United States Patent [19]

Mimino et al.

[11] **3,751,244**

[45] **Aug. 7, 1973**

[54] **AUSTENITIC HEAT RESISTING STEEL**

[76] Inventors: **Tohru Mimino; Kazuhisa Kinoshita; Isao Minegishi; Takayuki Shinoda,** all of c/o Gijutsa Kenkyushon, Nippon Kokan Kabushiki Kaisha, 2730 Minamiwatarida cho, Kawasaki, Japan

[22] Filed: **Dec. 14, 1970**

[21] Appl. No.: **97,854**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 773,786, Nov. 6, 1968, abandoned.

[52] **U.S. Cl.** ..... **75/128 G,** 75/128 T

[51] **Int. Cl.** **C22c 39/20**

[58] **Field of Search** ..... 75/128 T, 128 F, 75/128 G

[56] **References Cited**

UNITED STATES PATENTS

2,190,486	2/1940	Schafmeister	75/128 G
2,562,854	7/1951	Binder	75/128 F
2,602,028	7/1952	Urban	75/128 F
2,793,113	5/1957	Rait	75/128 F
2,801,916	8/1957	Harris	75/128 T
3,303,023	2/1967	Dulis	75/128 F

Primary Examiner—Hyland Bizot
Attorney—Flynn & Frishauf

[57] **ABSTRACT**

Cr-Ni type austenitic heat resisting steel having about twice the heat resistibility of common stainless steel is provided by the addition of 0.001 to 0.30 percent by weight Ti, 0.001 to 0.30 percent by weight Nb + Ta, and 0.0001 to 0.05 percent by weight B to a well-known Cr-Ni type steel composition for elevated temperature service, and maintaining a specified balance of [Ti + 0.5 (Nb+Ta)] to C and a specified balance of Ti to [Ti+0.5 (Nb+Ta)].

5 Claims, 2 Drawing Figures

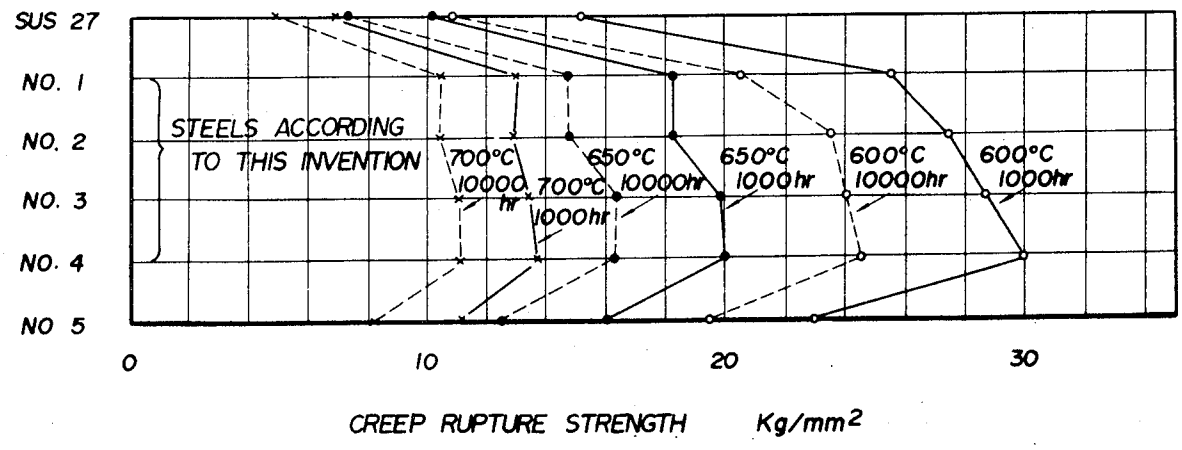


FIG. 1

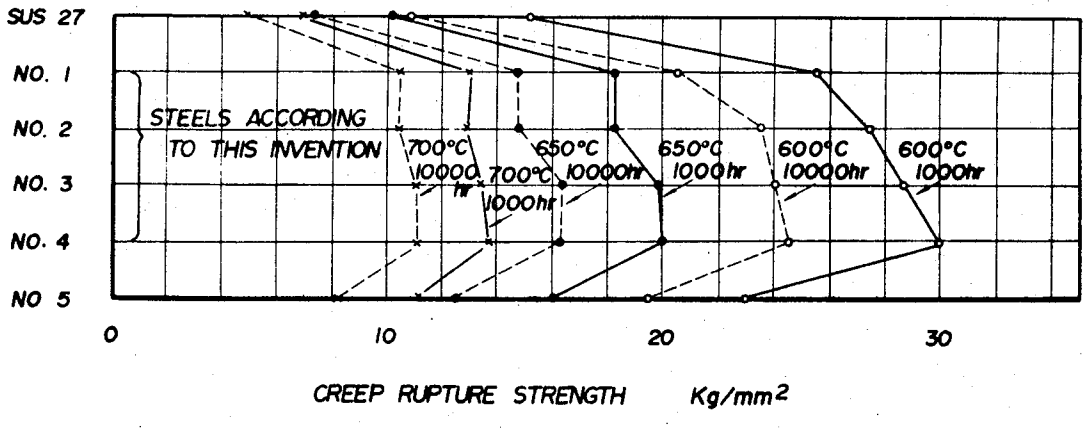
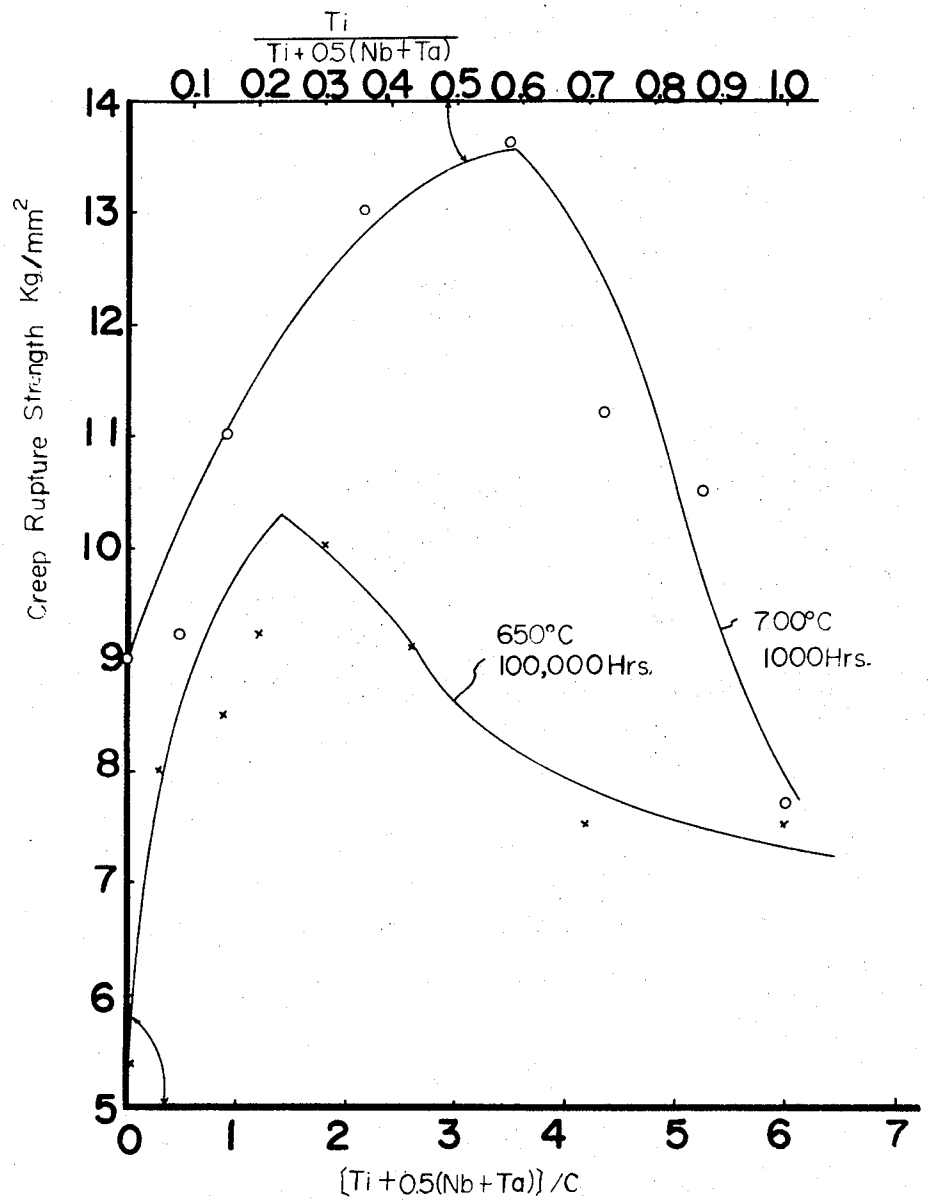

SUS 27
NO. 1
NO. 2
NO. 3
NO. 4
NO 5
STEELS ACCORDING TO THIS INVENTION
700°C 10000 hr
700°C 1000hr
650°C 10000hr
650°C 1000hr
600°C 10000hr
600°C 1000hr
0
10
20
30
CREEP RUPTURE STRENGTH Kg/mm²

FIG. 2


Ti / Ti+0.5(Nb+Ta)
0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
Creep Rupture Strength Kg/mm²
14
13
12
11
10
9
8
7
6
5
0 1 2 3 4 5 6 7
{Ti+0.5(Nb+Ta)}/C
650°C
100,000Hrs.
700°C
1000Hrs.

AUSTENITIC HEAT RESISTING STEEL

RELATED APPLICATION

This application is continuation-in-part of application Ser. No. 773,786, filed November 6, 1968 now abandoned.

FIELD OF THE INVENTION

This invention relates to Cr-Ni type austenitic stainless steels of improved heat resistibility for elevated temperature service.

BACKGROUND OF THE INVENTION

It is well-known that higher strength and oxidation resistibility of steel at high temperatures are required in some fields, e.g. the boiler industry. As boilers become larger in size and of an ultra-critical pressure type, steels of higher strength have been called for by said service.

At present, JIS (Japanese Industrial Standard) SUS-27, SUS-29, SUS-32 steels and the like (AISI-304, 321 and 316 steels as similar standards) among 18 Cr – 8 Ni austenitic stainless steels are generally employed for elevated temperature and high pressure services. The fact is that said SUS-32 steel (AISI-316 steel) among the above steels is commonly employed in view of its having superior strength at high temperatures in spite of a high cost which is due to a Mo content of 2.0 to 3.0 percent. The cost of SUS-27 steel (AISI-304 steel) is relatively low, while its high temperature strength is inferior to other stainless steels. SUS-29 steel (AISI-321 steel) formed by adding Ti to said SUS-27 steels, has higher heat resistibility than said SUS-27 steel. It is, however, found that the strength of said SUS-29 steel fails remarkably in service for a relatively long period of time such as 650°C at 100,000 hours. Consequently, the strength is substantially the same as that of said SUS-27 steel.

Thus, an inexpensive heat resisting steel having higher strength has not yet been provided for industrial circles. Accordingly, the development of more economical heat resisting steels is required today.

The present invention has been developed in order to meet the above requirement. The heat resisting steels of this invention are characterized by the addition of 0.001 to 0.30 percent by weight Ti, 0.001 to 0.30 percent by weight Nb+Ta and 0.0001 to 0.050 percent by weight B to compositions of the above Standards steels, and by critical values of Ti + 0.5(Nb + Ta)/C and Ti/Ti + 0.5(Nb+Ta).

SUMMARY OF THE INVENTION

In accordance with the present invention, there are provided steels of the following composition in weight percent:

C	0.03 to 0.30
Si	up to 1.00
Mn	up to 2.00
Cr	15.0 to 26
Ni	7.0 to 22
Ti	0.001 to 0.30
Nb + Ta	0.001 to 0.30
B	0.0001 to 0.050
Fe and unavoidable impurities	balance

and having a ratio of Ti + 0.5(Nb+Ta)/C of from about 0.25 to about 3, and a ratio of Ti/Ti + 0.5(Nb+Ta) of from about 0.15 to about 0.85.

BRIEF DESCRIPTION OF THE DRAWINGS

Additional objects of this invention will become apparent from the following description and the examples and the accompanying drawings in which:

FIg. 1 is a graph showing the relation of the creep rupture strength in the case where steels subjected to elevated temperature service are JIS SUS-27 (AISI-304), steels No. 1, No. 2, No. 3 and No. 4 according to this invention and No. 5 not containing B.

FIG. 2 is a graph illustrating the critical relationships Ti + 0.5(Nb+Ta)/C and Ti/Ti + 0.5(Nb+Ta), with respect to creep rupture strength.

SPECIFIC EMBODIMENTS OF THE INVENTION

As mentioned above, the Ti and Nb + Ta are effective for causing the agglomeration of produced carbides to disperse uniformly and finely by interaction of said additional elements.

The C content of the steels is chosen to be a relatively high value in order to cause Cr-carbides to precipitate and disperse around Ti and Nb-carbide and improve high temperature characteristics. However, as Cr-carbide has a tendency to agglomerate around said Ti and Nb-carbide, the addition of B is effective to stop said agglomeration and cause the higher strength to hold.

The content of Ti should be defined to be within the above-mentioned range. More than 0.30 percent Ti causes its carbide to coarsen and causes its strength to decrease at high temperatures, while less than 0.001 percent Ti brings about a decrease of the amount of Ti-carbide precipitated and is ineffective for improving its strength.

The effect of Nb + Ta, too, is similar to that of Ti. That is, both more than 0.30 percent Nb + Ta and less than 0.001 percent Nb + Ta are unable to cause high temperature strength to improve. It is to be understood that Nb or Ta can be used in place of mixtures of Nb and Ta; however, generally mixtures are employed.

Less than 0.0001 B is ineffective for improving its strength at high temperatures, while more than 0.050 percent B is undesirable because workability of said steel decreases exceedingly, even though the high temperature strength may possibly be improved.

Referring now to FIG. 1, each graph is plotted on the basis of the following examples.

The chemical composition (by weight percent) of the above examples is shown in Table 1.

TABLE 1

The composition of SUS-27 steel (AISI-304 steel) is based on the Standard.

TABLE 1

	C	Si	Mn	Cr	Ni	Ti	Nb + Ta	B
No. 1	0.14	0.54	1.56	12.46	9.74	0.10	0.10	0.001
No. 2	0.14	0.54	1.58	17.91	9.80	0.09	0.11	0.003
No. 3	0.13	0.54	1.56	19.91	9.80	0.06	0.09	0.007
No. 4	0.14	0.53	1.55	17.91	9.80	0.06	0.08	0.012
No. 5	0.12	0.68	1.20	20.28	9.16	0.02	0.098	------

NOTES.—1. All compositions No. 1, No. 2, No. 3, and No. 4 steel are within the ranges given above for steels of this invention. 2. The composition of No. 5 steel is not within the ranges given above in view of the omission of B.

SUS-27 steel and steels Nos. 1–5 were manufactured by using a conventional process, and were then subjected to a creep rupture test at 600°C, 650°C and 700°C in 10^3 hours and 10^4 hours, respectively. The results are shown in the following TABLE 2.

TABLE 2 (kg./mm.²)

	600° C.		650° C.		700° C.	
	10^3 hr.	10^4 hr.	10^3 hr.	10^4 hr.	10^3 hr.	10^4 hr.
SUS-27	15.1	10.8	10.2	7.3	7.0	4.9
No. 1	25.5	20.5	18.2	14.7	13.0	10.5
No. 2	27.5	23.5	18.2	14.7	13.0	10.5
No. 3	28.7	24.0	19.8	16.3	13.5	11.2
No. 4	30.0	24.5	20.0	16.5	13.8	11.2
No. 5	23.0	19.5	16.0	12.5	11.2	8.2

As mentioned above the only difference between the compositions of No. 1 to No. 4 steels and No. 5 steel was the presence of B. Referring now to the above Table 2 and FIG. **1**, it is clearly indicated that there is a great difference in creep rupture test values for the steels tested. That is, it should be understood that the existence of B has an important effect upon the creep rupture strength. Even such steel as No. 5 steel attained a higher strength as compared with said SUS-27 steel, by reason of the addition of Ti and Nb + Ta to said SUS-27 steel. This fact evidently explains that addition of Ti, Nb + Ta and B causes the high temperature strength to improve greatly.

As indicated above, the ratio Ti + 0.5(Nb +Ta)/C should be from about 0.25 to about 3, and preferably between about 0.6 and about 2.6. This critical relationship is revealed by data given below in TABLES **3** and **4**, and illustrated in FIG. **2**, with steels Nos. 11 through 19. It is to be noted that these steels do not contain B; however, as demonstrated above, the addition of B to such steels increases the effectiveness of Ti and Nb. The components of such steels are set forth (in weight percent) in TABLE 3.

TABLE 3

No.	C	Si	Mn	Ni	Cr	Ti	Nb + Ta	Ti + ½(Nb + Ta) / C
11	0.07	0.55	1.38	10.03	18.02	Tr.	Tr.	0
12	0.12	0.72	1.14	9.27	20.37	0.03	0.020	0.33
13	0.07	0.47	1.28	10.27	18.67	0.02	0.080	0.86
14	0.15	0.58	1.51	9.98	17.96	0.07	0.22	1.2
15	0.11	0.51	1.56	9.74	17.46	0.10	0.10	1.1
16	0.10	0.65	1.48	9.98	17.56	0.09	0.18	1.8
17	0.08	0.46	1.49	10.47	18.28	1.10	0.21	2.6
18	0.08	0.51	1.46	10.47	18.10	0.18	0.31	4.2
19	0.08	0.50	1.46	10.08	18.19	0.28	0.40	6.0

Steels **11**, **18** and **19** are included for comparative purposes, since the ratios fall outside the specified critical range. Steels **12** through **17** are illustrative of steels, except for their B content, come within the scope of this invention.

Steels **11–19** were hot rolled, heated at 1100°C. and solution treated with water cooling. A creep rupture test of 5,000 to 10,000 hours was conducted with each steel. From the test values obtained, the creep rupture strength at 650°C. for 100,000 hours was determined by extrapolation. The creep rupture values, at 650°C. for 100,000 hours, are given below in TABLE **4** and are also shown in FIG. **2**.

TABLE 4

No.	11	12	13	14	15	16	17	18	19
Kg./mm.²	5.3	8.0	8.5	9.2	10.0	10.0	9.1	7.5	7.5

As shown, steels **12** through **17** with ratios within a range of about 0.25 to 3, have substantially greater creep rupture values than steels **11, 18** and **19.** In particular, it is to be noted that steels **18** and **19** contain relatively large amounts of Ti and Nb + Ta, and yet are inferior to steels **12** through **17** which contain substantially lesser quantities of such components. This is unexpected.

The ratio Ti/Ti+0.5(Nb+Ta) is also controlled in order to achieve high creep rupture values. This ratio is maintained between about 0.15 and about 0.85, and preferably 0.15+0.75. Criticality is shown by data with steels Nos. 21 through **28.** Here again as with Nos. 11–19, such steels do not contain B. The components of Nos. **21–28** are given (in weight percent) in TABLE 5. The values [Ti+**0.5**(Nb+Ta)]/C of Nos. **21–28** range from 0.77 to 0.98.

TABLE 5

No.	C	Si	Mn	Ni	Cr	Ti	Nb + Ta	Ti + ½(Nb + Ta) / Ti
21	0.12	0.59	1.54	9.68	19.31	----	0.22	0
22	0.13	0.43	1.45	10.10	17.66	0.01	0.23	0.08
23	0.15	0.43	1.42	10.16	18.19	0.02	0.23	0.15
24	0.13	0.39	1.35	10.07	17.75	0.04	0.14	0.36
25	0.16	0.58	1.47	9.86	18.29	0.09	0.13	0.58
26	0.14	0.44	1.42	10.04	18.87	0.09	0.07	0.72
27	0.15	0.46	1.38	10.04	18.84	0.10	0.03	0.87
28	0.13	0.52	1.43	10.09	17.73	0.11	----	1.00

Steels Nos.**21, 22, 27** and **28** have ratios not within the range specified for steels of this invention. Steels **23-26,** except for their B content, come within the scope of the invention.

Steels Nos.**21–28** were heated at 1100°C. and were then subjected to a creep rupture test at 700°C. for 1000 hours. Results are given below in TABLE 6.

TABLE 6

No.	21	22	23	24	25	26	27	28
Kg./mm.²	9.0	9.2	11.0	13.0	13.6	11.2	10.5	7.7

Data in TABLE 6 are also shown graphically in FIG. **2.** Such data demonstrate that substantially higher creep rupture values are realized with steels having a value of from about 0.15 to about 0.85 for Ti/-Ti+0.5(Nb+Ia).

Thus, according to the present invention, the insufficient heat-resisting strength of the steel is improved remarkably at lower cost since relatively expensive Mo is omitted.

The austenitic heat-resisting steels of the present invention may be employed broadly in a variety of industrial circles.

What is claimed is:

1. An austenitic heat-resisting steel consisting essentially of, in weight percent,

C	0.03 to 0.30
Si	up to 1
Mn	up to 2
Cr	15.0 to 26
Ni	7.0 to 22
Ti	0.001 to 0.30
Nb+Ta	0.001 to 0.30
B	0.0001 to 0.050
Fe and unavoidable impurities	balance,

and having a ratio of Ti + 0.5(Nb+Ta)/C of from 0.25 to 3, and a ratio of Ti/Ti + 0.5(Nb+Ta) of from 0.15 to 0.85.

2. A steel of claim **1**, wherein the ratio of Ti + 0.5(Nb+Ta)/C is from 0.6 to 2.6.

3. A steel of claim **1**, wherein the ratio of Ti/Ti + 0.5(Nb+Ta) is from 0.15 to 0.75.

4. A steel of claim **1**, wherein the Ti content is from 0.02 to 0.10.

5. A steel of claim **1**, wherein the Nb+Ta content is from 0.02 to 0.23.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,751,244 Dated August 7, 1973

Inventor(s) TOHRU MIMINO et al

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

Abstract, line 5: replace "0.05" with --- 0.050 -- .

Column 3, Table 3, No. 17: under "Ti", replace "1.10" with ---0.10--- .

Column 4, Table 4, line 7: under "15", replace "10.0" with ---10.5--- .

Column 4, line 64: replace "Ia" with ---Ta--- .

Column 5, line 10: re-space "7.0 to 22" to fall in correct column beneath "15.0 to 26".

Signed and sealed this 1st day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
☆ U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334