United States Patent [19]

Mimino et al.

[11] **3,716,353**

[45] **Feb. 13, 1973**

[54] AUSTENITIC HEAT RESISTING STEEL

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[22] Filed: **March 10, 1970**

[21] Appl. No.: **18,245**

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

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

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

[56] **References Cited**

UNITED STATES PATENTS

3,337,331	8/1967	Ljunberg	75/128 T
2,159,724	5/1939	Franks	75/128 G
2,801,916	8/1957	Harris	75/128 G
3,303,023	2/1957	Dulis	75/128 T
2,602,737	8/1952	Binder	75/128 N
2,229,065	1/1941	Franks	75/128 N
3,523,788	8/1970	Bates	75/128 N

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[57] **ABSTRACT**

Cr–Ni system austenitic heat resisting steel having higher heat resistibility at elevated temperatures and for a longer time than common austenitic stainless steel by the multiplied effects of 0.03 to 0.30 C, Ti + Nb content and that the atomic ratio of Ti + Nb/C is within range of 0.05 to 1.0, 0.2 to 4.0% Mo and 0.04 to 0.15% N.

2 Claims, 4 Drawing Figures

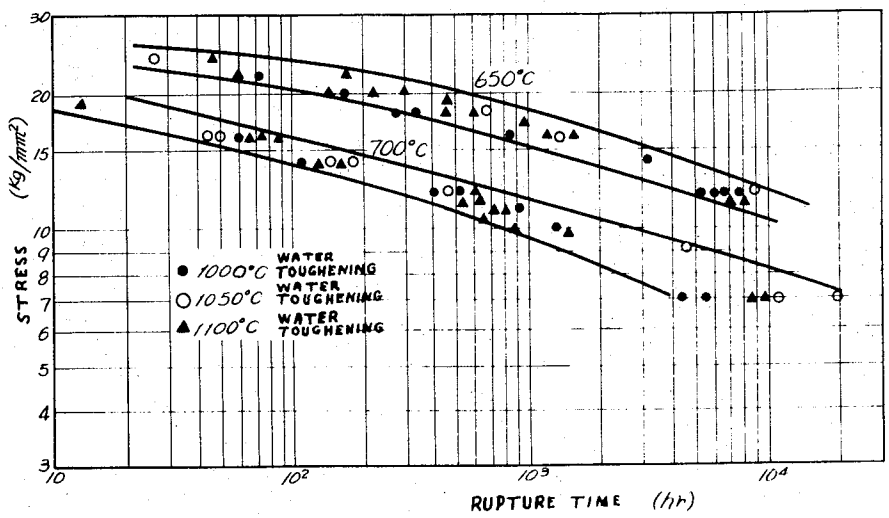
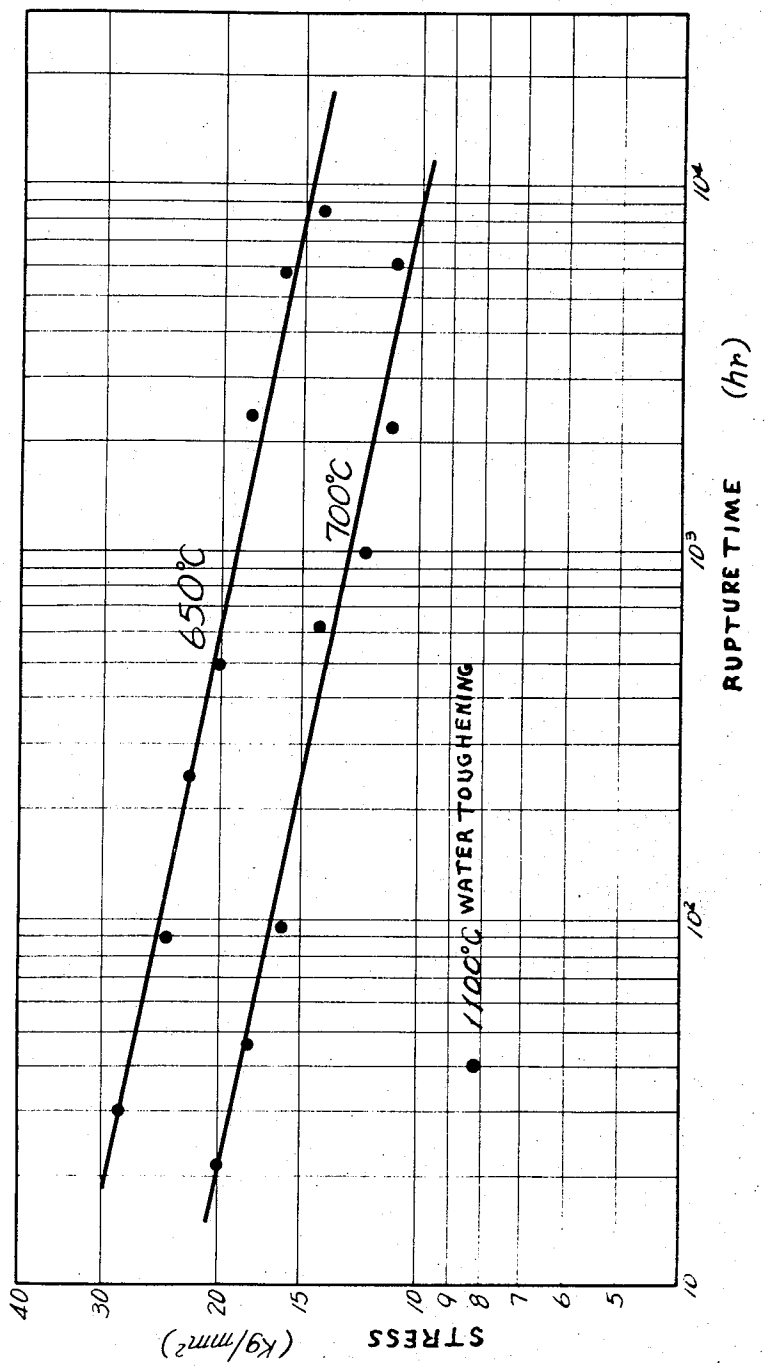


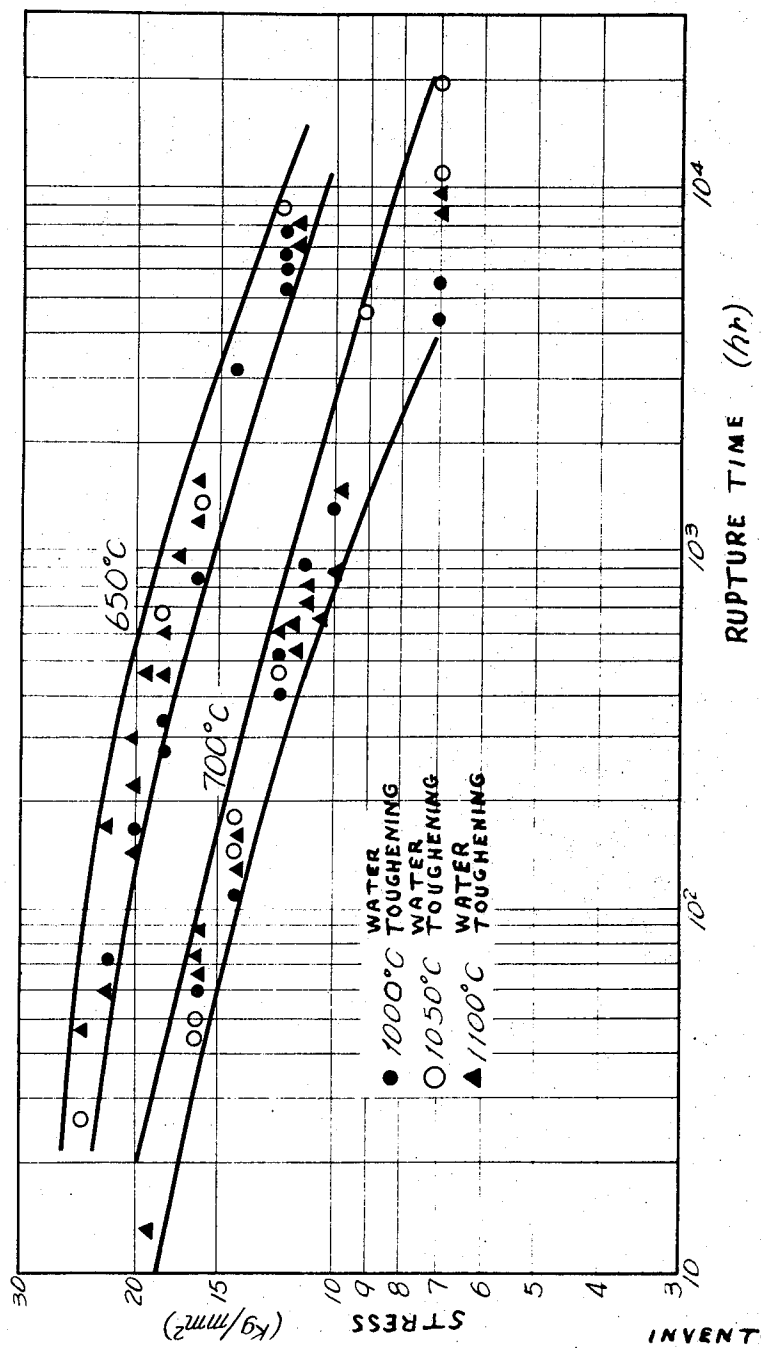
FIG. 1



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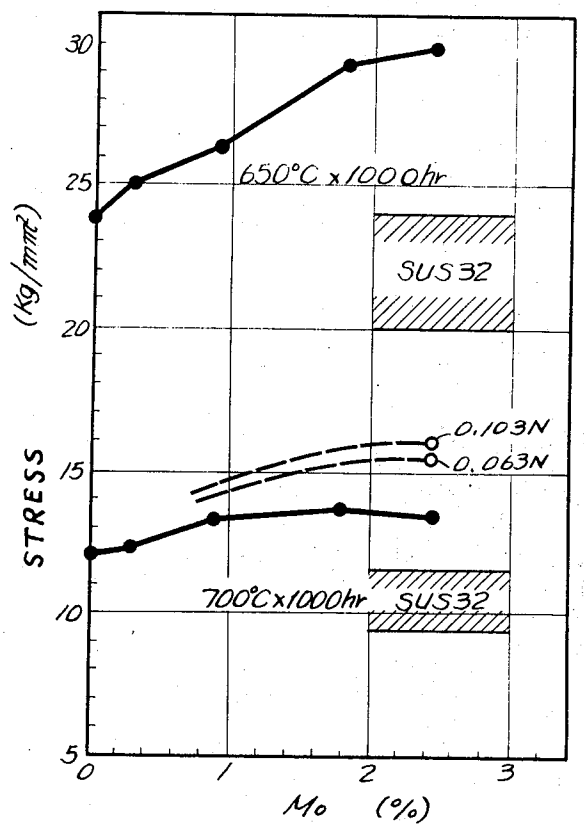
FIG. 2



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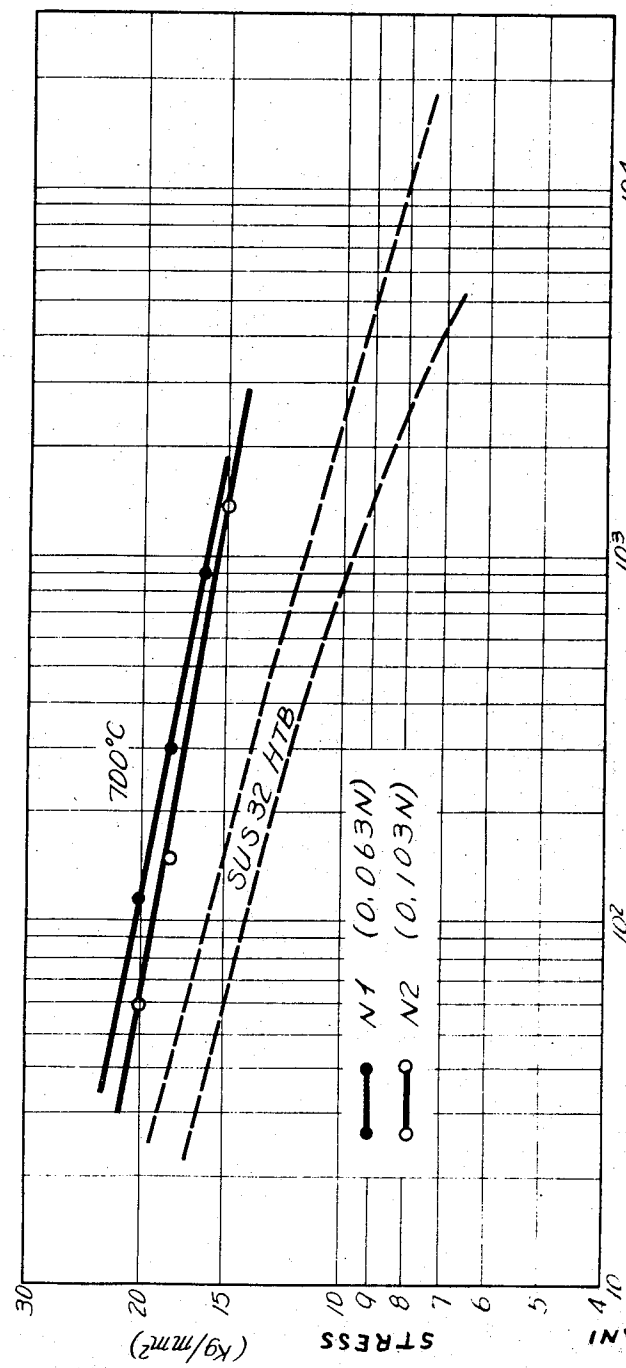
FIG. 3



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FIG. 4



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AUSTENITIC HEAT RESISTING STEEL

This invention relatives to a composition for improving the heat resistibility of Cr—Ni system austenitic stainless steel for elevated temperature services.

It is well known that higher strength and oxidation resistibility at elevated temperatures of steel are required in some services such as boiler industries. As boilers become larger and of the ultra-critical pressure type, a higher strength of the steels employed is required.

At present JIS (Japanese Industrial Standards) SUS–27, SUS–29, SUS–32 and the like (AISI–304, 321, 316 and the like as similar standards) among 18Cr–8Ni austenitic stainless steels are generally employed for elevated temperatures and high pressure services.

The fact is that said 18–8 Ti—Nb steel or SUS–32 steel (AISI–316 steel) is commonly employed in consideration of having superior strength at high temperatures in spite of a fault. The following table shows the chemical compositions of these steels.

TABLE I

	Percent										
	C	Si	Mn	P	S	Cr	Ni	Mo	Ti	Nb	N
18–8Ti NH	0.16	0.58	1.47	0.018	0.024	18.29	9.86	Trace	0.09	0.13	0.0130
SUS 32 (1)	0.08	0.46	1.56	0.031	0.009	17.04	12.56	2.47			0.0357
SUS 32 (2)	0.10	0.75	1.59	0.028	0.009	16.95	12.44	2.39			0.0396
SUS 32 (3)	0.06	0.58	1.65	0.020	0.014	17.60	13.09	2.44			0.0223

The above 18–8 Ti—Nb steel is subject to solution heat-treatment, which is water toughened at 1,100°C, and SUS–32 steel (AISI–316 steels), which is water-toughened at 1,100°C, 1,050°C and 1,100°C, respectively. The results of creep rupture test for these steels are shown in FIG. 1 and FIG. 2.

Referring now to FIG. 1 and FIG. 2, it is found that the creep rupture strength of 18–8 Ti—Nb steel is far higher than that of SUS–32 steels, which is marked for long test time on purpose, owing to the following reason, that is, the coexistance of Ti and Nb (containing Ta) in 18 Cr-8NI-Ti-Nb steel are effective for causing the coalescence of formed carbides, such as $M_{23}C_6$, to stop and for causing said carbides to disperse uniformly, which results in improving said high temperature and long service strength, while the coalescense of said carbides of SUS–32 steel (AISI–316 steel) is made to accelerate owing to Mo when being exposed at high temperatures for long time services and consequently the strength of said steel is lowered.

The present invention has been developed in order to improve the qualities of said 18 CR-8Ni-Ti-Nb steel and strength of said SUS–32 steel for long time services at high temperatures. That is, the heat resisting steel of this invention is characterized by contents of Ti+Nb (containing Ta) and that the atomic ratio of Ti+Nb/C is 0.05 to 1.0 in coexistence with up to 4.0% Mo and 0.04 to 0.15%N.

An object of the present invention is to provide an economical heat resisting steel having higher strength and heat resistibility for elevated temperature services than those of SUS–32 steel (AISI–316 steel as similar standard).

Another object of this strength is to provide a heat resisting steel having higher strength and heat resistibility for elevated temperature services than these of 18Cr-8Ni-Ti-Nb steel, which is based on multiplied (or synergestic) effect of Ti and Nb.

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

FIG. 1 is a graph showing creep rupture strength of 18Cr-8Ni-Ti-Nb steel, which is known;

FIG. 2 is a graph showing creep rupture strength of SUS–32 steel which is AISI–316 steel as similar Standard;

FIG. 3 is a graph showing creep rupture strength affected by added Mo contents; and

FIG. 4 is a graph showing creep rupture strength of the present invention steel.

According to the present invention, the steel has the following composition; that is

0.03 to 0.30% by weight C
up to 1.0% weight Si
up to 2.0% weight Mn
15.0 to 26.0% weight Cr
7.0 to 22.0% weight Ni
up to 4.0% weight Mo
0.04 to 0.15% weight Na
By weight Ti+Nb (containing Ta) contents and that the atomic ratio of Ti+Nb/C is 0.05 to 1.0

And a part or all of the above Ti is possible to be with Zr.

As mentioned above, the features of this invention consist in that Mo and N is made to coexist with said Ti+Nb. In this case, effects of added Mo to 18Cr-8Ni-Ti-Nb steel is as follows:

TABLE II

	Percent									
	C	Si	Mn	P	S	Cr	Ni	Mo	Ti	Nb
1	0.15	0.67	1.60	0.019	0.012	17.86	9.86	0.29	0.09	0.10
2	0.16	0.65	1.63	0.018	0.013	17.86	9.80	0.87	0.09	0.11
3	0.17	0.69	1.65	0.018	0.013	17.43	9.68	1.77	0.09	0.11
4	0.15	0.67	1.63	0.020	0.015	17.35	9.51	2.44	0.06	0.00

The creep rupture strength of these steels, which is water toughened at 1,100°C, at 650°C × 100 hr and 700°C × 1,000 hr is shown in FIG. 3 in comparison with that of SUS–32 steel (AISI–316 steel).

Referring now to FIG. 3, it will be understood that the curve of the creep rupture strength at 700°C × 1,000 hr tends toward the uppermost limit by the addition of about 1%Mo, while that at 650°C × 100 hr is on the rise, nearly straight.

It is, however, evident that the creep rupture strength of 18Cr-8Ni-Ti-Nb steel is still superior to that of SUS–32 (AISI–316) steel to which Mo is similarly added. Thus, for the purpose of improving said 18Cr-8Ni-Ti-Nb-Mo steel, N is further added in this present steel.

The following Table shows an example of the chemical compositions of this present steel.

TABLE III

(Chemical composition)

	Percent										
	C	Si	MN	P	S	Cr	Ni	MO	Ti	Nb	N
5	0.10	0.56	1.56	0.022	0.009	17.26	10.04	2.44	0.05	0.08	0.063
6	0.11	0.52	1.65	0.025	0.012	17.93	10.39	2.44	0.04	0.05	0.103

The creep rupture strength of these steels which is heat treated in the same manner as the above steels of Table II, at 700°C is shown in FIG. 4 in comparison with that of SUS-32 steel (AISI-316 steel).

Referring now to FIG. 4, the slope degree of the creep rupture strength for long time services is far gentler than that of said SUS-32 steel. This fact signifies the effect of the added N at elevated temperature and for long time services. It is needless to say that the required contents of N should be specially added in the steel-making stage through same addition agent, e.g. Mn-Nitride. Thus, the addition effect of Mo and N has not been discovered before.

The range of the chemical composition as mentioned above is determined by the following reasons.

C content of the present invention is chosen in relation to Ti+Nb content which is within the range of 0.03 to 0.30% More than 0.30%C is undesirable, because solution C in steel precipitates as $Cr_{23}C_6$ during elevated temperature services and then coalesces and results in the deterioration of the creep rupture strength. It is, conversely, difficult to improve said strength when C content is less than 0.03.

Ti+NB (containing Ta) content is determined in relation to the above C content. That is, the atomic ratio of Ti-Nb/C should be within the range of 0.05 to 1.0. Ti+Nb content exceeding the above ratio has no effect in improving the high temperature strength. In this invention, part or all of said Ti can be replaced with Zr.

It is confirmed by experiments that Mo can improve said strength in relation to N content even though the content of Mo was small. However, less than 0.02% Mo has little effect to improve said strength. More than 4.0% Mo has a tendency to form ferrite and is costly.

Up to 0.04% N is the common content in the usual steel-making process. It is, however, difficult to improve said strength even though the Mo content was increased. Accordingly, more than 0.04% N is required. On the other hand, more than 0.15% N will be impossible to be realized.

Less than 15.0% Cr makes said oxidation resistibility worse. When the Cr content is more than 26.0% a stable austenitic steel is difficult to be obtained. Ni is necessary to make a stable austenitic phase form. The content should be chosen within the range of 7.0 to 22.0% in relation to the Cr content.

It is, in the present invention, free from that some content of Si, Mn, or Al, which is added on purpose of deoxidation, is included in steel.

Thus, according to this invention, Cr—Ni system austenitic heat resisting steel for use at elevated temperatures and for long time services may be remarkably improved with a lower cost, and it is possible to be broadly employed in many fields of industrial circles

I claim:

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

0.03 to 0.03% by weight C,

15.0 to 26.0% by weight Cr,

7.0 to 22.0% by weight Ni,

0.2 to 4.0% by weight Mo,

0.04 to 0.15% by weight N and

Ti+Nb (containing Ta) content that the atomic ratio of Ti+Nb/C is within range of 0.05 to 1.0 and balance Fe.

2. The austenitic heat-resisting steel as set forth in claim 1 wherein at least part of said Ti is replaced with Zr.

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