AUSTENITIC C_r-M_n-C-N STEELS FOR ELEVATED TEMPERATURE SERVICE

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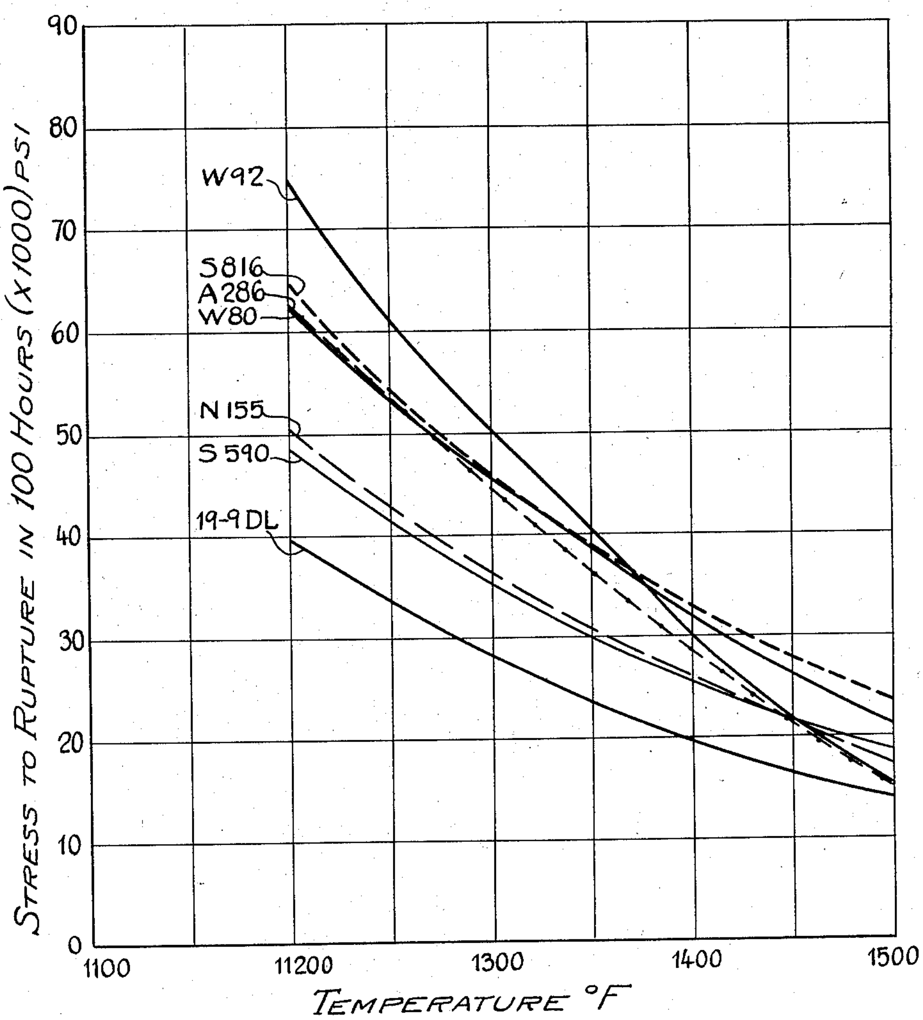

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AUSTENITIC Cr-Mn-C-N STEELS FOR ELEVATED TEMPERATURE SERVICE

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This invention pertains to austenitic steels for elevated temperature service and provides new and improved steels of this type which are characterized by exceptionally high strength at temperatures up to 1200–1500° F. or higher, and which require no additions of nickel or cobalt for imparting these properties, this in marked contrast to the conventional types of so-called "super alloys" in which these strategically critical elements are present in substantial or preponderant amounts.

The press toward ever higher supersonic speeds for planes, missiles and the like, and toward ever higher operating temperatures for jet and internal combustion engines, has confronted the industry with a continuous demand for new and better elevated temperature materials. The best of those developed to date require, as above stated, substantial or predominant amounts of nickel or cobalt or both, so much so that the majority cannot be classed as steels but rather as nickel and/or cobalt base alloys.

In contrast, the present invention provides a series of austenitic steels in which nickel and cobalt are present only in residual amounts and which contain as essential constituents in addition to iron, substantial amounts of manganese, chromium, carbon and nitrogen together with relatively small amounts of one or more of vanadium, tungsten, molybdenum and columbium, within critical ranges for each and in balanced proportions such as to impart to the steel a wholly austenitic structure and outstanding elevated temperature properties as discussed below.

Fully austenitic steels are desirable because of their superior hot working characteristics and superior elevated-temperature mechanical properties as compared to those steels containing delta ferrite at elevated temperatures. Although some martensitic steels are stronger than austenitic steels at temperatures below about 1150° F., the fully austenitic steels have superior strength characteristics above this temperature and the strength difference increases as the temperature increases. The compositions of the steels of this invention have been based on the ability of: (1) manganese to produce stabilized austenite; (2) chromium to impart oxidation resistance and stabilization of austenite; and (3) carbon and nitrogen to form austenite and to combine with the strengthening elements vanadium, tungsten, molybdenum and columbium to form the carbides and nitrides that increase the elevated-temperature strength.

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We have found that when the composition of steel containing about 0.1/0.8% C, 10/28% Mn, 12/28% Cr and 0.1/0.8% N, is balanced so that it is stably austenitic, as described in our copending application Serial No. 671,616, filed July 12, 1957, according to the formula percent (C+N) is equal to or greater than 0.078 (percent Cr—12.5), the strength of the steel at elevated temperatures generally increases as the sum of C+N increases, as shown in the following Table I.

TABLE I

Effect of C *plus* N *on stress rupture of stably austenitic* Mn—Cr *steels*

Steel	Composition Percent; Balance Fe					100 Hr. Rupture Stress (1,000 p.s.i.) at Indicated Temperatures (F.)			
	C	Mn	Cr	N	C+N	1,200	1,300	1,400	1,500
W88	.19	12.5	12.3	.28	.47	37	28	81	12
W76	.32	11.9	13.5	.30	.62	40	29	19	13
W82	.48	12.3	21.6	.54	1.02	52	37	21	12
W94	.64	12.4	24.4	.72	1.36	55.	35	17	11

NOTE.—All test pieces were solution treated at 2100° F. 30 min. except W94 which was treated at 2200° F. 30 min., and quenched.

However, when the testing temperature is above about 1200° F., steels that contain large amounts of nitrogen are subject to the formation of a lamellar microstructure (formed by a grain boundary reaction as discussed in a paper by C. M. Hsiao and E. J. Dulis, "Precipitation Reactions in Austenitic Cr—Mn—C—N Stainless Steels," Trans. ASM, vol. 49, 1957) that lowers the creep rupture strength of the steel.

Now we have found, and this is the crux of our present invention, that by adding one or more of the carbide forming elements V, W, Mo and Cb in proper proportions to the stably austenitic Cr—Mn—C—N steel aforesaid, we can appreciably enhance the strength of the steel, not only at 1200° F., but also at 1300° to 1500° F. Indeed, this enhanced strengthening is imparted to such a degree as to make the relatively low alloy, and nickel-and-cobalt-free steel of this invention comparable and even superior in stress rupture strength at 1200° to 1350° F. to the conventional types of super-alloys, high in nickel and cobalt content, as will be shown hereinafter. The increase in rupture strength at 1200° F. brought about by additions of one or more of the aforesaid carbide forming elements is shown in the following Table II.

TABLE II

Effects of additions of V, W, Mo, *and* Cb *on creep rupture strengths of stably austenitic* Cr—Mn—C—N *steels (all tests made at 1200° F. with stress of 65,000 p.s.i.)*

Steel	Composition Percent; Balance Fe									Hours to Rupture	Elong., Percent	R.A., Percent
	C	Mn	Cr	N	C+N	V	W	Mo	Cb			
W55	.40	12.5	18.4	.39	.79	------	------	------	------	2	19	23
W56	.41	11.7	18.7	.28	.69	1.2	------	------	------	24	5	4
W58	.38	11.8	18.3	.37	.75	------	6.0	------	------	48	13	13
W57	.41	12.0	18.2	.37	.78	------	------	3.1	------	55	15	20
W63	.43	12.4	17.1	.47	.90	------	------	------	2.5	3	13	18
W60	.40	12.4	18.6	.35	.75	0.5	3.2	------	------	10	6	8
W59	.43	12.6	17.9	.35	.78	0.6	------	1.5	------	11	6	9
W66	.43	12.5	16.6	.50	.93	0.5	------	------	1.3	18	6	9
W61	.39	12.3	18.2	.35	.74	------	3.1	1.5	------	30	11	14
W64	.43	12.2	17.2	.46	.89	------	3.2	------	1.4	50	9	13
W65	.44	12.1	16.8	.41	.85	------	------	1.5	1.4	29	9	12
W62	.37	12.5	17.4	.35	.72	0.6	2.2	1.1	------	10	6	11
W68	.42	12.1	16.9	.42	.84	0.3	2.1	------	0.9	30	9	9
W69	.40	12.5	17.1	.40	.80	0.4	------	1.0	0.9	20	9	13
W67	.41	12.1	16.6	.41	.82	------	2.1	1.0	0.9	18	10	13
W70	.40	12.4	16.9	.40	.80	0.2	1.4	0.7	0.6	24	10	10
W81	.54	13.2	19.7	.49	1.03	0.3	2.1	1.0	------	52	5	8
W80	.50	12.6	19.5	.46	.96	0.3	2.0	------	1.0	65	7	9
W79	.53	12.7	19.6	.49	1.02	0.4	------	1.0	1.1	69	7	10
W78	.50	12.5	19.6	.51	1.01	------	2.0	1.0	0.9	58	9	11
W77	.49	12.0	19.5	.50	.99	0.2	1.4	0.7	0.7	55	7	9
W93	.62	12.3	24.4	.70	1.32	0.4	2.1	1.0	------	98	5	6
W92	.62	12.3	24.5	.70	1.32	0.4	2.1	------	0.9	273	7	8
W91	.61	12.2	24.3	.68	1.29	0.4	------	1.0	0.9	183	9	6
W90	.62	12.5	24.4	.68	1.30	------	2.1	1.0	1.0	231	10	13
W89	.60	12.4	24.4	.71	1.31	0.4	1.5	0.7	0.7	118	8	6

NOTE.—All test pieces solution treated at 2100° F., 30 min. except those of W93, 92, 91, 90, and 89 which were treated at 2200° F., and quenched.

It is to be noted from the data in the above table, that the quantitative effects of the different carbide forming elements are different. This is to be expected since these various elements have different combining weights in forming compounds with carbon and nitrogen. It is also to be noted that although appreciable strength may be obtained with a rather large addition of one of these elements, as in steels W58 and W57, equally good and even better strength may be obtained by additions of smaller total amounts of two or more of these elements used at the same time, as in steels W77 to W81 and W89 to W93. In the latter steels the increases in Cr along with increases of C and N over the steels of the series W55 to W70 also contributed appreciably to the increase in strength. However, from the economic viewpoint, it is preferable to use Cr, C, and N rather than the more expensive elements V, W, Mo, and Cb. It is further to be noted that although Cb by itself, as in steel W63, appears to have little effect on the strength of the steel at 1200° F., nevertheless when it is present in conjunction with other carbide forming elements, it has an appreciable effect in raising the strength of the steel. This is particularly true in the series W89 to W93, in which steel W93 without Cb is appreciably inferior to the other four steels which contain Cb.

On the basis of these results and from the viewpoint of economy, we prefer to use small quantities of the carbide forming elements, that is, no more than 2.5% of each, and to use more than two of these elements at a time in the steel of this invention. We have found that when we use more than about 7% in total amount of the carbide forming elements V, W, Mo, and Cb in the Cr—Mn—C—N steel balanced so as to be stably austenitic, considerable difficulty is encountered in forging the steel. When the Cr is over about 26% in the properly balanced stably austenitic steel, the steel is also difficult to forge.

Additional data on creep rupture strength over the temperature range 1200° to 1500° F. for the steels of this invention are given in Table III below.

TABLE III

Stresses for rupture in 100 hours for 15–24% Cr *austenitic steels containing carbide forming, or strengthening, elements*

Steel No.	Nominal Base Comp. (Percent)	Strengthening Elements (Percent)				100-Hrs. Rupture Stress (1,000 p.s.i.) at Indicated Temperature (° F.)			
		V	W	Mo.	Cb	1,200°	1,300°	1,400°	1,500°
W71	.3 C, 12 Mn, 15 Cr, .4 N	.2	1.4	.7	.7	53	38	25	17
W75		.3	2	1	.9	55	42	27	17
W72		------	2	1	.9	51	38	24	15
W73		.3	------	1	1	51	38	25	17
W74		.4	2	------	.9	53	38	26	17
W75a		.4	2	1	------	51	39	26	17
W76		------	------	------	------	40	29	19	13
W70	.4 C, 12 Mn, 18 Cr, .4 N	.2	1.4	.7	.6	57	42	29	18
W56		1	------	------	------	56	41	26	17
W58		------	6	------	------	60	41	28	18
W57		------	------	3	------	60	40	28	18
W63		------	------	------	2.5	49	36	23	15
W60		.5	3	------	------	53	40	27	18
W59		.5	------	1.5	------	54	40	------	------
W66		.5	------	------	1.3	55	40	26	16
W61		------	3	1.5	------	58	41	29	18
W64		------	3	------	1.3	54	41	27	17
W65		------	------	1.5	1.3	56	40	27	18
W62		.6	2	1	------	54	41	29	18
W68		.3	2	------	.9	58	42	28	19
W69		.4	------	1	.9	56	42	28	18
W67		------	2	1	.9	56	42	29	19
W55		------	------	------	------	44	31	20	13
W77	.5 C, 12 Mn, 21 Cr, .5 N	.2	1.4	.7	.7	61	44	29	17
W78		------	2	1	.9	61	44	29	18
W79		.4	------	1	1	63	44	30	19
W80		.3	2	------	.9	63	46	31	21
W81		.3	2	1	------	60	42	26	15
W82		------	------	------	------	52	37	21	12
W89	.6 C, 12 Mn, 24 Cr, .7 N	.4	1.5	.7	.7	66	47	26	14
W90		------	2	1	1	73	49	27	16
W91		.4	------	1	.9	71	49	29	15
W92		.4	2	------	.9	75	50	30	17
W93		.4	2	1	------	65	44	24	14
W94		------	------	------	------	55	35	17	11

Complete analyses of the above steels are given in Tables I and II, supra, except for steels W71–W76, inc., the compositions of which are given in the following Table IV.

TABLE IV

Compositions of steels W71–W76, inc.

Steel	Composition Percent; Balance Fe								
	C	Mn	Cr	N	C+N	V	W	Mo	Cb
W71	.28	11.9	14.0	.28	.56	.20	1.4	0.7	0.7
W75	.32	11.9	13.6	.33	.65	.28	1.9	1.0	0.9
W72	.31	11.8	13.7	.29	.60	------	1.9	1.0	0.9
W73	.33	13.9	13.9	.31	.64	.28	------	1.0	1.1
W74	.30	12.4	15.4	.35	.65	.36	1.9	------	0.9
W75a	.30	11.8	15.2	.34	.64	.38	2.2	1.0	------
W76	.32	11.9	13.5	.30	.62	------	------	------	------

That the values for some of these steels, particularly W80 and W92, are quite outstanding can be appreciated when the values for these steels are compared with those of the well known super-alloys. A set of curves for stress for 100 hr. rupture versus test temperature is shown graphically in the accompanying drawing. The nominal compositions of the super-alloys used for comparison are given in the following Table V.

TABLE VII

*Creep and creep-rupture properties of 0.6C—12*Mn*—24*Cr*—0.7*N *steels that contained strengthening elements*

Steel[1] No. and Strengthening Elements	Test Condition		Results			
	Temp. (° F.)	Stress (×1,000 p.s.i.)	Rupt. Life (Hrs.)	Elong. (Percent)	R.A. (Percent)	Min. Creep Rate (Percent/hr.)
W90 (—)-1.0 Mo— 2.1 W-1.0 Cb	1,200	65	231	10	13	----------
	1,300	50	75	11	16	.097
	1,350	40	90	15	23	.067
	1,400	30	53	10	16	.055
	1,500	20	18	26	20	----------
	1,500	15	47	7	24	.112
	1,800	7	20	36	40	----------
	1,800	5	49	33	47	----------
	2,000	3	5	70	64	----------
W91 .40 V-1.0 Mo— (—)-.91 Cb	1,200	65	183	9	6	----------
	1,350	40	110	8	14	.037
	1,500	20	27	23	24	.30
	1,600	10	39	28	33	.20
	1,800	4	43	57	48	----------
W92 .40 V-(—)— 2.1 W-.91 Cb	1,200	65	273	7	8	----------
	1,300	50	133	11	15	.048
	1,350	40	128	13	16	.024
	1,400	30	88	11	14	.057
	1,500	20	33	11	22	----------
	1,500	20	21	9	23	----------
	1,500	15	57	11	12	.094
	1,600	10	50	23	20	----------
	1,800	6	25	20	37	----------

[1] Complete analyses appear in Table II.
NOTE.—All samples were solution treated at 2200° F., 30 min. water quenched.

TABLE V

Compositions of conventional super-alloys

	Composition, percent								
	C	Mn	Cr	Ni	Co	W	Mo	Cb	Others
S816	0.38	1.5	20.0	20.0	43.0	4.0	4.0	4.0	3.0 Fe.
S590	0.40	1.5	20.0	20.0	20.0	4.0	4.0	4.0	Bal. Fe.
N155	0.15	1.5	21.0	20.0	20.0	2.5	3.0	1.0	0.15 N, Bal. Fe.
A286	0.05	1.35	15.0	26.0	------	------	1.3	------	0.2 Al, 2.0 Ti. 0.3 V, Bal. Fe.
19-9DL	0.30	1.10	19.0	9.0	------	1.2	1.3	0.4	0.3 Ti, Bal. Fe.

More detailed creep rupture test data on steels of this invention are given in the following Tables VI and VII.

TABLE VI

*Creep and creep-rupture properties of 0.5C—12*Mn*—21* Cr*—0.5*N *steels that contained strengthening elements*

Steel[1] No. and Strengthening Elements	Test Condition		Results			
	Temp. (° F.)	Stress (×1,000 p.s.i.)	Rupt. Life (Hrs.)	Elong. (Percent)	R.A. (Percent)	Min. Creep Rate (Percent/hr.)
W77 .20 V-.71 Mo— 1.4 W-.70 Cb	1,200	65	55	7	9	----------
	1,300	40	254	11	15	.022
	1,500	20	46	22	27	.14
W78 (—)-.99 Mo— 2.0 W-.87 Cb	1,200	65	58	9	11	----------
	1,300	40	239	18	28	.033
	1,500	20	50	19	27	.17
W79 .36 V-1.0 Mo— (—)-1.1 Cb	1,200	65	69	7	10	----------
	1,300	40	218	9	22	.012
	1,500	20	69	23	33	----------
W80 .30 V-.95 Mo— 2.1 W-(—)	1,200	65	65	7	9	----------
	1,300	40	138	9	9	.027
	1,500	20	22	19	22	----------

[1] Complete analyses appear in Table II.
NOTE.—All samples were solution treated at 2100° F., 30 min. water quenched.

It will be noted from the above data that all of the steels have relatively good elongation at rupture, that is, all the steels have an elongation of at least 5%.

As was pointed out above with reference to our mentioned copending application on the straight

Cr—Mn—C—N

steels referred to, a stably austenitic structure is imparted by so proportioning the carbon and nitrogen in relation to the chromium content according to the formula:

$$\text{(1)}\quad \text{Percent } (C+N)_{\text{Min.}} = 0.078\ (\text{percent Cr} - 12.5)$$

Since, however, the steels of the present invention contain in addition to the active ferrite former, chromium, also one or more of the additional active ferrite formers vanadium, tungsten, molybdenum and columbium, it is necessary to substitute in the above formula the total chromium equivalent of all ferrite forming elements present in the steels of the instant invention. This chromium equivalent, designated Cr_{eq} is expressed by the following formula:

$$\text{(2)}\quad Cr_{eq} = \text{Percent Cr} + 2.3\%\ V + 0.63\%\ W + 1.4\%\ Mo + 2.8\%\ Cb$$

Thus in any given composition of steel according to this invention, the chromium equivalent comprises the actual percent of chromium present in the alloys plus the weighted percents according to Formula 2 of V, W, Mo and Cb present. And for assuring a wholly austenitic structure for the steels of this invention, Formula 1 above becomes:

(3) Percent $(C+N)_{Min.}=0.078\ (Cr_{eq}—12.5)$

The broad and preferred ranges for the steels of this invention are:

	Composition, percent	
	Broad	Preferred
C	0.20/0.80	0.35/0.65.
Mn	10/14	11/13.
Si	up to 2	0.2/0.7.
Cr	14/26	16/24.
N	0.20/0.80	0.30/0.70.
(C+N)	over 0.078 $(Cr_{eq}—12.5)$	0.65/1.35.
V	up to 1	up to 0.5.
W	0.5 to 2.5	0.7 to 2.0.
Mo	up to 2	up to 1.5.
Cb	0.3 to 1.5	0.5 to 1.
Balance	Substantially Fe	Substantially Fe.

In the appended claims the expression "chromium equivalent" shall have the meaning defined by the above Formula 2.

What is claimed is:

1. An alloy steel containing about: 0.2 to 0.8% carbon, 10 to 14% manganese, 14 to 26% chromium, 0.2 to 0.8% nitrogen, 0.5 to 2.5% tungsten, 0.3 to 1.5% columbium, up to 1% vanadium, up to 2% molybdenum, up to 2% silicon, balance substantially all iron, the carbon plus nitrogen content of said alloy being greater than 0.078 (chromium equivalent—12.5) and the total content of the elements vanadium, tungsten, molybdenum and columbium present in said alloy being from about 2 to 7%, said alloy being characterized by a wholly austenitic structure and by high creep strength at elevated temperatures in excess of 1100° F.

2. An alloy steel containing about: 0.35 to 0.65% carbon, 11 to 13% manganese, 16 to 24% chromium, 0.3 to 0.7% nitrogen, 0.7 to 2% tungsten, 0.5 to 1% columbium, up to 0.5% vanadium, up to 1.5% molybdenum, 0.2 to 0.7% silicon, balance substantially all iron, the carbon plus nitrogen content of said alloy being greater than 0.078 (chromium equivalent—12.5) and the total content of the elements vanadium, tungsten, molybdenum and columbium present in said alloy being from about 3 to 5%, said alloy being characterized by a wholly austenitic structure and by high creep strength at elevated temperatures in excess of 1100° F.

3. An alloy steel containing about: 0.2 to 0.8% carbon, 10 to 14% manganese, 14 to 26% chromium, 0.2 to 0.8% nitrogen, 2 to 7% of at least one element selected from the group consisting of molybdenum, vanadium, tungsten and columbium, up to 2% silicon, balance substantially all iron, the carbon plus nitrogen content of said alloy being greater than 0.078 (chromium equivalent—12.5), said alloy being characterized by a wholly austenitic structure and by high creep strength at elevated temperatures in excess of 1100° F.

4. An alloy steel containing about: 0.35 to 0.65% carbon, 11 to 13% manganese, 16 to 24% chromium, 0.3 to 0.7% nitrogen, 3 to 5% of at least one element selected from the group consisting of molybdenum, vanadium, tungsten and columbium, 0.2 to 0.7% silicon, balance substantially all iron, the carbon plus nitrogen content of said alloy being greater than 0.078 (chromium equivalent—12.5), said alloy being characterized by a wholly austenitic structure and by high creep strength at elevated temperatures in excess of 1100° F.

5. An alloy steel containing about: 0.2 to 0.8% carbon, 10 to 14% manganese, 14 to 26% chromium, 0.2 to 0.8% nitrogen, 2 to 7% of a plurality of elements selected from the group consisting of molybdenum, vanadium, tungsten and columbium, up to 2% silicon, balance substantially all iron, the carbon plus nitrogen content of said alloy being greater than 0.078 (chromium equivalent—12.5), said alloy being characterized by a wholly austenitic structure and by high creep strength at elevated temperatures in excess of 1100° F.

6. An alloy steel containing about: 0.35 to 0.65% carbon, 11 to 13% manganese, 16 to 24% chromium, 0.3 to 0.7% nitrogen, 3 to 5% of a plurality of elements selected from the group consisting of molybdenum, vanadium, tungsten and columbium, 0.2 to 0.7% silicon, balance substantially all iron, the carbon plus nitrogen content of said alloy being greater than 0.078 (chromium equivalent—12.5), said alloy being characterized by a wholly austenitic structure and by high creep strength at elevated temperatures in excess of 1100° F.

7. An alloy steel containing about: 0.2 to 0.8% carbon, 10 to 14% manganese, 14 to 26% chromium, 0.2 to 0.8% nitrogen, 2 to 7% of a plurality of elements selected from the group consisting of molybdenum, vanadium, tungsten and columbium, including 0.3 to 1.5% columbium, up to 2% silicon, balance substantially all iron, the carbon plus nitrogen content of said alloy being greater than 0.078 (chromium equivalent—12.5), said alloy being characterized by a wholly austenitic structure and by high creep strength at elevated temperatures in excess of 1100° F.

8. An alloy steel containing about: 0.35 to 0.65% carbon, 11 to 13% manganese, 16 to 24% chromium, 0.3 to 0.7% nitrogen, 3 to 5% of a plurality of elements selected from the group consisting of molybdenum, vanadium, tungsten and columbium, including 0.5 to 1% columbium, 0.2 to 0.7% silicon, balance substantially all iron, the carbon plus nitrogen content of said alloy being greater than 0.078 (chromium equivalent—12.5), said alloy being characterized by a wholly austenitic structure and by high creep strength at elevated temperatures in excess of 1100° F.

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