143,157
9 Claims. (Cl. 75—126)

This invention pertains to stainless steel and particularly to stainless steel exhibiting very high strength at room and elevated temperatures. More particularly, the invention pertains to stainless steel having very high strength and exhibiting good oxidation and corrosion resistance under substantially atmospheric conditions at both ambient and elevated temperatures.

Concerning the various steels of the prior art, those known as austenitic stainless steels may be characterized as resistant to corrosion and oxidation and as having good strength at elevated tempertaures. A disadvantage of such steels, however, is their relatively low strength at ambient and moderately elevated temperatures. On the other hand, some steels of a heat-treatable nature and having a martensitic structure attain desired high strengths at ambient temperature which are retained at elevated temperatures. Exemplary of such steels are those covered by U.S. Patent No. 2,986,463, issued May 30, 1961, which was copending herewith. These steels, however, are not characterized by good resistance to corrosion and oxidation. Other martensitic steels having chromium contents of about 12% by weight have improved corrosion and oxidation resistance while similarly exhibiting relatively good strength at low temperatures and fairly high strength at elevated temperatures. The latter martensitic steels, however, are limited in chromium content to a maximum value of about 12%. Above this value, the microstructure of the steel is characterized by the presence of substantial amounts of free ferrite. Free ferrite in substantial amounts is undesirable, being generally regarded as the probable cause of many hot-working difficulties as well as excessive variations in product properties with regard to the direction of working.

Another group of heat-treatable stainless steels, the so-called semiaustenitic steels, have chromium contents up to about 17%, but their applicability at temperatures above about 900° to 1000° F. is very limited. At such temperatures, particularly after prolonged exposure, these steels have relatively low strength values.

In accordance with a principal object of the present invention, steels are provided which are heat-treatable to very high strength levels and which retain an unusually high percentage of such strength at temperatures up to 1200° F. or higher. These steels offer particularly high strengths, in both short-time and prolonged exposures, at temperatures ranging from about 1000° to 1200° F. and

in addition exhibit high resistance to corrosion and oxidation. The inventive steels constitute a substantial improvement over the elevated-temperature structural materials known to the art and are particularly well suited for construction of aircraft and engine parts subjected to wide variations in operating temperatures.

The steels of the invention comprise iron-base alloys of the following broad composition ranges:

	Percent
Carbon	0.01 to 0.25
Nitrogen	0.01 to 0.25
Sum of carbon and nitrogen	0.06 to 0.35
Manganese	Up to 1.0
Silicon	Up to 1.0
Chromium	11 to 16
Vanadium	Up to 1.0
Molybdenum	Up to 10
Tungsten	Up to 10
Sum of molybdenum and tungsten	3.5 to 20
Cobalt	10 to 20
Aluminum	Up to 0.25
Boron	Up to 0.025

Preferred composition ranges of the inventive steels are as follows:

Carbon	0.05 to 0.17%	00.08 to 0.17%.
Nitrogen	0.01 to 0.07%	0.05 to 0.15%.
Sum of Carbon and Nitrogen	0.10 to 0.20%	0.20 to 0.30%.
Manganese	0.10 to 0.40%	0.10 to 0.40%.
Silicone	0.10 to 0.40%	0.10 to 0.40%.
Chromium	12.0 to 16.0%	12.0 to 16.0%.
Vanadium	Up to 1.0%	Up to 1.0%.
Molybdenum	4.0 to 6.0%	4.0 to 6.0%.
Tungsten	Up to 5.0%	Up to 5.0%.
Cobalt	12.0 to 15.0%	10.0 to 12.0%.

In addition to the elements listed in the above broad and preferred composition ranges, the steels may contain impurities commonly encountered in the steelmaking practice (such as sulfur and phosphorus) and "tramp" elements.

The steels of this invention are typified by Steels 77 and 107, the chemical compositions of which, together with those of a sizeable number of steels of similar compositions are given in Tables I–A and I–B. Table I–A lists these steels according to significant compositional variable, whereas Table I–B lists the same steels according to identification number. Microstructural characteristics of the steels as determined by microstructural examination and mechanical properties of the steels as determined by hardness, tension, and creep-rupture tests are set forth in Tables II through VI.

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TABLE I–A

Chemical Compositions of Steels Investigated [1]

Steel	C	Cr	V	Mo	Co	N	Al	Other
121	*0.014*	14.16	<.01	5.38	13.43	0.054	-------	
116	*0.023*	14.48	0.46	4.99	13.56	0.016	0.040	
115	*0.06*	14.48	0.48	4.96	13.56	0.016	0.050	
91	*0.08*	14.48	0.46	4.99	13.56	0.071	0.033	
92	*0.12*	14.40	0.41	4.99	13.45	0.028	0.046	
95	*0.15*	14.60	0.41	5.02	13.48	0.022	0.046	
77	*0.16*	14.36	0.48	4.90	13.60	0.05	0.042	
93	*0.21*	14.52	0.43	5.09	13.48	0.025	0.033	
94	*0.21*	14.58	0.46	5.02	13.45	0.018	0.046	
77	0.16	*14.36*	3.48	4.90	13.60	0.05	0.042	
97	0.145	*15.54*	0.41	4.99	13.41	0.03	0.033	
98	0.16	*16.20*	0.41	5.09	13.41	0.03	0.067	
99	0.16	14.36	*0.0*	5.15	13.45	0.028	0.067	
95	0.15	14.60	*0.41*	5.02	13.48	0.022	0.046	
77	0.16	14.36	*0.48*	4.90	13.60	0.05	0.042	
100	0.16	14.34	*0.87*	5.09	13.45	0.038	0.050	
103	0.16	14.36	*0.41*	*3.04*	13.64	0.026	0.025	
101	0.157	14.36	*0.97*	*3.01*	13.33	0.025	0.054	
102	0.146	13.72	0.41	*0.15*	13.11	0.025	0.084	
103	0.16	14.36	0.41	*3.04*	13.64	0.026	0.025	
77	0.16	14.36	0.48	*4.90*	13.60	0.05	0.042	
104	0.166	14.24	0.41	*7.15*	13.60	0.026	0.042	
111	0.17	13.98	0.46	5.09	*0.02*	0.057	0.037	
112	0.155	14.04	0.43	4.96	*3.98*	0.032	0.084	
113	0.15	14.04	0.43	4.99	*8.03*	0.03	0.084	
76	0.155	14.26	0.46	4.93	*10.55*	0.03	0.042	
106	0.154	14.36	0.41	5.09	*12.23*	0.03	0.042	
77	0.16	14.36	0.48	4.90	*13.60*	0.05	0.042	
78	0.155	13.56	0.40	4.70	*16.20*	0.04	0.042	
67	0.15	14.02	0.38	4.83	*18.70*	0.02	0.046	
115	0.06	14.48	0.48	4.96	13.56	*0.016*	0.050	
91	0.08	14.48	0.46	4.99	13.56	*0.07*	0.033	
96	0.07	14.48	0.46	5.06	13.49	*0.15*	0.046	
107	0.164	14.40	0.41	5.28	*11.74*	*0.13*	*0.14*	
89	0.17	14.48	0.41	5.22	*11.41*	*0.12*	*0.13*	
77	0.16	14.36	0.48	4.90	13.60	0.05	0.042	0 W.
75	0.177	13.44	0.46	*3.01*	*19.46*	0.04	0.042	*2.35 W.*
122	0.162	14.50	0.52	*0.04*	13.21	0.04	-------	*5.11 W.*
105	0.154	14.26	0.41	5.09	13.64	0.033	0.025	*0.007 B.*
118	0.15	14.56	0.48	5.34	*0.02*	0.023	-------	*3.32 Ni.*
120	0.144	13.80	0.43	5.25	*0.02*	0.022	-------	*7.52 Ni.*
114	0.167	14.46	0.46	5.09	*0.04*	0.037	0.084	*10.14 Ni.*
108	0.164	14.46	0.41	5.12	13.41	0.026	0.046	*0.36 Mn.*
109	0.161	14.50	0.41	5.09	13.41	0.024	0.037	*0.67 Si.*
110	0.16	14.64	0.43	5.12	13.41	0.037	0.037	*0.51 Mn. 0.79 Si.*

[1] Grouped according to significant compositional variable; the significant compositional variable or variables are italicized.

TABLE I–B

Chemical Compositions of Steels Investigated [1]

Steel	C	Cr	V	Mo	Co	N	Al	Other
67	0.15	14.02	0.38	4.83	*18.70*	0.02	0.046	
75	0.177	13.44	0.46	*3.01*	*19.46*	0.04	0.042	*2.35 W.*
76	0.155	14.26	0.46	4.93	*10.55*	0.03	0.042	
77	*0.16*	*14.36*	*0.48*	*4.90*	*16.60*	0.05	0.042	
78	0.155	13.56	0.40	4.70	*16.20*	0.04	0.042	
89	0.17	14.48	0.41	5.22	*11.41*	*0.12*	*0.13*	
91	*0.08*	14.48	0.46	4.99	13.56	0.071	0.033	
92	*0.12*	14.40	0.41	4.99	13.45	0.028	0.046	
93	*0.21*	14.52	0.43	5.09	13.48	0.025	0.033	
94	*0.21*	14.58	0.46	5.02	13.45	0.018	0.046	
95	*0.15*	14.60	*0.41*	5.02	13.48	0.022	0.046	
96	0.07	14.48	0.46	5.06	13.49	*0.15*	0.046	
97	0.145	*15.54*	0.41	4.99	13.41	0.03	0.033	
98	0.16	*16.20*	0.41	5.09	13.41	0.03	0.067	
99	0.16	14.36	*0.0*	5.15	13.45	0.028	0.067	
100	0.16	14.34	*0.87*	5.09	13.45	0.038	0.050	
101	0.157	14.36	*0.97*	*3.01*	13.33	0.025	0.054	
102	0.146	13.72	0.41	*0.15*	13.11	0.025	0.084	
103	0.16	14.36	*0.41*	*3.04*	13.64	0.026	0.025	
104	0.166	14.24	0.41	*7.15*	13.60	0.026	0.042	
105	0.154	14.26	0.41	5.09	13.64	0.033	0.025	*0.007 B.*
106	0.154	14.36	0.41	5.09	*12.23*	0.03	0.042	
107	0.164	14.40	0.41	5.28	*11.74*	*0.13*	*0.042*	
108	0.164	14.46	0.41	5.12	13.41	0.026	0.046	*0.36 Mn.*
109	0.161	14.50	0.41	5.09	13.41	0.024	0.037	*0.67 Si.*
110	0.16	14.64	0.43	5.12	13.41	0.037	0.037	*0.51 Mn. 0.79 Si.*
111	0.17	13.98	0.46	5.09	*0.02*	0.057	0.037	
112	0.155	14.04	0.43	4.96	*3.98*	0.032	0.084	
113	0.15	14.04	0.43	4.99	*8.03*	0.03	0.084	
114	0.167	14.46	0.46	5.09	*0.04*	0.037	0.084	*10.14 Ni.*
115	*0.06*	14.48	0.48	4.96	13.56	*0.016*	0.050	
116	*0.023*	14.48	0.46	4.99	13.56	0.016	0.040	
118	0.15	14.56	0.48	5.34	*0.02*	0.023	-------	*3.32 Ni.*
120	0.144	13.80	0.43	5.25	*0.02*	0.022	-------	*7.52 Ni.*
121	*0.014*	14.16	<.01	5.38	13.43	0.054	-------	
122	0.162	14.50	0.52	*0.04*	13.21	0.04	-------	*5.11 W.*

[1] Steels listed in numerical order.

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TABLE II

Results of Microstructural Examination and Hardness Tests [1]

Steel	Austenitized at 1,000° F.			Austenitized at 2,000° F.		
	Free Ferrite (percent)	Hardness (R_c) after Tempering 2+2 hr. at:		Free Ferrite (percent)	Hardness (R_c) after Tempering 2+2 hr. at:	
		1,100° F.	1,200° F.		1,100° F.	1,200° F.
67	0	48	48	0	48	48
75	0	52	49	0	49	50
76	5	51	44	10	52	46
77	0	53	47	0	54	47
78	0	54	49	0	55	49
89	0	54	50	1–5	56	53
91	<1	54	48	0–1	54	51
92	<1	53	47	0–1	53	49
93	0	53	47	0	55	50
94	0	53	47	0	56	51
95	0	53	47	1	54	50
96	0	54	50	0	54	52
97	0	52	49	5	53	49
98	10	52	48	30	41	41
99	0	53	48	0	54	50
100	<1	53	47	10	55	51
101	0	47	40	0	47	41
102	0	36	33	0	36	34
103	0	47	39	0	46	42
104	0	55	49	25	56	53
105	0	53	47	0	55	50
106	1	51	46	5	53	48
107	0	54	49	0	56	51
108	0	49	49	1–5	55	49
109	0	49	49	1	57	52
110	0	51	52	0	41	50
111	100	18	17	90	24	23
112	50	35	23	50	36	37
113	30	44	43	30	49	43
114	0	R_b, 87	R_b, 89	0	R_b, 84	R_b, 83
115	20	50	46	30	51	47
116	30	48	44	40	47	43
118	50	38	35	50	41	37
120	0	R_b, 92	R_b, 92	5	R_b, 87	R_b, 85
121	0	50	44	20	50	45
122	0	49	45	0	50	46

[1] Heat treatment: Austenitized at the indicated temperature (1,900° or 2,000° F.), oil quenched, refrigerated at −100° F. for ½ hr., and tempered at 1,100° F. for 2+2 hr.

TABLE III

Results of Tension Tests at Room Temperature [1]

Steel	Austenitizing Temperature (° F.)	0.2% Offset Yield Strength (1,000 p.s.i.)	Tensile Strength (1,000 p.s.i.)	Elong. in 1 Inch (Percent)	Reduction of Area (Percent)
67	1,900	126	259	10	32
75	1,900	163	280	8	16
76	2,000	204	275	14	49
77	1,900	214	289	9	27
	2,000	222	294	14	36
78	2,000	185	283	12	39
89	2,000	223	310	10	38
91	1,900	188	292	12	35
	2,000	192	294	16	51
	2,100	191	292	12	34
92	2,000	192	288	16	49
93	2,000	229	305	6	12
94	2,000	222	306	12	33
95	2,000	204	308	12	46
96	2,000	169	295	4	5
97	1,900	186	285	9	32
	2,000	195	299	14	46
99	2,000	212	300	12	43
100	2,000	225	308	12	45
101	2,000	180	232	14	44
102	2,000	144	164	16	44
103	2,000	179	234	14	43
104	2,000	212	319	4	6
105	2,000	218	304	11	40
106	1,900	209	274	12	41
	2,000	218	289	13	49
107	2,000	239	312	10	38
108	2,000	196	296	12	44
109	2,000	205	309	4	6

[1] Heat treatment: Austenitized at the indicated temperature, oil quenched, refrigerated at −100° F. ½ hr., and tempered at 1,100° F. 2+2 hr.

TABLE IV

Results of Tension Tests at 1100° F.[1]

Steel	Austenitizing Temperature (° F.)	0.2% Offset Yield Strength (1,000 p.s.i.)	Tensile Strength (1,000 p.s.i.)	Elong. in 1 Inch (Percent)	Reduction of Area (Percent)
77	2,000	123	180	19	52
89	2,000	142	194	19	52
91	2,000	132	180	23	67
	2,100	120	177	19	59
92	2,000	132	176	23	66
93	2,000	120	185	16	51
94	2,000	122	186	18	53
95	2,000	117	186	24	66
96	2,000	121	182	12	41
97	2,000	120	176	17	63
99	2,000	127	182	18	42
100	2,000	140	191	19	61
101	2,000	106	140	20	68
102	2,000	73	89	25	71
103	2,000	103	139	26	69
104	2,000	125	194	14	43
105	2,000	139	189	16	46
106	1,900	124	163	16	57
	2,000	128	174	20	67
107	2,000	144	197	16	51
108	2,000	138	182	25	67
109	2,000	135	188	22	65
110	2,000	137	190	21	58

[1] Heat treatment: Austenitized at the indicated temperature, oil quenched, refrigerated at −100° F. ½ hr., and tempered at 1,100° F. 2+2 hr.

TABLE V

Results of Creep-Rupture Tests at 1100° F.[1]

Steel	Aust. Temp. (° F.)	Stress (p.s.i.)	Rupture		
			Life (hr.)	Elong. (percent)	Red. of Area (percent)
67	2,000	75,000	112	8	11
75	1,900	75,000	239	8	10
	2,000	[2] 75,000	365	5	9
76	2,000	75,000	224	17	51
	2,100	75,000	195	13	35
	1,900	75,000	221	13	31
	1,900	90,000	137	21	47
77	2,000	75,000	366	8	14
	2,000	90,000	194	13	15
	2,100	75,000	406	4	7
78	2,000	75,000	243	5	8
	2,100	75,000	259	3	8
89	2,000	75,000	620	9	9
	2,000	90,000	308	11	11
	1,900	75,000	296	13	16
91	2,000	75,000	369	7	12
	2,100	75,000	275	5	11
92	2,000	75,000	214	12	23
93	2,000	75,000	269	11	21
94	2,000	75,000	224	9	22
95	2,000	75,000	259	8	15
96	2,000	75,000	242	7	13
97	1,900	75,000	109	12	30
	2,000	75,000	254	11	20
99	2,000	75,000	189	11	27
100	2,000	75,000	274	13	26
101	2,000	75,000	75	19	55
102	2,000	75,000	0.1	21	61
103	2,000	75,000	115	21	49
104	2,000	75,000	212	13	30
105	2,000	75,000	276	5	8
106	1,900	75,000	185	20	55
107	2,000	75,000	694	8	14
109	2,000	75,000	257	11	28
110	2,000	75,000	338	11	17
122	2,000	75,000	782	5	7

[1] Heat treatment: Austenitized at the indicated temperature, oil quenched, refrigerated at −100° F. ½ hr., and tempered at 1,100° F. for 2+2 hr.

[2] Heat treatment: Austenitized at the indicated temperature, oil quenched, refrigerated at −100° F. ½ hr., and tempered at 1,100° F. for 2+2+2+2 hr.

TABLE VI

Results of Creep-Rupture Tests at 1200° F. Under a Stress of 35,000 p.s.i.[1]

Steel	Aust. Temp. ° F.	Rupture		
		Life (hr.)	Elong. (percent)	Red. of Area (percent)
75	2,000	96	13	13
76	2,000	148	16	26
77	2,000	103	18	17
78	2,000	76	16	24
89	2,000	94	11	11
91	1,900	63	32	50
	2,000	135	21	28
	2,100	109	25	33
92	2,000	65	27	27
93	2,000	63	17	22
94	2,000	66	51	47
95	2,000	75	16	19
96	2,000	69	9	9
97	1,900	21	29	54
	2,000	73	32	43
99	2,000	84	7	12
100	2,000	56	21	39
101	2,000	27	16	21
102	2,000	6	19	31
103	2,000	36	8	19
104	2,000	72	43	38
105	2,000	103	11	15
106	1,900	54	42	53
	2,000	98	13	28
107	2,000	146	16	17
108	2,000	76	22	24
109	2,000	82	27	38
110	2,000	101	25	33
122	2,000	175	11	13

[1] Heat treatment: Austenitized at the indicated temperature, oil quenched, refrigerated at −100° F. ½ hr., and tempered at 1100° F. for 2+2 hr.

Graphical illustrations of the foregoing, as well as graphical comparisons of the steel of the invention with prior-art steels, are depicted by the drawings, wherein:

FIG. 1 shows the effect of molybdenum on tensile properties and hardness;

FIG. 2 shows the effect of molybdenum on creep-rupture strength;

FIG. 3 shows the effect of cobalt on tensile properties, hardness and microstructure;

FIG. 4 shows the effect of cobalt on creep-rupture strength;

FIG. 5 shows the effect of vanadium on creep-rupture strength;

FIG. 6 shows the creep-rupture strength of various prior-art steels together with that of a steel typical of the invention;

FIG. 7 shows the tensile strength of various prior-art steels together with that of a steel typical of the invention;

FIG. 8 shows the oxidation resistance of various prior-art steels together with that of a steel typical of the invention.

As indicated by the test data set out in the aforementioned tables and drawings, steels within the invention are capable of exhibiting hardness of Rockwell "C" 48 or greater and tensile strength of 250,000 p.s.i. or greater at room temperature, tensile strength of 170,000 p.s.i. or greater at a temperature of 1100° F., creep-rupture life of 100 hours or more for an applied stress of 75,000 p.s.i. at a temperature of 1100° F., and creep-rupture life of 50 hours or more for an applied stress of 35,000 p.s.i. at a temperature of 1200° F. In addition to exhibiting superior strength properties the steels of the invention exhibit good ductility at both room and elevated temperatures and have excellent weldability.

In accordance with the basic concepts of the present invention, the foregoing superior mechanical properties are obtained only upon the achievement of a proper compositional balance and the application of a proper heat treatment. Such heat treatment may involve the steps of austenitizing at an elevated temperature, preferably in the range of 1900° to 2100° F., cooling to

room temperature, and heating at an elevated temperature below about 1500° F. Refrigeration at a subzero temperature, e.g., —100° F., is preferably included in the heat-treating schedule immediately following the austenitizing step for the purpose of facilitating the transformation of austenite. While the recited sequence of heat-treating steps has been found admirably suited for the contemplated purpose, it is well to note that other sequences of heat-treating steps, including conditioning treatments, may be employed, the principal criteria being the complete or substantially complete elimination of free ferrite at elevated temperatures and the complete or substantially complete elimination of austenite thereafter as well as the obtention of high strength.

It is also understood that a combination of thermal and mechanical treatments may result in further improvement of some of the important properties of the inventive steels. For example, when a sheet sample of Steel 77 was cold reduced 50% in thickness and subsequently heated at 1100° F. for two plus two hours, a tensile strength of 341,000 p.s.i. and an elongation of 6% were obtained at room temperature. In contrast, it will be noted from Table III that thermal treatment alone of Steel 77 resulted in a maximum tensile strength of only 294,000 p.s.i.

It is well known to the art that in order for a steel to exhibit satisfactory corrosion resistance at ambient temperature and satisfactory oxidation resistance at temperatures up to about 1200° F., the chromium content of such steel should be about 12% or more. In general, the higher the chromium content of the steel, the higher its corrosion and oxidation resistance. In view of these considerations, chromium has been included as an essential element in the steels of the invention, the minimum content thereof being set at 11%. As it is desirable to maintain the chromium content at the highest level compatible with desired microstructural characteristics, i.e., essential freedom from free ferrite and retained austenite, the maximum chromium content of the inventive steels has been set at about 16%. The latter figure finds support in the accompanying data wherein it is observed from Tables I–A and II that when the compositional variable is chromium, values of 14.36% (Steel 77) and 15.54% (Steel 97) result in a microstructure having no free ferrite after an austenitizing treatment at 1900° F., whereas, a value of 16.20% (Steel 98) results in a microstructure having 10% free ferrite after the same austenitizing treatment.

Molybdenum has been included in the steels of the invention as an effective strengthener. Supporting data therefor were obtained by testing steels of the basic inventive composition wherein the molybdenum content was varied (see Table I–A, Steels 102, 103, 77 and 104). As shown in FIGS. 1 and 2, all the important strength properties, i.e., yield and tensile strengths at room temperature and at 1100° F., hardness after tempering at 1100° F. and 1200° F., and rupture times in creep-rupture tests at 1100° F. and 1200° F., are steadily enhanced as the molybdenum content is increased from about 0.1 to about 5%. Tables III through VI indicate that for this same molybdenum range, ductility is maintained at a high level. Molybdenum contents in excess of about 5% have some additional strengthening effects in short-time tests; however, the tendency for formation of free ferrite at high temperatures is increased. Therefore, although molybdenum contents up to about 10% are included within the broad scope of the invention, a molybdenum content of about 4 to 6% is preferred for an optimum combination of properties. In addition to its strengthening role, molybdenum functions to increase significantly the corrosion resistance of the invention steels in such media as chloride solutions.

Tungsten is also an effective elevated-temperature strengthener in the inventive steels. For example, a steel containing 5.11% tungsten and only 0.04% molybdenum (Steel 122) exhibited a higher creep-rupture life (782 hours) than any other steel when tested at 1100° F. under a stress of 75,000 p.s.i. (see Table V). Similarly, when tested at 1200° F. under a stress of 35,000 p.s.i., this same steel again exhibited a higher creep-rupture life (175 hours) than any other steel tested (see Table VI).

In addition to the benefits derived from the individual uses of tungsten and molybdenum, test data show that a combination of these elements is an effective strengthening agent in the inventive steels. In support thereof, it will be noted that Steel 75, containing 3.01% molybdenum and 2.35% tungsten, exhibited a creep-rupture life of 365 hours when tested at 1100° F. under a stress of 75,000 p.s.i. (see Table V).

Cobalt has been incorporated as an essential ingredient in the inventive steels for the purpose of obtaining desired microstructural characteristics, a critical cobalt range of 10 to 20% having been determined therefor. In this regard, Table II strikingly reveals that cobalt values below about 10% (Steels 111, 112 and 113) result in the formation of excessive amounts of free ferrite, and that cobalt values above about 10% (Steels 76, 106, 77, 78 and 67) permit the complete or substantial elimination of free ferrite by proper compositional balance and/or heat-treatment selection. On the other hand, cobalt contents in excess of about 15% permit the retention of increasing amounts of austenite, the effect of which is to lower the room-temperature strength properties of the steels to some extent. This is graphically depicted in FIGS. 3 and 4, wherein it is observed that optimum strength values at both room temperature and 1100° F. are obtained in a cobalt range of about 13 to 15% and that said values fall off with increasing cobalt content until an extrapolated maximum of about 20% cobalt is reached, beyond which value strength properties become unsatisfactory.

In addition to the employment of a critical cobalt range, the invention contemplates as a preferred embodiment a proper balancing of the cobalt content within said range with the nitrogen content. This proper balancing, as evidenced by Steels 76, 106, 77, 78 and 67, involves the restriction of the cobalt content to values in excess of 12% where the steel is essentially nitrogen-free or low in nitrogen, i.e., less than about 0.1%. Where the nitrogen present amounts to about 0.10% or greater, the cobalt content may be lowered to the range 10 to 12%. It will be noted from Table II after an austenitizing treatment at 1900° F. that Steel 76, embraced within the broad concept of the invention, exhibits 5% free ferrite and that Steels 106, 77, 78 and 67, comprising preferred embodiments of the invention, exhibit not more than 1% free ferrite after the same austenitizing treatment.

As is known to the art, the alloying elements cobalt and nickel are interchangeable to some extent for the formation of an austenitic structure and for the elimination of free ferrite in steel. As increasing amounts of nickel up to 10.14% (Steels 118, 120 and 114) were used in the steels of this invention as a replacement for cobalt, it became evident that while nickel effectively caused the amount of free ferrite to decrease, it also stabilized the austenitic structure of the steel so that when the free ferrite was fully eliminated (as in Steel 114 containing 10.14% nickel), the steel was not hardenable and thus incapable of exhibiting very high strengths at ambient and moderately elevated temperatures. Therefore, it is recognized that although to some extent nickel may be substituted for cobalt in these steels, no complete or substantial replacement of cobalt with nickel is possible.

The elements carbon and nitrogen both constitute strong austenite formers and are essential in the steels of this invention for the elimination or minimization of free ferrite in the microstructure. Quantitatively, it appears that about 0.06 to 0.35% carbon plus nitrogen (combined) is required to avoid substantially the formation of free ferrite upon heat treatment at high temperatures.

However, it is important to select quantities within the foregoing range so as to maintain a proper compositional balance vis-à-vis ferrite formers, lest the ferritizing effect of the latter become dominant. For example, where the sum of carbon plus nitrogen is less than about 0.1% the presence of vanadium (a strong ferrite former) cannot be tolerated above about 0.1%. In this regard it will be noted that Steel 121 (containing 0.068% carbon plus nitrogen and no intentionally added vanadium) was heat-treatable to zero percent free ferrite, while Steel 115 and 116 (containing 0.076% carbon plus nitrogen and 0.039% carbon plus nitrogen, respectively as well as about one-half percent each of vanadium) were heat-treatable to no less than 20% and 30% free ferrite, respectively. On the other hand, it has been found that high carbon plus nitrogen contents have an adverse effect on ductility at high strength levels and promote the retention of austenite in the microstructure. Therefore, to ensure proper compositional balance, it is preferred in the steels of this invention to keep the carbon plus nitrogen content between about 0.10% and 0.20% when the content of cobalt (as indicated heretofore, also a strong austenite former) is about 12% or higher, and between about 0.20% to 0.30% when the content of cobalt is below about 12%.

Vanadium in amounts up to about 1.0% may be added to the steels of this invention to improve certain properties. As shown in FIG. 5, additions of vanadium to the steels of the invention increased rupture life at 1100° F., as determined by creep-rupture tests, the highest rupture life being obtained with a steel containing about 0.5% vanadium.

It is generally agreed that tungsten has alloying effects in steels quite similar to those of molybdenum except that the amounts (in weight percent) necessary to produce the effects with tungsten are about twice as great as those of molybdenum because of the substantial difference in the atomic weights of these two elements. In the steels of this invention we consider tungsten as at least a partial replacement for molybdenum.

For the purpose of comparing relative strength and corrosion properites, an investigation was undertaken along these lines with respect to the steels of the invention and prior-art steels of the semiaustenitic, the 12% chromium high-strength, and the chromium hot-work tool-steel types. The nominal compositions of representative examples of the latter steel types are set forth in Table VII.

TABLE VII

Nominal Compositions of Comparison Steels

Designation	C	Mn	Si	Cr	Ni	V	Mo	W	Al	N	Fe
Semiaustenitic Steels:											
AM 350 [1]	0.10	1.00	0.40	16.5	4.25	----	2.75	----	----	----	Bal.
AM 355 [1]	0.15	1.00	0.40	15.5	4.25	----	2.75	----	----	0.10	Bal.
17-7PH [2]	0.09	----	----	17.0	7.1	----	----	----	1.1	----	Bal.
PH15-7Mo [2]	0.09 max.	1.0 max.	1.0 max.	14.0–16.0	6.5–7.75	----	2.0–3.0	----	0.75–1.50	----	Bal.
12% Cr High-Strength Steels:											
Crucible 422 [5]	0.22	0.65	0.36	12.0	0.70	0.25	1.00	1.00	----	----	Bal.
Crucible 422M [5]	0.28	0.84	0.25	12.0	0.20	0.50	2.25	1.70	----	----	Bal.
Lapelloy [4]	0.30	1.0	0.25	12.0	0.30	0.25	2.75	----	----	----	Bal.
Hot-Work Steels:											
H-11 [3]	0.38–0.43	0.20–0.40	0.80–1.00	4.75–5.25	----	0.40–0.60	1.20–1.40	----	----	----	Bal.
Crucible 218 [5]	0.35	0.35	1.00	5.00	----	0.45	1.40	----	----	----	Bal.

[1] Grade of Allegheny-Ludlum Steel Co.
[2] Grade of Armco Steel Co.
[3] AISI Type.
[4] Grade of General Electric Co.
[5] Grade of Crucible Steel Co. of America.

Comparative data relating to creep-rupture strength and elevated-temperature tensile strength for the steels in Table VII, representative of the types recited therein, and a sample of Steel 77, representative of the steels of the invention, are given in Tables VIII and IX, respectively.

TABLE VIII

Comparison of Creep-Rupture Strengths

Steel	100-Hour Creep-Rupture Strength (1,000 p.s.i.)				
	800° F.	900° F.	1,000° F.	1,100° F.	1,200° F.
Semiaustenitic Steels:					
AM 350	164	107	63	----	----
17-7PH	110	78	----	----	----
PH15-7Mo	174	125	----	----	----
12% Cr High-Strength Steels					
Crucible 422	----	----	63	46	25
Crucible 422M	----	----	86	61	26
Lapelloy	----	----	----	50	28
Hot-Work Steel: Crucible 218	----	155	100	40	----
Steel of this Invention:					
Steel 77	----	----	160	90	35

TABLE IX

Comparison of Elevated-Temperature Tensile Strengths

Steel	Condition	R.T.	200° F.	300° F.	400° F.	500° F.	600° F.	700° F.	800° F.	900° F.	1,000° F.	1,100° F.	1,200° F.
Semiaustenitic Steels:													
AM-355	SCT [1]	222	----	208	208	----	208	----	197	180	----	----	----
AM-350	SCT	200	----	----	185	191	179	190	179	165	105	68	45
PH15-7Mo	RH950 [2]	238	227	----	211	----	203	----	182	161	130	----	----
12% Chromium High-Strength Steels:													
Crucible 422	Q & T [3]	243	----	----	----	----	230	----	216	----	169	----	57
Crucible 422M	Q & T	----	----	----	----	----	----	----	----	----	----	101	74
Hot-Work Steel: H-11	Q & T	280	----	----	260	----	243	----	230	----	185	150	100
Steel of the Invention: Steel 77	Q & T	290	286	----	----	----	259	----	----	233	214	176	121

[1] Subzero-cooled and tempered.
[2] Roll-hardened at room temperature and aged 950° F.
[3] Quenched and tempered.

Graphical depiction of the foregoing data is shown in FIGS. 6 and 7, wherein the superiority of the steels of the invention over the comparison steels of the prior art is clearly evident.

To assess the corrosion resistance of the steels of this invention, a heat-treated sample of Steel 77 was subjected to the water-vapor-column corrosion test and to the CASS test along with heat-treated samples of a number of the aforementioned prior-art comparison steels. These tests have been used for many years as laboratory tests to indicate the relative corrosion resistance of stainless steels under essentialy atmopheric conditions.

In the water-vapor-column test, the samples are exposed to water vapor condensation for a period of 8 hours and then allowed to dry for a period of 4 hours. This procedure is repeated several times. Results of this test after six wet-and-dry cycles showed the H–11 specimen to be covered with heavy rust, and the Crucible 422 steel to contain local rust spots, whereas it showed Steel 77 of this invention to be only slightly stained, as were the samples of AM 350 and PH15–7Mo.

In the so-called CASS test, the specimens are sprayed with an acidified aqueous solution of NaCl and $CuCl_2$ for 16 hours at 120° F. The samples are then cleaned with a detergent and the surface appearance is rated by visual examination. In this test the H–11 sample was severely attacked and Crucible 422 was seriously pitted; Steel 77 along with other stainless steels showed only slight pitting and all to about the same degree.

To determine the oxidation resistance, samples of Steel 77 were exposed to a static air atmosphere at 1200° F. and measurements of weight gain were made periodically; in this test, a higher rate of weight gain indicates a higher rate of deterioration (scaling) of the steel in air at the test temperature. The results of this test, given in FIG. 8, show clearly that Steel 77 of this invention exhibited a superior resistance to oxidation attack.

For the purpose of evaluating welding characteristics of steels of the invention, welding tests were conducted on sheet samples of Steel 77 using the semiautomatic inert-gas-shielded-tungsten-arc process. The tests involved tension testing of one-eighth inch thick specimens, both welded and unwelded. The average results of these tests are given in Table X.

TABLE X

Welding Test

Condition	0.2% Offset Yield Strength (p.s.i.)	Tensile Strength (p.s.i.)
Hot-rolled, 2,000° F. for 15 min., welded, —100° F. for ½ hr., 1,100° F. for 2+2 hours	218,000	285,000
Hot-rolled, 2,000° F. for 15 min., unwelded, —100° F. for ½ hour, 1,100° F. for 2+2 hours	219,000	290,000

These results indicate a weld efficiency (i.e., ratio of tensile strengths of the welded specimens to those of the unwelded specimens) of 98%. Also, it is important to note that no high-temperature heat treatment is needed after the welding operation. This feature is extremely important in fabrication, since it virtually precludes any difficulties resulting from scaling and warping of a formed and welded article.

While the invention has been described and disclosed in connection with specific embodiments thereof, it will be understood that the invention is not limited thereto but may be otherwise embodied or practiced within the scope of the appended claims.

We claim:

1. A stainless steel having enhanced strength and useful ductility over a temperature range from subzero to about 1200° F., consisting essentially, by weight percent, of:

Element:	Percent
Carbon+nitrogen	0.06 to 0.35.
Chromium	From 11 to 16.
Molybdenum+½ tungsten	From 3 to less than 7.
Nickel	Up to 3.
Vanadium	Up to 1.
Nickel+cobalt	10 to 20.
Manganese	Up to 1.
Silicon	Up to 1.
Aluminum	Up to 0.25.
Boron	Up to 0.025.
Iron	Balance.

wherein vanadium is present on the low side of its range when the sum of carbon+nitrogen is on the high side of the combined range of those elements.

2. A stainless steel having enhanced strength and useful ductility over a temperature range from subzero to about 1200° F., consisting essentially, by weight percent, of:

Element:	Percent
Carbon+nitrogen	0.10 to 0.30.
Chromium	12 to 16.
Molybdenum+½ tungsten	More than 3 to 6.
Nickel	Up to 3.
Nickel+cobalt	12 to 16.
Vanadium	Up to 0.5.
Manganese	Up to 1.
Silicon	Up to 1.
Aluminum	Up to 0.25.
Boron	Up to 0.025.
Iron	Balance.

where the sum of carbon+nitrogen is in the range of 0.10 to 0.20 when the sum of nickel+cobalt is at least 12% and is in the range of 0.20 to 0.30 when the sum of nickel+cobalt is less than 12%.

3. A stainless steel having enhanced strength and useful ductility over a temperature range from subzero to about 1200° F., consisting essentially, by weight percent, of:

Element:	Percent
Carbon	0.01 to 0.25.
Nitrogen	Less than 0.15.
Carbon+nitrogen	0.06 to 0.35.
Chromium	12 to 15.5.
Molybdenum+½ tungsten	4 to 6.
Cobalt	12 to 14.
Vanadium	Up to 0.5.
Manganese	Up to 0.4.
Silicon	Up to 0.4.
Aluminum	Up to 0.25.
Boron	Up to 0.025.
Iron	Balance.

4. A heat-treated stainless steel consisting essentially of the composition of claim 1, said steel being characterized by the following minimum mechanical properties:

Hardness	Rockwell "C" 48
Tensile strength (room temperature)	p.s.i. 250,000
Tensile strength (1100° F.)	p.s.i. 170,000

5. A heat-treated stainless steel consisting essentially of the composition of claim 2, said steel being characterized by the following minimum mechanical properties:

Hardness	Rockwell "C" 48
Tensile strength (room temperature)	p.s.i. 250,000
Tensile strength (1100° F.)	p.s.i. 170,000

6. A heat-treated stainless steel consisting essentially of the composition of claim 3, said steel being characterized by the following minimum mechanical properties:

Hardness	Rockwell "C" 48
Tensile strength (room temperature)	p.s.i. 250,000
Tensile strength (1100° F.)	p.s.i. 170,000

7. A heat-treated stainless steel as in claim 4, said steel being additionally characterized by the following minimum mechanical properties:

	Hrs.
Creep-rupture life (75,000 p.s.i. at 1100° F.)	100
Creep-rupture life (35,000 p.s.i. at 1200° F.)	50

8. A heat-treated stainless steel as in claim 5, said steel being additionally characterized by the following minimum mechanical properties:

	Hrs.
Creep-rupture life (75,000 p.s.i. at 1100° F.)	100
Creep-rupture life (35,000 p.s.i. at 1200° F.)	50

9. A heat-treated stainless steel as in claim 6, said steel being additionally characterized by the following minimum mechanical properties:

	Hrs.
Creep-rupture life (75,000 p.s.i. at 1100° F.)	100
Creep-rupture life (35,000 p.s.i. at 1200° F.)	50

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,154,412 October 27, 1964

August Kasak et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, TABLE I-A, under the heading "V", line 10, thereof, for "3.48" read -- 0.48 --; same column, same table, under the heading "Al", line 34 thereof, for "0.14", in italics, read -- 0.042 --, in italics; column 7, line 71, for "invention" read -- inventive --; column 9, line 10, for "Steel" read -- Steels --; column 11, line 12, for "essentialy atmopheric" read -- essentially atmospheric --.

Signed and sealed this 27th day of July 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents