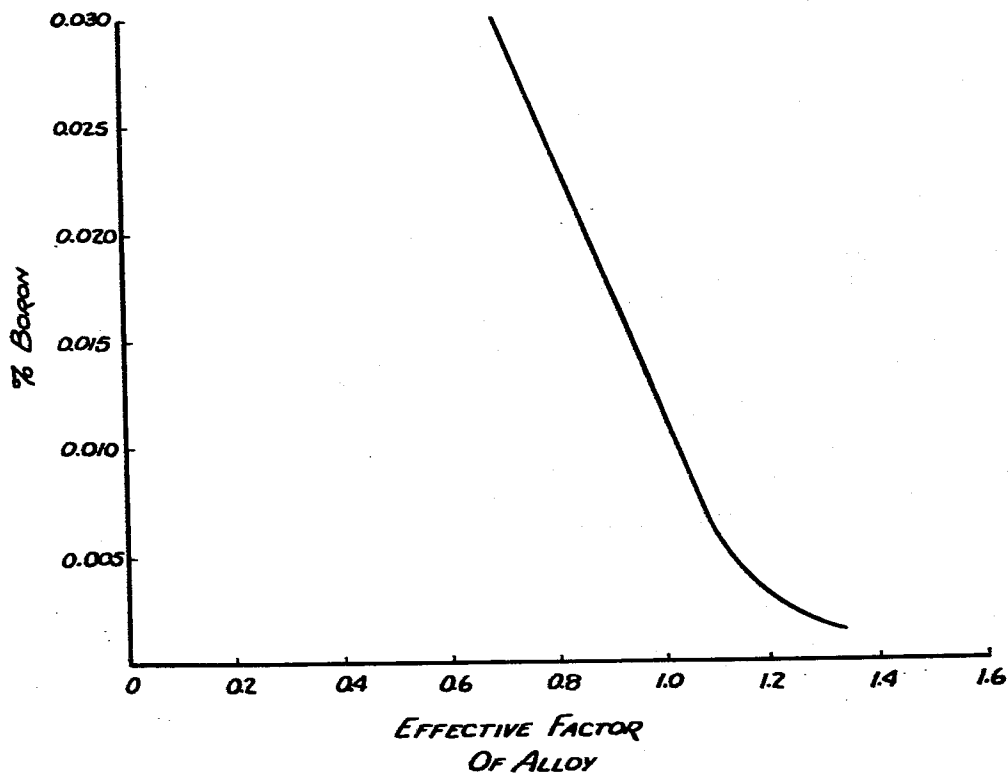


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R. A. KOZLIK ET AL
UNFIRED PRESSURE VESSEL

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UNFIRED PRESSURE VESSEL

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11 Claims. (Cl. 75-124)

The present invention relates to austenitic stainless
steels and, more particularly, to nickel-containing stain-
less steels and the manufacture of structures therefrom.

It is well known that extra-low carbon grades of
nickel-containing stainless steels have many metallurgi-
cally attractive advantages which have led to their adop-
tion in many areas of manufacturing. However, for the
production of unfired pressure vessels for use up to and
above 800° F., these grades of stainless steels have sub-
stantially limited commercial utilization since the engi-
neering boiler codes have imposed extremely severe stress
penalties attendant their use and, as a matter of fact,
do not authorize the use of certain grades of stainless
steel for unfired pressure vessels operating at tempera-
tures in excess of 800° F. These officially imposed stress
penalties are based in part upon a recognition that steels
within the normally accepted composition limits for low
and extra-low carbon stainless steels have widely varying
high temperature stress characteristics which could not
heretofore with certainty be predicted. In view of this
fact, the extra-low carbon grades of nickel-containing stain-
less steels are not now commercially accepted for use in
unfired pressure vessels operating at temperatures of the
order of 500° F. to 800° F. or higher, regardless of
whatever other attractive advantages may be afforded by
the alloys. Although many attempts were made to
provide extra-low carbon stainless steels which can be
employed in unfired pressure vessels used at high tem-
peratures, none, as far as we are aware, was entirely
successful when carried into practice commercially on
an industrial scale.

It has now been discovered that by maintaining speci-
fied and coordinated ranges of elements inherently co-
present with nickel, chromium and iron in commercially
produced stainless steels in a further coordinated rela-
tionship with specified amounts of alloying ingredients,
stainless steels can be provided which are particularly
suited for the manufacture of pressure vessels employable
at elevated temperatures.

It is an object of the present invention to provide a
novel stainless steel pressure vessel for use at elevated
temperatures of the order of 800° F. and higher.

Another object of the invention is to provide a novel
and improved method for the production of stainless steel
structures such as pressure vessels utilizable at tempera-
tures of the order of 800° F. and higher.

The invention also contemplates providing a unique
stainless steel particularly adapted to be employed in the
construction of pressure vessels utilizable at tempera-
tures of the order of 800° F. and higher.

Other objects and advantages will become apparent
from the following description taken in conjunction with
the accompanying drawing which is a graphical plot of the
effective factor of an alloy as hereinafter defined
versus the boron content thereof.

Generally speaking, the present invention contemplates
the manufacture of articles, structures and the like, such
as unfired pressure vessels operable at temperatures of the
order of about 800° F. to about 1200° F., from wrought
alloys consisting essentially in weight percent of about
8% to about 14% nickel, about 15% to about 21%
chromium, about 0.0015% to about 0.03% boron, about
0.008% to about 0.08% nitrogen, up to about 2% man-

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ganese, up to about 0.15% carbon, up to about 0.2%
aluminum, up to about 0.5% copper, up to about 1%
silicon, with the balance being essentially iron together
with correlated and controlled amounts of one or more
of the elements columbium, titanium, vanadium and
molybdenum, in addition to closely restricted amounts
of elements unavoidably present as impurities in com-
mercially manufactured stainless steels. The alloys from
which the articles of the present invention are formed by
working techniques including rolling, forging, extrusion
and the like are adjusted while molten prior to casting to
contain up to about 0.25% columbium, up to about 0.2%
vanadium, up to about 0.25% titanium and up to about
1% molybdenum. The wrought alloys operable in ac-
cordance with the present invention are stably austenitic
and can contain silicon in amounts up to 1%, for ex-
ample, about 0.4% to about 0.9%, but the silicon con-
tent is advantageously so controlled that when the alloy
contains less than about 0.02% carbon, 10% nickel and
0.03% nitrogen, the sum of the percentages of silicon
and chromium does not exceed about 19.8%.

In the manufacture of the articles of the present in-
vention and, in particular, when manufacturing said ar-
ticles by hot working an air melted alloy which contains
at least about 0.02% nitrogen, less than about 0.01%
titanium and advantageously less than about 0.03% car-
bon, care must be taken to avoid excessive amounts of
contaminating impurities during all stages of manufacture
including melting, casting, working, welding, machining
and the like. Low melting metals such as lead should
be held to an absolute minimum in the alloy composition.
Thus, lead which can be picked up during melting, cast-
ing, etc., should be present in the alloy of the finished
article in amounts no greater than, for example, about
0.01%. Tin and zinc should likewise be maintained at
as low a level as is commercially practical. Phosphorus
and sulfur advantageously are maintained at a maximum
of about 0.02% each. Zirconium in the alloy of the fin-
ished article should be no greater than about 0.02% and,
advantageously, is less than 0.01%.

When making articles in accordance with the present
invention, a molten bath of alloy is produced and adjusted
in composition so that the alloy as cast therefrom and
as subsequently worked and formed, contains interrelated
amounts of nitrogen and one or more of the elements
columbium, vanadium, titanium and molybdenum which
in turn are related in a particular manner to the boron
content. The effective amount of columbium and/or
vanadium and/or titanium and/or molybdenum and nitro-
gen in the alloy articles of the present invention termed,
for convenience, the effective factor (E.F.) of the alloy,
are defined by the appropriate algebraic expression set
forth in Table I in which percent (when used in con-
junction with a chemical symbol of an element) indi-
cates the numerical value of the percentage by weight
of said element. As indicated in Table I, the effective
factor of the alloy is determined with reference to the
particular contents of titanium and nitrogen in the alloy.

Table I

4% N to percent Ti	Effective factor
<-0.01-----	7.8 [percent Ti to 4% N minus 0.01] plus K* ¹ .
-0.01 to 0.01-----	K* ¹
0 to 0.12-----	4.9 [4% N to percent Ti] plus K* ¹
0.12 to 0.22-----	1.5 [4% N to percent Ti minus 0.12] plus K* ¹ plus 0.588.
>0.22-----	0.4 [4% N to percent Ti minus 0.22] plus K* ¹ plus 0.738.

¹ K* equals 6% Cb plus 1.9% V plus 0.9 [percent Mo minus 0.2] minus
2 [percent Cu minus 0.28]. When the quantity [percent Mo minus 0.2]
or the quantity [percent Cu minus 0.28] employed in the definitions set
forth in Table I is equal to a negative number, it is to be disregarded and
treated as equal to zero.

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In order to provide useful structures adapted to be employed in the temperature range of 800° F. to about 1200° F. in accordance with the concepts of the present invention, it is necessary to correlate the E.F. of the alloy comprising said structure with the boron content thereof. As mentioned heretofore, this correlation is essentially inverse and is more particularly exemplified as set forth in Table II.

Table II

Percent boron ¹	Minimum E.F., percent
0.0015	1.33
0.005	1.28
0.008	1.07
0.010	1.02
0.015	0.94
0.020	0.86
0.025	0.78
0.030	0.70

¹ Determined by spectrographic analyses which analyses closely approximate boron percentages added to alloy following final deoxidation.

This relationship between the minimum effective factor of the alloy and the percentage of boron is also exemplified in the drawing. Referring now thereto, it is to be observed that articles in accordance with the present invention are made from alloys which are adjusted in composition so as to be represented by a point lying to the right of the curve when the boron content is plotted against the effective factor of the alloy.

In carrying the invention into practice, it is advantageous to adjust the composition of the molten bath so that the cast alloy which is wrought into the novel articles of the present invention contains amounts of alloying ingredients as set forth in Table III correlated as set forth hereinbefore.

Table III

Element	Range, Percent				
	Alloy A	Alloy B	Alloy C	Alloy D	Alloy E
Ni	9-12	9-12	9-12	9-12	9-12
Cr	16-19	16-19	16-19	16-19	16-19
Mn	1-2	1-2	1-2	1-2	1-2
Si	0.3-0.9	0.3-0.9	0.3-0.9	0.3-0.9	0.3-0.9
B	0.0015-0.003	0.010-0.025	0.0015-0.003	0.003-0.025	0.002-0.025
Cb	0.1-0.15	0.15 max	0.1-0.15	0.1-0.15	0.10-0.15
C	0.015-0.035	0.015-0.035	0.015-0.035	0.015-0.035	0.08 max
N	0.03-0.04	0.03-0.04	0.01-0.04	0.01-0.04	0.03-0.06
Ti	0.01 max	0.01 max	0.04 max	0.1 max	0.1 max
V	0.15 max	0.15 max	0.1-0.15	0.10-0.15	0.15 max
Al	0.1 max	0.1 max	0.1 max	0.1	0.1 max
Cu	0.3 max	0.3 max	0.3 max	0.5 max	0.3 max
Mo	0.7 max	0.7 max	0.7 max	0.7 max	0.7 max
Fe	Bal. E. ¹	Bal. E. ¹	Bal. E. ¹	Bal. E. ¹	Bal. E. ¹

¹ Balance essentially.

In correlating the alloying ingredients to adjust the composition of the alloy in accordance with the concepts of the present specification and claims, it is to be noted that for any given alloy range the effective factor of the alloy is defined with respect to the ranges of nitrogen and titanium. For example, with respect to Alloy A as set forth in Table III, since 4 times (×) the percentage of nitrogen (percentage N) minus (−) the percentage of titanium (percentage Ti), i.e., the nitrogen-titanium factor (N-T-F), can be a maximum of 0.16 and a minimum of 0.11 the effective factor of this alloy is defined when the nitrogen-titanium factor is from 0.11 up to 0.12 by the expression

$$6 \times \% \text{Cb} + 1.9 \times \% \text{V} + 0.9 [\% \text{Mo} - 0.2] - 2 [\% \text{Cu} - 0.28] + 4.9 [4 \times \% \text{N} - \% \text{Ti}]$$

and when the nitrogen-titanium factor is in excess of 0.12 the E.F. of the alloy is defined by the expression

$$6 \times \% \text{Cb} + 1.9 \times \% \text{V} + 0.9 [\% \text{Mo} - 0.2] - 2 [\% \text{Cu} - 0.28] + 1.5 [4 \times \% \text{N} - \% \text{Ti} - 0.12] + 0.588$$

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After the molten bath of the alloy is so adjusted, the alloy is cast and wrought to form heat-resistant articles. The articles thus made in accordance with the present invention exhibit excellent high temperature stability when subjected to temperatures of the order of 800° F. to 1200° F. by virtue of the fact that they are comprised of a non age-hardenable alloy possessing a coordinated chemical composition specifically designed to minimize the formation of deleterious microstructures when subjected for extended periods of time to stress at elevated temperatures.

To illustrate more fully the advantages of the present invention, alloys illustrative of alloys which can be employed in the novel process and articles of the present invention are set forth in Table IV.

Table IV

Element	Percent by weight				
	Alloy No. 1	Alloy No. 2	Alloy No. 3	Alloy No. 4	Alloy No. 5
Ni	10.95	11.01	9.4	10.3	11.14
Cr	18.68	18.5	18.7	16.4	18.5
Mn	1.11	1.2	1.19	1.31	1.17
Si	0.48	0.5	0.56	0.67	0.3
C	0.017	0.032	0.02	0.015	0.05
N	0.031	0.031	0.022	0.029	0.054
V	0.04	0.082	0.12	0.12	0.016
Cb	0.12	0.03	0.12	0.14	0.14
Ti	<0.01	<0.01	0.014	0.03	<0.01
Al	0.098	0.027	<0.01	<0.01	0.012
B	0.0015	0.017	0.0024	0.0053	0.019
Cu	—	0.09	0.30	0.34	—
Mo	—	<0.01	0.25	0.64	<0.01
Fe	Bal. E.	Bal. E.	Bal. E.	Bal. E.	Bal. E.

¹ Balance essentially.

When formed into wrought articles, the alloys set forth in Table IV are ductile, weldable and exceptionally resistant to the deleterious effects of stress at elevated

temperatures of the order of 1200° F. The data in Table V shows the 100-hour rupture stress at 1200° F. in pounds per square inch (p.s.i.) of articles made from the alloys set forth in Table IV.

Table V

Alloy No.	100-hour rupture stress at 1200° F. (p.s.i.)	Alloy No.	100-hour rupture stress at 1200° F. (p.s.i.)
1	33,200	4	37,500
2	35,000	5	38,500
3	36,250		

The data set forth in Table V is to be compared to data with regard to alloys which are similar in chemical composition but which are outside the scope of the present invention. The 100-hour rupture stress of such similar alloys outside the scope of the present invention can be as low as 18,000 p.s.i. or even 15,000 p.s.i. In addition, al-

loys outside the scope of the present invention can form deleterious microstructural constituents during processing or service in articles exposed to elevated temperatures. Thus, if the articles contain too much chromium, molybdenum and/or silicon and/or too little nickel, carbon and/or nitrogen, deleterious amounts of ferrite can form in the substantially completely austenitic matrix of the alloy article. Excessive amounts of columbium, molybdenum and titanium can induce the formation of deleterious carbides. Excessive amounts of vanadium tend to reduce ductility and increase the tendency of the alloy articles to be notch sensitive. When nitrogen is present in the alloy in amounts in excess of about 0.01%, amounts of titanium in excess of about 0.01% are to be avoided in order to minimize and/or eliminate the formation of deleterious amounts of titanium nitrides and/or carbonitrides. To minimize the formation of deleterious amounts of carbides, the carbon content of the alloy articles of the present invention must not exceed 0.15%, should not exceed about 0.10% or 0.08% and, advantageously, is less than 0.03%. Excessive amounts of aluminum over 0.2% can weaken the alloy articles of the present invention. Excessive amounts of boron can induce undue difficulties in welding said articles but advantageously at least about 0.002% boron is present in the alloys. When producing the alloy articles in accordance with the present invention, small amounts of cobalt can be introduced along with nickel and small amounts of tantalum can be introduced along with columbium. Such small incidental amounts of cobalt and tantalum are not deleterious to the characteristics of the alloy articles of the present invention.

Alloy articles made in accordance with the present invention and adapted to be employed at temperatures of the order of 800° F. and higher, exhibit 100-hour rupture stresses at least in excess of 30,000 p.s.i. at 1200° F. Such alloy articles include hydrogenation equipment, high temperature oil and steam piping, superheater elements, furnace parts such as retorts, muffles, radiant tubes, mesh belts, chain link belts, etc., heat exchangers, 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. An unfired pressure vessel for use at temperatures of about 800° F. to about 1200° F. made of a stable, non-age hardenable austenitic alloy consisting essentially of about 8% to about 14% nickel, about 15% to about 21% chromium, about 0.0015% to about 0.03% boron, about 0.008% to about 0.08% nitrogen, up to about 2% manganese, up to about 0.15% carbon, up to about 0.2% aluminum, up to about 0.25% titanium, up to about 0.5% copper, up to about 1% silicon, up to about 0.25% columbium, up to about 0.2% vanadium, up to about 1% molybdenum with the balance being essentially iron, the elements in said alloy being so correlated that when the effective factor of said alloy is plotted against the boron content thereof, the alloy is representable by a point lying to the right of the curve in the accompanying drawing.

2. An unfired pressure vessel in accordance with claim 1 made of an alloy containing up to about 0.08% carbon.

3. An unfired pressure vessel in accordance with claim 1 made of an alloy containing less than about 0.01% titanium.

4. An unfired pressure vessel in accordance with claim

1 made of an alloy containing up to about 0.035% carbon.

5. An unfired pressure vessel in accordance with claim 4 made of an alloy containing less than about 0.01% titanium.

6. An unfired pressure vessel in accordance with claim 4 made of an alloy containing at least about 0.002% boron.

7. An unfired pressure vessel for use at temperatures of about 800° F. to about 1200° F. made of a stable, non-age hardenable austenitic alloy consisting essentially of about 9% to about 12% nickel, about 16% to about 19% chromium, about 0.0015% to about 0.003% boron, about 0.03% to about 0.04% nitrogen, about 1% to about 2% manganese, about 0.015% to about 0.035% carbon, up to about 0.1% aluminum, up to about 0.01% titanium, up to about 0.3% copper, about 0.3% to about 0.9% silicon, about 0.1% to about 0.15% columbium, up to about 0.15% vanadium, up to about 0.7% molybdenum with the balance being essentially iron, the elements in said alloy being so correlated that when the effective factor of said alloy is plotted against the boron content thereof, the alloy will be represented by a point lying to the right of the curve in the accompanying drawing.

8. An unfired pressure vessel for use at temperatures of about 800° F. to about 1200° F. made of a stable, non-age hardenable austenitic alloy consisting essentially of about 9% to about 12% nickel, about 16% to about 19% chromium, about 0.01% to about 0.25% boron, about 0.03% to about 0.04% nitrogen, about 1% to about 2% manganese, about 0.015% to about 0.035% carbon, up to about 0.1% aluminum, up to about 0.01% titanium, up to about 0.3% copper, about 0.3% to about 0.9% silicon, up to about 0.15% columbium, up to about 0.15% vanadium, up to about 0.7% molybdenum with the balance being essentially iron, the elements in said alloy being so correlated that when the effective factor of said alloy is plotted against the boron content thereof, the alloy will be represented by a point lying to the right of the curve in the accompanying drawing.

9. An unfired pressure vessel for use at temperatures of about 800° F. to about 1200° F. made of a stable, non-age hardenable austenitic alloy consisting essentially of about 9% to about 12% nickel, about 16% to about 19% chromium, about 0.0015% to about 0.003% boron, about 0.01% to about 0.04% nitrogen, about 1% to about 2% manganese, about 0.015% to about 0.035% carbon, up to about 0.1% aluminum, up to about 0.04% titanium, up to about 0.3% copper, about 0.3% to about 0.9% silicon, about 0.1% to about 0.15% columbium, about 0.1% to about 0.15% vanadium, up to about 0.7% molybdenum with the balance being essentially iron, the elements in said alloy being so correlated that when the effective factor of said alloy is plotted against the boron content thereof, the alloy will be represented by a point lying to the right of the curve in the accompanying drawing.

10. An unfired pressure vessel for use at temperatures of about 800° F. to about 1200° F. made of a stable, non-age hardenable austenitic alloy consisting essentially of about 9% to about 12% nickel, about 16% to about 19% chromium, about 0.003% to about 0.025% boron, about 0.01% to about 0.04% nitrogen, about 1% to about 2% manganese, about 0.015% to about 0.035% carbon, up to about 0.1% aluminum, up to about 0.1% titanium, up to about 0.5% copper, about 0.3% to about 0.9% silicon, about 0.1% to about 0.15% columbium, about 0.10% to about 0.15% vanadium, up to about 0.7% molybdenum with the balance being essentially iron, the elements in said alloy being so correlated that when the effective factor of said alloy is plotted against the boron content thereof, the alloy will be represented by a point lying to the right of the curve in the accompanying drawing.

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11. An unfired pressure vessel for use at temperatures of about 800° F. to about 1200° F. made of a stable, non-age hardenable austenitic alloy consisting essentially of about 9% to about 12% nickel, about 16% to about 19% chromium, about 0.002% to about 0.025% boron, about 0.03% to about 0.06% nitrogen, about 1% to about 2% manganese, up to about 0.08% carbon, up to about 0.1% aluminum, up to about 0.1% titanium, up to about 0.3% copper, about 0.3% to about 0.9% silicon, about 0.1% to about 0.15% columbium, up to about 0.15% vanadium, up to about 0.7% molybdenum with

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the balance being essentially iron, the elements in said alloy being so correlated that when the effective factor of said alloy is plotted against the boron content thereof, the alloy will be represented by a point lying to the right of the curve in the accompanying drawing.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,107,997

October 22, 1963

Roland A. Kozlik 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 1, line 66, for "nad" read -- and --; column 2, lines 60 to 68, Table I, should appear as shown below instead of as in the patent:

4% N - % Ti	:	Effective Factor
<-0.01	:	$7.8 [\% \text{ Ti} - 4\% \text{ N} - 0.01] + K^*$
-0.01 to 0	:	K^*
>0 to 0.12	:	$4.9 [4\% \text{ N} - \% \text{ Ti}] + K^*$
>0.12 to 0.22	:	$1.5 [4\% \text{ N} - \% \text{ Ti} - 0.12] + K^* + 0.588$
>0.22	:	$0.4 [4\% \text{ N} - \% \text{ Ti} - 0.22] + K^* + 0.738$

column 6, line 30, for "0.25%" read -- 0.025% --.

Signed and sealed this 12th day of May 1964.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents