United States Patent

Hachisu et al.

[15] **3,658,516**

[45] **Apr. 25, 1972**

[54] AUSTENITIC CAST STEEL OF HIGH STRENGTH AND EXCELLENT DUCTILITY AT HIGH TEMPERATURES

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[73] Assignee: **Hitachi, Ltd.,** Tokyo, Japan

[22] Filed: **Sept. 5, 1969**

[21] Appl. No.: **855,716**

[52] **U.S. Cl.**.....**75/128 E,** 75/128 A, 75/128 T, 75/128 R

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

[58] **Field of Search** .....75/128 E, 128 T, 128 R

[56] **References Cited**

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[57] **ABSTRACT**

An austenitic cast steel having high strength and excellent ductility at temperatures higher than, for example, 700° C. consisting essentially of C in the range from 0.30 to 0.55 percent, Si in the range from 0.2 to 2.0 percent, Mn in the range from 0.5 to 3.0 percent, Ni in the range from 15 to 40 percent, Cr in the range from 20 to 30 percent, Ti in the range from 0.05 to 0.6 percent, a rare earth metal alloy containing Ce and La as the main components in the range from 0.05 to 0.5 percent (as the additive amount) and the balance substantially iron. The steel may further contain from 0.07 to 0.7 percent by weight of Nb.

19 Claims, 23 Drawing Figures

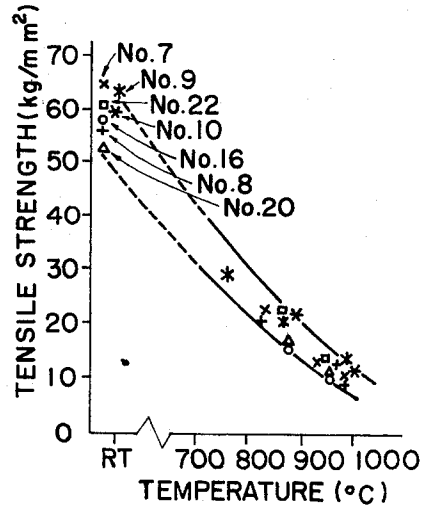


FIG. 1

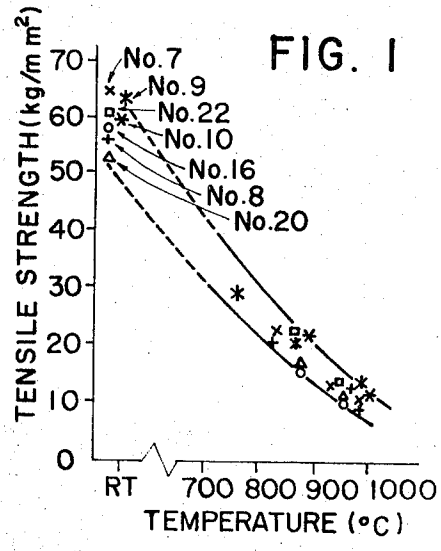


FIG. 2

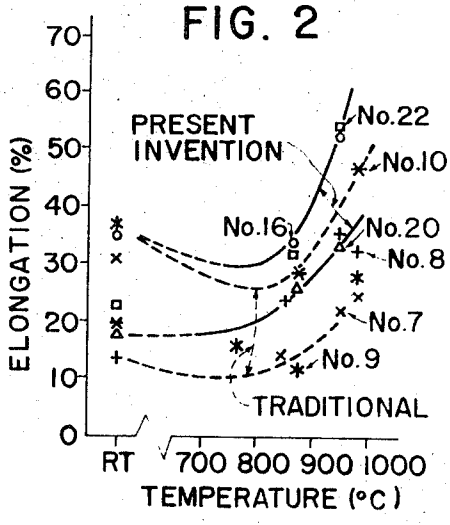
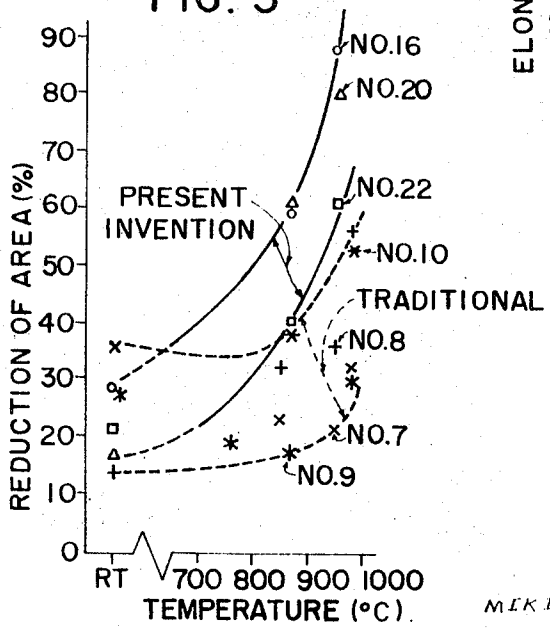


FIG. 3



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FIG. 4

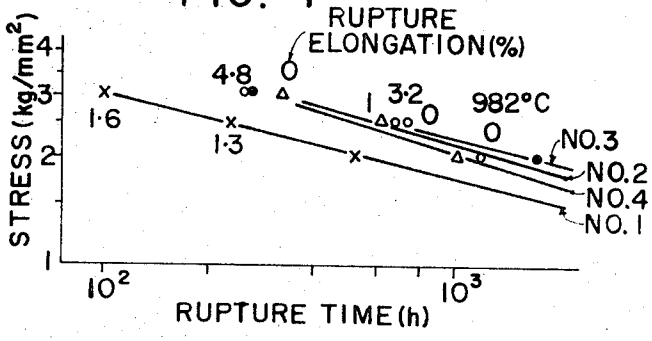


FIG. 5

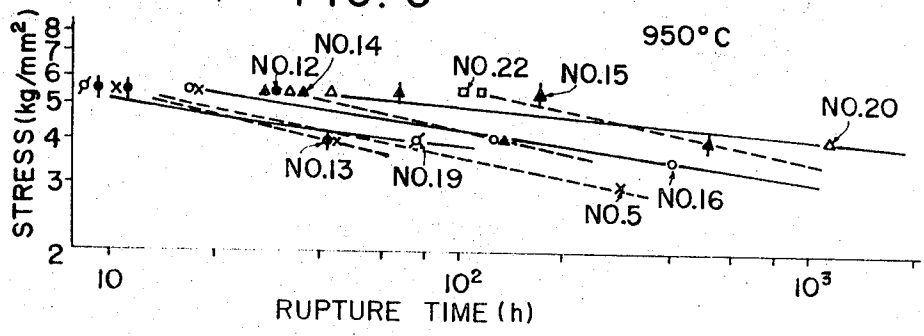
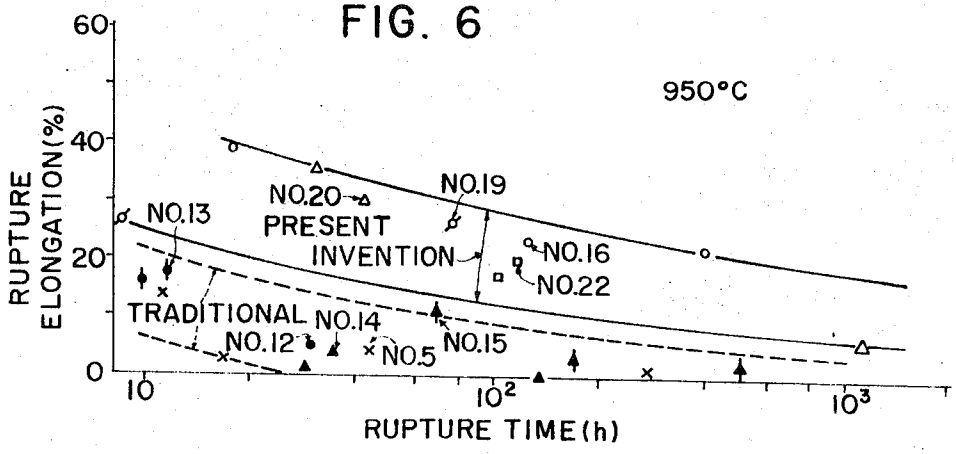


FIG. 6



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FIG. 7

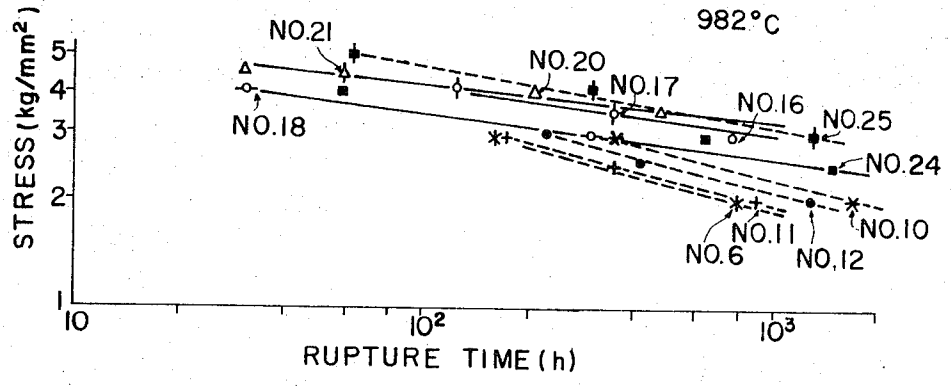
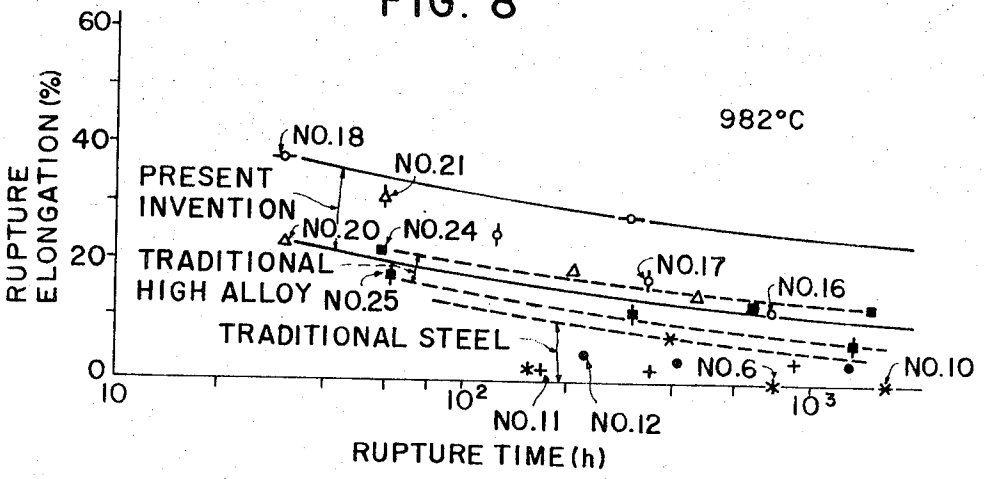


FIG. 8



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FIG. 9

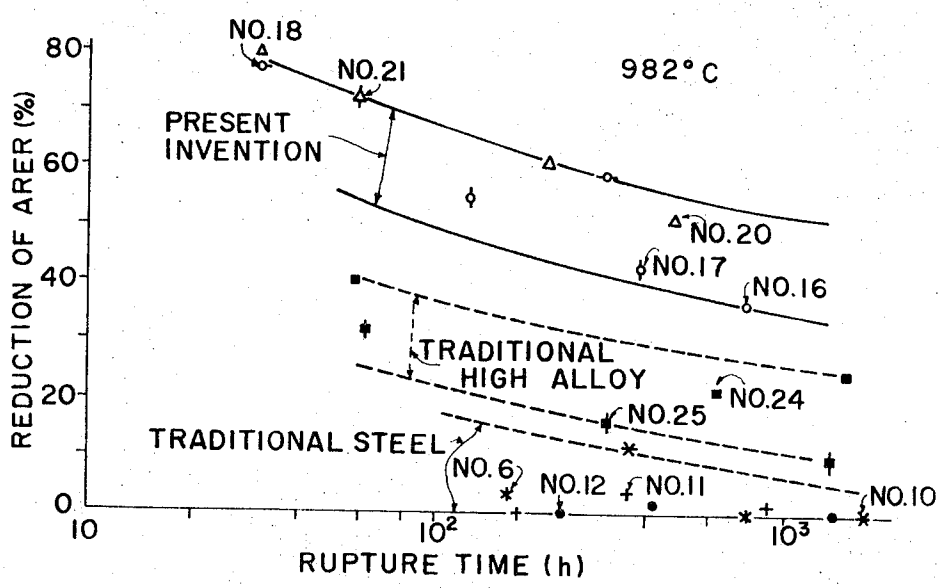
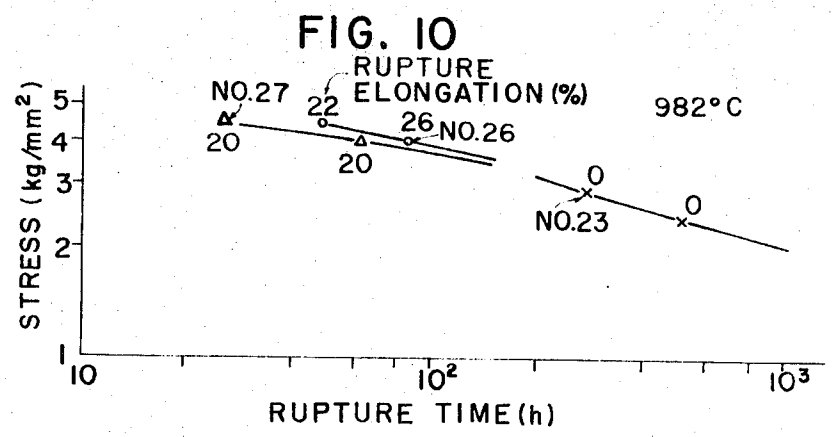


FIG. 10



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FIG. 11

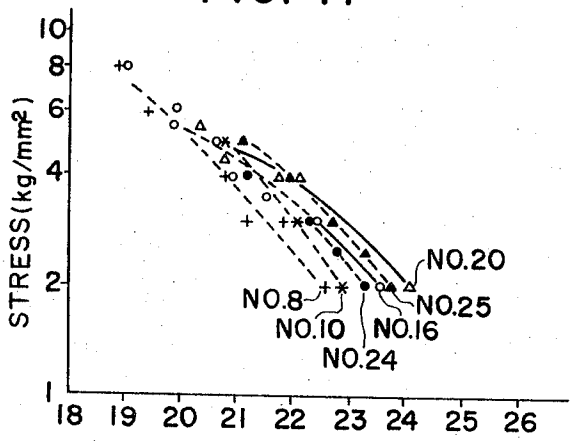
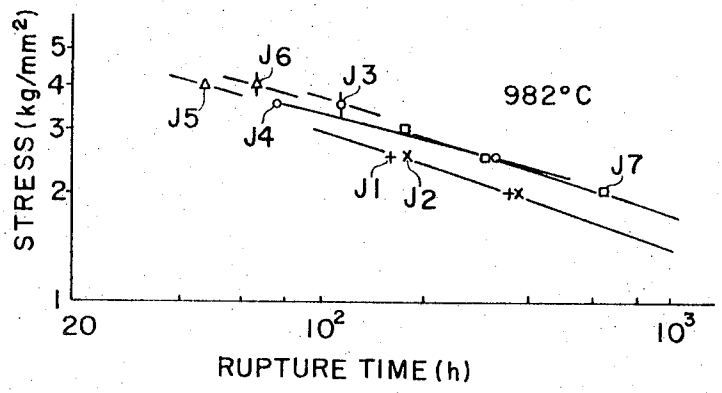


FIG. 16



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FIG. 12

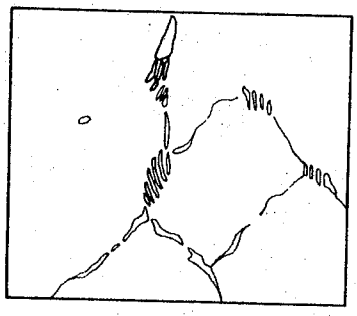


FIG. 13

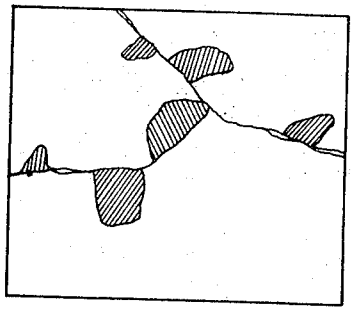


FIG. 14

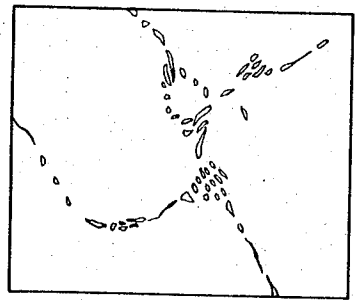
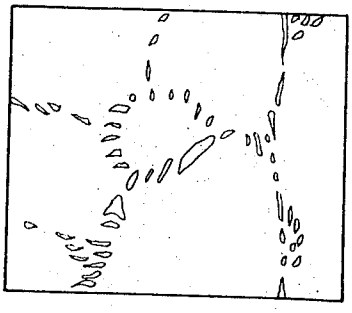


FIG. 15



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FIG. 17

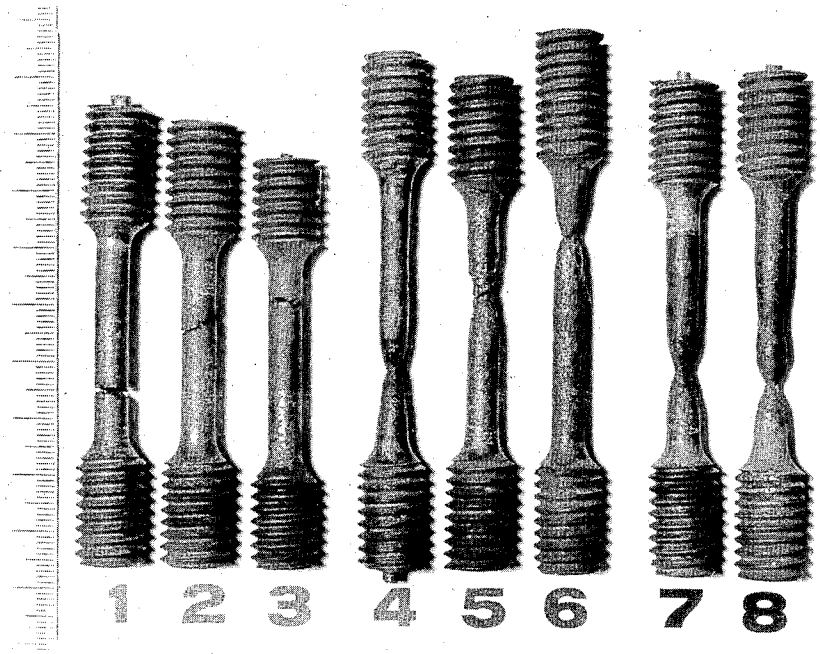


FIG. 18a

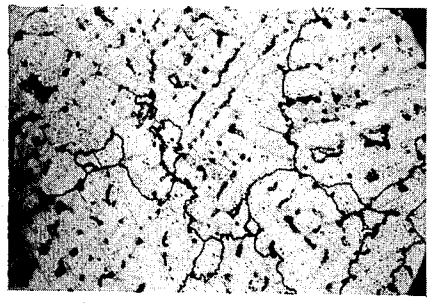


FIG. 18b

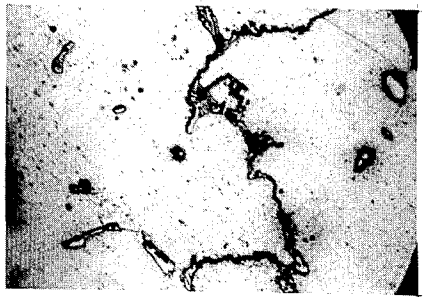


FIG. 18c

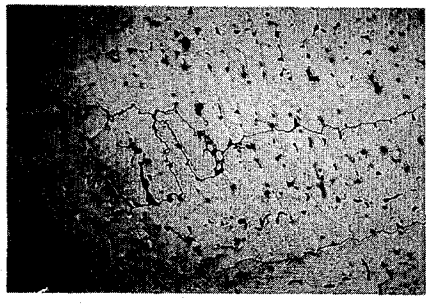


FIG. 18d

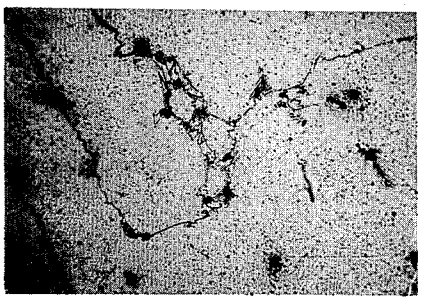


FIG. 18e

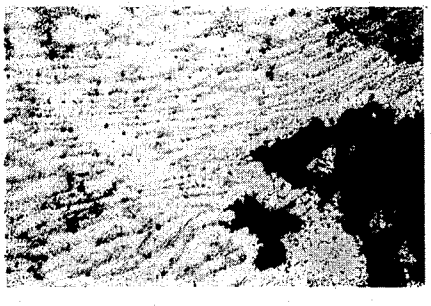
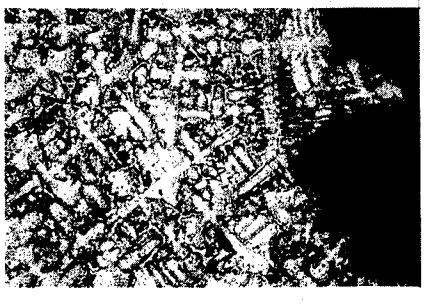


FIG. 18f



AUSTENITIC CAST STEEL OF HIGH STRENGTH AND EXCELLENT DUCTILITY AT HIGH TEMPERATURES

BACKGROUND OF THE INVENTION

This invention relates to an austenitic cast steel having high strength and excellent ductility at high temperatures. More particularly, it relates to an austenitic cast steel having high strength and excellent ductility, particularly at temperatures greater than about 700° C., containing particular amounts of carbon, silicon, manganese, nickel, chromium, titanium and a rare earth metal alloy.

In recent years, the petrochemical industry has grown steadily, particularly in the production of, for example, hydrogen, ammonia and ethylene. A great tendency toward using high temperature and high pressure procedures in order to improve the yields of products has been noted. For the reformer tubes and the cracker tubes occupying the main parts of petrochemical plants, centrifugal casting tubes of 25Cr–20Ni steel or 25Cr–35Ni steel have been used. High alloy casting steels such as 25Cr–20Ni steel, 25Cr–35Ni steel or those steels including W and Co have been used for the bend tubes and the supports. Although such centrifugal casting tubes and casting steels have a high carbon content and show a high strength at high temperatures, they display defects such as being low in ductility especially in the elongation and the reduction of area in creep rupture tests. Accordingly, these steels have a tendency to develop cracks in the tubes and supports with repetitions of the thermal stresses encountered during starting and stopping or during variations in the loads placed upon the apparatus.

SUMMARY OF THE INVENTION

The present invention is concerned with improving the elongation, reduction of area and strength on the creep rupturing and of the elongation and reduction of area on the tensile testing at increased temperatures by adding a small amount of Ti, Nb and a rare earth metal alloy to 25Cr–20Ni steel or to 25Cr–35Ni steel. In general, materials having an increased elongation and reduction of area show an increased durability against repeated thermal stresses.

Heretofore, Cr–Ni austenite steels having Nb, W and Co added thereto showed improved strength, elongation and reduction of area. However, these prior art steels have the disadvantage of being expensive owing to the comparatively great amount of said additives needed in the steel. Moreover, these steels are difficult to weld.

In contrast thereto, the steel according to the present invention contains comparatively small amounts of additives of Ti, Nb and the rare earth metal alloy, thereby making it relatively inexpensive. At the same time, an increased strength, elongation and reduction of area at the creep rupture point are obtained, while maintaining an excellent weldability property.

One of the objects of the present invention is to provide heat-resisting cast steels which are significantly less expensive than the conventional high alloy cast steels.

Another object of the invention is to provide heat-resisting cast steels having a high strength and an excellent ductility at high temperatures.

A further object of the invention is to provide heat-resisting cast steels for use in, for example, petrochemical plants.

A still further object of the invention is to provide austenitic cast steels having increased strength, elongation and reduction of area, particularly at the creep rupture point, and an excellent weldability property.

These and other objects and advantages of the present invention will become apparent to those skilled in the art from a consideration of the following specification and claims, taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. **1**, **2** and **3** show the results of tensile tests taken with respect to certain kinds of conventional cast steels and the novel austenitic cast steels according to the present invention.

Specifically, FIGS. **1**, **2** and **3** show, respectively, the relationship between temperature and tensile strength, rupture elongation and reduction of area;

FIG. **4** shows the results of creep rupture tests;

FIG. **5** and FIG. **7** show the results of creep rupture tests with centrifugal casting tubes and sand mold casting steels, respectively;

FIG. **6** and FIG. **8** show the creep rupture elongation of centrifugal casting tubes and sand mold casting steels, respectively;

FIG. **9** shows the reduction of area after creep rupture tests;

FIG. **10** shows the results of creep rupture tests with centrifugal casting tubes;

FIG. **11** shows a Larson-Miller parameter diagram which represents the creep rupture curves of centrifugal casting tubes;

FIGS. **12**, **13**, **14** and **15**, respectively, are rough sketches of microscopic photographs of cast steels;

FIG. **16** shows the results of creep rupture strength tests with welded joints;

FIG. **17** is a photograph showing the appearances of creep rupture specimens; and

FIGS. **18***a*–**18***f*, respectively, are microscopic photographs of conventional cast steels and the novel cast steels of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples are given merely as illustrative of the present invention and are not to be considered as limiting.

The chemical compositions of the tested samples are shown in Table 1 hereinbelow. Sample Nos. 1–4 were prepared by melting 2.8 to 4 kg. thereof in a high frequency induction furnace. The melt was poured into a metallic mold coated with a coating material of approximately 1 mm. thickness thereon and surrounded with fire bricks, said mold being 60 mm./100 mm./170–25 mm. in dimensional size. An anti-piping material was included in the mold in order to obtain directional solidification.

Sample Nos. 5–18, Nos. 20–23, No. 26 and No. 27 were obtained by preparing a melt in a high frequency induction furnace of approximately 200 to 500 kg. capacity. The melts were casted into a tube-shaped rotary metallic mold coated with a coating material on its inner surface. Centrifugal casting tubes of 70–180 mm. in outer diameter/13–20 mm. in thickness/1,000–3,000 mm. in length were obtained. The Misch metal (tradename, sold by Santoku Metal Industries, Japan) used as the rare earth metal alloy additive has a composition of 52 percent by weight of Ce, 24 percent by weight of La, 18 percent by weight of Nd and 5 percent by weight of Pr. As the Misch Metal is very easily oxidizable, these steels were casted within a shorter time immediately after de-oxidation with Si, Mn and a small amount of Al and the addition of Ti and said Misch metal.

The sample of No. 19 was prepared by casting a sand mold of 22 mm. in diameter × 150 mm. in length provided with a sufficient riser.

Sample Nos. 24 and 25 were purchased on the commercial market, the former being a casted tube of 100 mm. in diameter × 21 mm. in thickness and the latter being a centrifugal casting pipe of 111 mm. in diameter × 13 mm. in thickness.

The steels of the invention are sample Nos. 16–22, No. 26 and No. 27.

Sample Nos. 1–23, No. 26 and No. 27 were subjected for testing under the as-cast condition, while sample Nos. 24 and 25 were tested under the as-purchased condition.

The testing of tensile strength was carried out by the use of a sample of 6 mm. in diameter × 40 mm. in length at its parallel part at room temperature to 982° C. The distance between each standard point for measuring the elongation was $4\sqrt{A}=28$ mm. (wherein A is the cross-sectional area of the sample) at room temperature and $5D = 40$ mm. (wherein D is the diameter of the sample in mm.) at high temperature.

As to the testing of creep rupture, a testing sample of 6 mm. in diameter × 30 mm. in length at its parallel part and of $5D=$ 30 mm. for the gauge length was used, and testing was carried out at a temperature of 800°–1,050° C.

TABLE 1

No.	Chemical composition of cast steels (percent by weight)													P.p.m.		
	C	Si	Mn	P	S	Cu	Ni	Cr	Mo	Ti	Nb	Misch metal[1]	Other additives	N	O	H
1	0.38	1.14	2.55				19.25	24.40								
2	0.38	1.05	1.03				19.08	22.80		0.24						
3	0.38	1.11	2.32				19.88	23.10			0.38					
4	0.40	1.16	2.33				19.85	24.05				(0.35)				
5	0.40	0.73	1.01	0.016	0.022	0.01	19.80	25.35	0.07					456	114	2.2
6	0.41	0.80	1.02	0.016	0.013		20.40	24.80	0.05							
7	0.38	0.82	0.75	0.014	0.024		21.82	24.80	0.08					713	66	9.4
8	0.40	0.87	0.84	0.014	0.017		12.80	24.00	0.08					429	181	7.2
9	0.40	0.53	0.70	0.013	0.027		19.40	25.00	0.06							
10	0.37	1.45	0.40	0.035	0.014		20.99	26.35	0.04					471	136	3.6
11	0.36	1.35	1.08	0.020	0.021		19.10	24.35								
12	0.42	1.22	1.12	0.018	0.004		19.12	24.0				(0.35)				
13	0.38	0.70	0.93	0.016	0.020		19.85	25.40						1,090	104	3.8
14	0.40	0.81	0.94	0.016	0.020		19.65	25.20		0.04				990	31	3.0
15	0.40	0.74	0.01	0.016	0.020		19.65	25.55		0.09	0.35			552	19	4.7
16	0.38	0.75	0.98	10.09	0.018		19.60	25.33	10.0	0.17		(0.35)		233	11	6.7
17	0.41	0.83	0.85	0.014	0.014	0.06	20.72	24.65	0.27	0.26		(0.35)				
18	0.39	0.80	0.87	0.013	0.013	0.06	19.50	24.55	0.08	0.31		(0.3)				
19	0.41	0.93	0.83	0.102	0.025	0.06	21.12	24.60	0.11	0.24		(0.3)				
20	0.40	0.82	1.05	0.020	0.013		19.52	25.52	0.10	0.16	0.32	(0.35)		172	12	7.2
21	0.41	0.75	0.85	0.015	0.014	0.06	20.80	15.03	0.14	0.16	0.31	(0.35)		345	19	9
22	0.45	0.81	0.10	0.018	0.012		19.28	25.38	0.09	0.08	0.30	(0.35)		795	45	2.5
23	0.40	0.82	0.68	0.015	0.015	0.05	34.30	25.60	0.08							
24	0.47	1.86	0.28				51.47	23.40	0.05				5.73W	266	69	5.5
25	0.52	1.73	0.40				34.10	24.20	0.09				5.48W 14.68 Co	750	24	5.3
26	0.40	0.68	0.70	0.015	0.016	0.05	34.35	25.60	0.08	0.22		(0.35)				
27	0.39	0.77	0.68	0.014	0.017	0.05	34.20	25.40	0.08	0.18	0.22	(0.35)				

[1] Amounts of Misch metal are additive amounts.

FIGS. 1, 2 and 3 show the results of testing of the tensile strength at room temperature and at high temperature for sample Nos. 7–10 of centrifugal casting tubes made of a prior art steel and sample Nos. 16, 20 and 22 of centrifugal casting tubes made of the steel according to the present invention. The tensile strength does not differ greatly between the steel of the invention and the steels of the prior art. For example, the difference is 52.4 to 64.5 kg./sq. mm. at room temperature and 15.3 to 20.8 kg./sq.mm. at a temperature of 871° C. These differences are mainly caused by a variation in the working conditions, such as the difference in the composition within the defined range, the manner in which the melting is carried out, the casting temperature and the tube size to be tested.

Insofar as the elongation is concerned, that of the steel of the invention is 18 to 35 percent, which is within the range of the prior art steel having an elongation of 13 to 37 percent at room temperature. However, at higher temperatures, the elongation of the steel of the present invention increases, for example, to about 33 to 54 percent at 950° C. as compared with 20 to 40 percent for the prior art steels.

The superiority in the ductility of the steel according to the invention will be apparent by noting the testing results for the reduction of area. Hence, a 17 to 29 percent reduction of area for the steel according to the invention is within the range of 14 to 36 percent for the prior art steels at room temperature. However, at higher temperatures the value increases greatly as compared with that of the prior art steels, for example, the result obtained with the steels of the invention is about 60 to 88 percent, which is greater than that of the prior art steels by about 21 to 50 percent at 950° C. These advantageous results obtained for the steels of the present invention for the elongation and reduction of area as compared with those of the prior art steels at high temperatures make a great contribution in preventing the causes of cracking owing to the thermal fatigues experienced by apparatus on a practical industrial scale.

The tensile strength of No. 25, a high alloyed steel including approximately 5 percent by weight of W and about 15 percent by weight of Co, is 62 kg./sq.mm., which is about the same as the values for the prior art steels shown in FIG. 1. The elongation and the reduction of area are, respectively, 7 and 6 percent, which values are lower than those of the prior art steels as shown in FIG. 2 and FIG. 3.

FIG. 4 shows the results of the creep rupture test at 982° C. for sample Nos. 1–4, the cast steel prepared by directional solidification. The numerals at the testing point show the rupture elongation. When a small amount of Ti, Nb and Misch metal, respectively, is added to the steel and individually to the 25Cr–20Ni steel, the creep rupture strength is increased. However, the elongation is not improved, the value being less than 5 percent.

FIG. 5 shows the creep rupture strength of a sand mold casting steel No. 19 and centrifugal cast tubes No. 5, Nos. 12–16, Nos. 20 and No. 22 at 950° C. FIG. 6 shows the creep rupture elongation. Comparing these strengths, the strength is minimum for the ordinary centrifugal casting tubes No. 5 and No. 13 which include N as an additive, and the strength is increased when Ti and Nb are added to the steel, such as sample Nos. 14 and 15. The creep rupture strength is gradually increased with the addition of Ti, Misch metal, Nb and furthermore N as shown in steel No. 16, No. 19, No. 20 and No. 22 according to the invention, the gradient of the creep rupture curve becoming small. Particularly, high strength is shown at the side of longer time. Further properties of the steel according to the invention are in the increased creep rupture elongation as compared with prior art steels, as shown in FIG. 6. The increase of the elongation is not obtained by a single addition of Ti, Nb or Misch metal, but can be established by the composite addition of these elements. The steel according to the invention is increased in the reduction of area, for example, the reduction of area of the steel of the invention is increased to 20 to 55 percent when breaking after 100 hours, as compared with 2 to 11 percent for the prior art steels.

Concerning the testing results of creep breaking at 982° C., FIG. 7 shows the creep rupture strength of centrifugal casting tubes No. 6 and Nos. 10–12 of prior art 25Cr–20Ni steel, centrifugal casting tubes Nos. 16–18 and Nos. 20–22 of 25Cr–20 Ni steel including Ti and Misch metal or Ti, Nb and Misch metal according to the present invention and centrifugal casting pipe Nos. 24 and 25 of prior art high alloyed steel including W and Co. FIG. 8 shows the creep rupture elongation of these steels. FIG. 9 shows the reduction of area after testing for the creep breaking. Steel Nos. 16–18 and 20–22 are smaller in the inclination of the curve of creep breaking in comparison with prior art steels No. 6 and Nos. 10–12 and are high in the strength for the long time period, the latter being equal to the high alloy steels No. 24 and No. 25.

Referring to the creep rupture elongation as shown in FIG. 8, the steel of the invention shows a considerably increased improvement in the rupture elongation as compared with prior art 25Cr–20Ni steel as well as with prior art high alloy steel because of the fine dispersion of eutectic carbides owing to the addition of W thereto. Even for the reduction of area, as shown in FIG. 9, the steel according to the invention is superi-

or to prior art carbon steels and alloy steels. Furthermore, necking is displayed by the steel according to the invention which shows the high values of the creep strength.

FIG. **17** is a photograph showing the rupture appearances of specimens subjected to the creep rupture test and show the cause of the necking indicating the increase in elongation and reduction of area for the steel Nos. **4** to **8** according to the invention as compared with prior art steels **1** to **3**. The steel according to the invention consists essentially of 25Cr–20Ni or 25Cr–35Ni steel containing Ti, Nb, Misch metal and N.

FIG. **10** shows the testing results of creep rupture at 982° C. of centrifugal casting tube No. **23** of prior art 25Cr–35Ni steel and centrifugal casting tubes Nos. **26** and **27** of the steel of this invention. The steel according to the present invention has a tendency of decreasing the inclination of the creep rupture curve and in showing a high strength at the side of longer time. Concerning the elongation and the reduction of area of creep rupture, the value becomes extremely low or near zero percent for prior art steels. However, the steels of the invention show a high value of 20 to 26 percent and 25 to 41 percent.

FIG. **11** is a Larson-Miller parameter diagram which is prepared by a Larson-Miller parameter method with respect to the results of creep rupture tests at 800°–1,050° C. on each centrifugal casting pipe. No. **16** and No. **20** of the steels according to the invention are superior in strength to No. **8** and No. **10** of prior art 25Cr–20Ni steels, and at the locations of increased parameter (higher temperature and higher time), No. **16** and No. **20** show higher strength than No. **24** of high alloy steel including W and No. **25** of high alloy steel including Co and W, respectively. Thus, it is very advantageous practically to obtain the higher strength, elongation and reduction of area than the values of the high alloy steels containing W or Co by adding a small amount of Misch metal and Ti and/or Nb to the base of 25Cr–20Ni steel.

In many cases, the centrifugal casting pipes have been made for practical use by solidification from the outer sides, making the macrostructure to the columnar crystals, collecting the impurity layer within the inner surface portion and cutting said inner surface portion off to remove said impurity layer from the casting tubes. Although the elongation on creep rupture becomes increased by making said centrifugal casting tube of equiaxial structure in order to make it easier to deform the grains, as the impurities and the defective parts tend to be included therein and it is difficult to obtain said equiaxial structure industrially in a stable and reproducible manner, castings having said columnar crystals have been produced on a large scale. The steel according to the present invention has columnar crystals and has increased values in the elongation of creep rupture than those of prior art steels having said equiaxial crystals. However, as the characteristics of the present invention can be obtained even in the case of equiaxial crystals, no problems in using castings having said equiaxial crystals are encountered.

FIGS. **12**, **13**, **14** and **15** are rough sketches of microscopic photographs of centrifugal casting tubes No. **5** and No. **13** of 25Cr–20Ni steels of the prior art, centrifugal casting pipe No. **16** of steel according to the invention and centrifugal casting pipe No. **25** of high alloy steel including 5 percent by weight of W. FIG. **12** shows the microstructure consisting of thin carbides at the grain boundaries and larger eutectic carbides as are generally noted. FIG. **13** shows the microstructure as often seen in the cases of increased O and N when using scraps of low grade as the melting materials and in the case of N addition, wherein lamellar Cr carbides other than thin carbides at the grain boundaries are recognized. This structure makes the strength, the elongation and the weldability low and, accordingly, quite disadvantageous. FIG. **14** shows the microstructure of the steel according to the invention, wherein the thin carbides at the grain boundaries and the eutectic carbides are divided. As the steel of this invention includes Ti, Misch metal or further includes Nb, even if scraps of low quality are used for melting, the oxygen and nitrogen are removed by the deoxidizing and denitrizing action of these additives. Even if the steel contains N additive, the harmful lamellar Cr carbides are not formed owing to combination with said added Ti and Nb. The steels according to the invention having a low content of O, high in toughness for the austenite matrix, and having finely divided hard carbides, are high in the elongation and the reduction of area on tensile tests at higher temperatures and on creep rupture tests. The elongation and the reduction of area are not improved only in the case when the Ti and Nb, respectively, are added singly although the carbides are divided as in the case with a high content of O, and when only Misch metal is added, although the O content is low and the toughness of the austenite matrix is high, as the carbides are not divided. The present invention is based upon the finding that only when a composite additive of carbide-forming elements of Ti, Nb and the deoxidizer of Misch metal is employed, the strength, elongation and reduction of area are improved. These effects can be expected not only for the centrifugal casting tubes, but also for cast steels using metallic molds and sand molds.

FIG. **15** shows the microstructure of centrifugal casting tube No. **25**. No. **24** also shows a similar structure. Although the steel in this case contains 5 percent by weight of W and the eutectic carbides are divided, as the austenite matrix is low in toughness, the elongation and the reduction of area are low as mentioned above, and the creep rupture elongation and reduction of area are higher than those of prior art centrifugal casting tubes of 25Cr–20Ni steels, but lower than those of steels according to the present invention as shown in FIGS. **8** and **9**. This factor tends to cause welding cracks because of the high content of W.

FIGS. **18***a*–**18***f* show the micrographs of prior art steels and the steel according to the invention. FIG. **18***a* is a photomicrograph (100 magnifications) of a prior art steel having a structure similar to No. **13**, and FIG. **18***b* is the same photomicrograph at 400 magnifications. As described above with reference to FIG. **12**, the prior art steels have a large amount of eutectic carbides and the boundary carbides are thick. In contrast thereto, for the steel of the invention as shown in FIGS. **18***c* and **18***d*, only a small amount of eutectic carbide is present and fine carbides are dispersed in the grains. FIG. **18***c* is a photomicrograph (100 magnifications) of steel No. **16** and FIG. **18***d* is a photomicrograph (400 magnifications) of the same steel No. **16** FIGS. **18***e* (sample No. **16**) and **18***f* (sample No. **13**) show photomicrographs of the ruptured specimens by creep rupture tests on and the steel according to the invention and the prior art steel, respectively. The dendrite cells of the steel of the invention flow in the direction of stress, and this shows that the steel of the invention has a comparatively high elongation. In the case of the prior art steels, the flow of the dendrite cells in the direction of stress is not found. It is this factor which contributes to the fact that the elongation of the prior art steels is inferior comparatively to that of the present invention.

Welding was effectuated about the centrifugal casting pipes of the prior art 25Cr–20Ni steel and the steel of this invention. The welded conditions were sound for all of the cases as determined from a color check, a bending test and a microscopic examination. FIG. **16** shows the results of the creep rupture test at 982° C. for these welded joints. The joints J1 and J2 were prepared by welding the centrifugal casting tube of prior art 25Cr–20Ni steel with an ordinary welding wire by means of the TIG (tungsten inert gas arc welding) method. The compositions of the wire employed for welding the steel according to the invention are shown in Table 2.

TABLE 2

	Chemical composition of welding wires (percent by weight)										P.p.m.		
No.	C	Si	Mn	P	S	Ni	Cr	Ti	Nb	Misch metal	N	O	H
W1	0.41	0.69	1.57	0.014	0.008	19.62	26.47	0.22	-------	(0.1)	82	11	1.0
W2	0.42	0.71	1.67	0.003	0.009	19.49	26.42	0.28	0.30	(0.1)	69	12	1.5
W3	0.42	0.58	1.81	0.003	0 008	20.66	26.72	0.34	0.31	(0.35)	125	35	1.0

It is preferred to use as small an amount of Misch metal additive as is possible. The joints J3 and J4 were prepared by welding the centrifugal casting tube No. 16 of the steel of the invention with the welding wires W1 and W2, respectively, according to Table 2, by means of the TIG method. The welded joints J5 and J6 were prepared with wires W1 and W3, respectively. The creep rupture strengths of the welded joints J3–J6 of the steel according to the invention are higher than those of the prior art welded joints J1 and J2. The welded joint J7 prepared by welding the steel No. 22 of this invention with an ordinary welding wire by means of the TIG method has more strength than the prior art joints J1 and J2 because of a strengthening of the deposited metal by dilution of the base metal. The wires were prepared by melting in a high frequency induction furnace, in a vacuum for the wires W1 and W2 and in air for the wire W3, and drawing to a wire of 3.2 mm. in diameter and 1.6 mm. in diameter, respectively, after having been forged and rolled. In the case of the vacuum melting procedure, it is preferred that the amount of Misch metal added be less as compared with the air melting procedure.

As described above, the steel according to the present invention shows an increase in the creep rupture strength for a long time and an improved elongation and reduction of area on the creep rupture test and the tensile test by adding Ti, Misch metal, Nb and N to the 25Cr–20Ni steel and the 25Cr–35Ni steel. Although steels having an improved strength by singly adding these elements to the steel have been known in the prior art, steels having decreased oxygen and sulfur contents together with a division of the carbides and showing an improvement in the elongation and the reduction of area by the composite addition with Misch metal have never been proposed heretofore. Also, the steels of the invention can be welded similarly as the prior art 25Cr–20Ni steel.

As the carbides can be divided by an addition of 5 percent by weight of W, as seen in No. 24 and No. 25, the elongation and the reduction of area are increased to a greater extent than those of the prior art 25Cr–20Ni steel, but less than those of the steel of this invention. Moreover, this type of steel is difficult to weld. The cost thereof becomes expensive because a high content of Ni is needed because of its inferiority in oxidation resistance and its tendency to cause the σ-phase owing to the high content of W.

The steel in accordance with the present invention contains the following additives: 0.30 to 0.55 percent by weight of C, 0.3 to 2.0 percent by weight of Si, 0.5 to 3.0 percent by weight of Mn, 15 to 40 percent by weight of Ni, 20 to 30 percent by weight of Cr, 0.05 to 0.6 percent by weight of Ti, 0.05 to 0.5 percent by weight of Misch metal in an additive amount, 0.07 to 0.7 percent by weight of Nb as needed, less than 50 p.p.m. of O and less than 1,000 p.p.m. of N. The reasons behind the particular stated ranges for each of these elements in the steels of the invention are as follows:

C; 0.30 to 0.55 percent

C is added to increase the strength and to stabilize the austenite structure. When added in an amount less than 0.3 percent by weight, both of these properties are insufficient. The 0.55 percent by weight upper limit is based upon the fact that as the C content increases, the ductility and machinability goes down. A particularly preferred range of content of carbon is 0.35 to 0.48 percent by weight.

Si: 0.2 to 2.0 percent

Si is added for deoxidation reasons. When added in an amount less than 0.2 percent by weight, a sufficient deoxidation is not obtained. The upper limit of 2.0 percent by weight is based upon the fact that when the content of silicon is over this amount, the weldability becomes inferior and a tendency to cause σ-phase brings about an embrittlement. The range of 0.5 to 1.2 percent by weight is most preferred.

Mn: 0.5 to 3.0 percent

Mn is added as a deoxidizer and a desulfurizer. When added in an amount less than 0.5 percent by weight, these actions are not sufficient. And, when an amount higher than the stated range is employed, the oxidation resistance property and the creep rupture strength go down, hence the upper limit of 3.0 percent by weight. The preferred range of this additive is 0.7 to 2.0 percent by weight.

Ni: 15 to 40 percent

Ni is added to produce the austenite structure and to increase the strength. When added in an amount less than 15 percent by weight, not only is the stable austenite structure not obtained, but also the brittle σ-phase is created. Although the austenite structure becomes stable and the resistance to carbon cementation is higher as the nickel content increases, a sufficient amount is 40 percent by weight. Thus, the stated range is 15 to 40 percent by weight, taking into account these factors as well as the factor of cost. The preferred range is 18 to 38 percent by weight.

Cr: 20 to 30 percent

Cr is added to give an anti-oxidizing property and the hot corrosion resistance property at high temperatures to the steel. When added in an amount less than 20 percent by weight, these properties are not sufficient. Although these properties are improved as the chromium content increases, there is no problem in an amount of 30 percent by weight until a temperature of 1,100° C. is reached. Moreover, higher contents of Cr cause the σ-phase to be formed. Thus, the range of 20 to 30 percent by weight is thought to be advantageous. The preferred range is 23 to 28 % by weight.

Ti: 0.05 to 0.6 percent

Ti prevents the production of the lamellar carbides, divides the carbides finely, has a deoxidizing action and increases the elongation and the reduction of area on the high temperature tensile strength by the composite addition together with Misch metal. Also, the creep rupture strength is increased by the fine precipitation of titanium carbide, titanium nitride and titanium carbonitride. When an amount less than 0.05 percent by weight is employed, these effects are not achieved. When more than 0.6 percent by weight is used, the inclusions are increased and the inner impurity layer becomes thicker. The preferred range is 0.15 to 0.35 percent by weight.

Rare Earth Metal Alloy: 0.05 to 0.5 percent

A rare earth metal alloy such as Misch metal composed of mixtures of rare earth elements having Ce and La as the main component has a strong deoxidizing action as well as denitrizing and desulfurizing actions, makes the O, N and S content of the steel low, increases the ductility of the austenite matrix, prevents the production of the lamellar carbide and increases the elongation and the reduction of area on the tensile test at high temperatures and on the creep rupture test significantly together with a facility for dividing the carbides. Since this additive is susceptible to oxidation loss in the melt, the steel must be casted as soon as possible immediately after the addition thereof. A part of the rare earth metal alloy additive makes it possible to increase a creep rupture strength and the resistance property to oxidation as an alloying element. The results shown in Table 3 were obtained by the analysis of La and Ce contained in the castings of sample Nos. 16–20.

TABLE 3

Sample Number--	16	17	18	19	20	21	22
Percent by wt.:							
La		0.0009	0.0043	0.0043	0.0004		
Ce		0.006	0.014	0.014	0.005		

Thus, it was recognized that Misch metal added as the rare earth metal alloy had been consumed to below one one-hundredth or less of the amount added to the casting. In one case, the analysis value could not be detected even though there had been an addition of Misch metal to the steel. However, even in this case, the effect of the addition of the Misch metal can be recognized in the excellence of the mechanical properties and the small O content in the steel. Although a range of additive amount of Misch metal is disclosed hereinabove, it must be noted that said amount does not mean the content thereof in the casting. The amount proposed as the amount of addition is for the sake of convenience. When the amount added is less than 0.05 percent by weight, the effects as mentioned above are very small. Although the advantageous pro-

perties become noticeable as the additive amount increases, a sufficient amount is 0.6 percent by weight. The addition of more than this amount increases the number of inclusions and makes the inner incomplete layer become thicker. In the case of vacuum melting, the amount to be added may be preferably smaller, as compared with the case of melting in air, because the smaller content of O reduces the amount of Misch metal consumed by oxidation.

Nb: 0.07 to 0.7 percent

Nb is a carbide-forming element similar to Ti and prevents the formation of the lamellar carbide, divides the boundary carbides and the eutectic carbides finely and increases the elongation and the reduction of area on the high temperature tensile test and the creep rupture test by the composite effect with the deoxidizing action provided by the Misch metal additive. Also, the niobium increases the creep rupture strength by precipitating finely as niobium carbide and niobium carbonitride. Particularly, the creep rupture strength at the side of higher temperature and longer time is increased by the composite addition of Ti and Misch metal. The effectiveness on the strength and the ductility is not obtained when the Nb is added in an amount less than 0.07 percent by weight. An addition of more than 0.7 percent by weight increases the amount of the inclusions and makes the oxidation resistance property inferior. The preferred range is 0.1 to 0.4 percent by weight.

O: Below 50 p.p.m.

Oxygen is normally included in ordinary steels in an amount of about 60 to 150 p.p.m. because a high content of O has a tendency to make the austenite matrix brittle and to cause a formation of the harmful lamellar carbide; the lesser amounts are preferred in order to increase the elongation and the reduction of area. Although the O content in the steel according to the present invention is considerably low due to the addition of Ti and Misch metal, said O content varies according to the material to be molten and the melting method. However, the content should be below 50 p.p.m. by consideration of the ductility property. In fact, a content below 30 p.p.m. is most preferable. It has been found that the elongation and the reduction of area were not improved even though the O content was decreased by only vacuum melting and vacuum casting. This is caused by not having fine carbides. Accordingly, a cast steel having a small content of oxygen and also finely divided carbides can be obtained in accordance with the present invention, said steel having excellent mechanical properties.

N: Below 1,000 p.p.m.

Nitrogen is normally included in conventional austenite steel, in a range of approximately 300 to 600 p.p.m. In the case of adding N in order to increase the strength of the steel, about 1,000 p.p.m. of N is included. Although such a high content of N increases the tensile strength and the short time creep rupture strength, as the inclination of the creep rupture curve becomes large, the long time strength becomes inferior and harmful lamellar carbides are created. It is thus preferable not to use too much nitrogen in the steel. Even though a relatively high content of N is used in the steel of the present invention, said lamellar carbides are not formed due to the included Ti, Misch metal and Nb additives. Thus, nitrogen contents of up to approximately 1,000 p.p.m. can be employed in the steel of the invention when high tensile strength and short time creep rupture properties are important. However, from the point of view of the long time creep rupture strength and the ductility property, a content below 400 p.p.m. is preferred.

It can be seen from the above description that the steels of the present invention have advantageous properties which make them highly useful and adaptable in the production of many products, such as reformer tubes, cracker tubes, supports and bends, pipes, ties and the like.

The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included herein.

It is claimed:

1. An austenitic heat-resisting cast steel consisting essentially of C in the range from 0.30 to 0.55 percent, Si in the range from 0.2 to 2.0 percent, Mn in the range from 0.5 to 3.0 percent, Ni in the range from 15 to 40 percent, Cr in the range from 20 to 30 percent, Ti in the range from 0.05 to 0.6 percent, a rare earth metal alloy containing Ce and La as the main components added in the range from 0.05 to 0.5 percent and the balance substantially iron, the percents all being by weight, said cast steel being substantially free from gaseous impurities and possessing excellent ductility at temperatures higher than about 700° C.

2. An austenitic heat-resisting cast steel consisting essentially of C in the range from 0.35 to 0.48 percent, Si in the range from 0.5 to 1.2 percent, Mn in the range from 0.7 to 2.0 percent, Ni in the range from 18 to 38 percent, Cr in the range from 23 to 28 percent, Ti in the range from 0.15 to 0.35 percent, a rare earth metal alloy containing Ce and La as the main components added in the range from 0.20 to 0.45 percent and the balance substantially iron, the cast steel containing not more than 50 p.p.m. of oxygen and 400 p.p.m. of nitrogen, respectively, the percents all being by weight, said cast steel possessing high creep rupture strength and excellent ductility at temperatures higher than 700° C.

3. An austenitic heat-resisting cast steel consisting essentially of C in the range from 0.30 to 0.55 percent, Si in the range from 0.2 to 2.0 percent, Mn in the range from 0.5 to 3.0 percent, Ni in the range from 15 to 40 percent, Cr in the range from 20 to 30 percent, Ti in the range from 0.05 to 0.6 percent, a rare earth metal alloy containing Ce and La as the main components added in the range from 0.05 to 0.5 percent and the balance substantially iron, the cast steel containing not more than 50 p.p.m. of oxygen and 400 p.p.m. of nitrogen, respectively, the percents all being by weight, said cast steel possessing tensile strength greater than 7 kg./mm.^{2}, an elongation larger than about 23 percent and a reduction of area larger than about 35 percent at temperatures ranging between 850° and 1,000° C.

4. An austenitic heat-resisting cast steel consisting essentially of C in the range from 0.30 to 0.55 percent, Si in the range from 0.2 to 2.0 percent, Mn in the range from 0.5 to 3.0 percent, Ni in the range from 15 to 40 percent, Cr in the range from 20 to 30 percent, Ti in the range from 0.05 to 0.6 percent, Misch metal containing Ce and La as the main components added in the range from 0.05 to 0.5 percent and the balance substantially iron, the percents all being by weight, said cast steel possessing excellent ductility at temperatures higher than about 700° C.

5. The austenitic cast steel of claim 4, wherein the Misch metal has composition of 52 percent by weight of Ce, 24 percent by weight of La, 18 percent by weight of Nd, and 5 percent by weight of Pr.

6. An austenitic heat-resisting cast steel consisting essentially of C in the range from 0.35 to 0.48 percent, Si in the range from 0.5 to 1.2 percent, Mn in the range from 0.7 to 2.0 percent, Ni in the range from 18 to 38 percent, Cr in the range from 23 to 28 percent, Ti in the range from 0.15 to 0.35 percent, Misch metal containing Ce and La as the main components added in the range from 0.20 to 45 percent and the balance substantially iron, the cast steel containing not more than 50 p.p.m. of oxygen and 400 p.p.m. of nitrogen, respectively the percents all being by weight, said cast steel possessing high creep rupture strength and excellent ductility at temperatures higher than about 700° C.

7. The austenitic cast steel of claim 6, wherein the Misch metal has composition of 52 percent by weight of Ce, 24 percent by weight of La, 18 percent by weight of Nd, and 5 percent by weight of Pr.

8. An austenitic heat-resisting cast steel of high creep rupture strength and excellent ductility at temperatures higher than about 850° C. for use in chemical apparatus consisting essentially of C in the range from 0.30 to 0.55 percent, Si in the range from 0.2 to 2.0 percent, Mn in the range from 0.5 to 3.0 percent, Ni in the range from 18 to 38 percent, Cr in the range from 23 to 28 percent, Ti in the range from 0.05 to 0.6 per-

cent, a rare earth metal alloy containing Ce and La as the main components added in the range from 0.20 to 0.45 percent and the balance substantially iron, the cast steel containing not more than 50 p.p.m. of oxygen and 400 p.p.m. of nitrogen, respectively, the percents all being by weight.

9. A welding wire comprised of an austenitic heat-resisting steel material consisting essentially of C in the range from 0.30 to 0.55 percent, Si in the range from 0.2 to 2.0 percent, Mn in the range from 0.5 to 3.0 percent, Ni in the range from 15 to 40 percent, Cr in the range from 20 to 30 percent, Ti in the range from 0.05 to 0.6 percent, a rare earth metal alloy containing Ce and La as the main components added in the range from 0.05 to 0.5 percent and the balance substantially iron, the amount of oxygen contained in the steel being less than 50 p.p.m., the percents all being by weight.

10. An austenitic heat-resisting cast steel consisting essentially of C in the range from 0.30 to 0.55 percent, Si in the range from 0.2 to 2.0 percent, Mn in the range from 0.5 to 3.0 percent, Ni in the range from 15 to 40 percent, Cr in the range from 20 to 30 percent, Ti in the range from 0.05 to 0.6 percent, a rare earth metal alloy containing Ce and La as the main components added in the range from 0.05 to 0.5 percent, Nb in the range from 0.07 to 0.7 percent, and the balance substantially iron, the percents all being by weight, said cast steel being substantially free from gaseous impurities and possessing excellent ductility at temperatures higher than about 700° C.

11. An austenitic heat-resisting cast steel consisting essentially of C in the range from 0.30 to 0.55 percent, Si in the range from 0.2 to 2.0 percent, Mn in the range from 0.5 to 3.0 percent, Ni in the range from 15 to 40 percent, Cr in the range from 20 to 30 percent, Ti in the range from 0.05 to 0.6 percent, a rare earth metal alloy containing Ce and La as the main components added in the range from 0.05 to 0.5 percent and the balance substantially iron, wherein an amount of oxygen contained in the steel is not greater than 50 p.p.m. and an amount of nitrogen contained is not greater than 1,000 p.p.m., said cast steel possessing excellent ductility at temperatures higher than about 700° C.

12. An austenitic heat-resisting cast steel consisting essentially of C in the range from 0.35 to 0.48 percent, Si in the range from 0.5 to 1.2 percent, Mn in the range from 0.7 to 2.0 percent, Ni in the range from 18 to 38 percent, Cr in the range from 23 to 28 percent, Ti in the range from 0.15 to 0.35 percent, a rare earth metal alloy containing Ce and La as the main components added in the range from 0.20 to 0.45 percent, Nb in the range from 0.1 to 0.4 percent and the balance substantially iron, the cast steel containing not more than 50 p.p.m. of oxygen and 400 p.p.m. of nitrogen, respectively, the percents all being by weight, said cast steel possessing high creep rupture strength and excellent ductility at temperatures higher than about 700° C.

13. An austenitic heat-resisting cast steel consisting essentially of C in the range from 0.30 to 0.55 percent, Si in the range from 0.2 percent, Mn in the range from 0.5+ to 3 percent, Ni in the range from 15 to 40 percent, Cr in the range from 20 to 30 percent, Ti in the range from 0.05 to 0.6 percent, a rare earth metal alloy containing Ce and La as the main components added in the range from 0.05 to 0.5 percent, Nb in the range from 0.07 to 0.7 percent and the balance substantially iron, the cast steel containing not more than 50 p.p.m. of oxygen and 400 p.p.m. of nitrogen, respectively, the percents all being by weight, said cast steel possessing a tensile strength greater than about 7 kg./mm.^{2}, an elongation larger than about 35 percent and a reduction of area larger than about 35 percent at temperatures ranging between 850° and 1,000° C.

14. An austenitic heat-resisting cast steel consisting essentially of C in the range from 0.30 to 0.55 percent, Si in the range from 0.2 to 2.0 percent, Mn in the range from 0.5 to 3.0 percent, Ni in the range from 15 to 40 percent, Cr in the range from 20 to 30 percent, Ti in the range from 0.05 to 0.6 percent, Nb in the range from 0.07 to 0.7 percent, Misch metal containing Ce and La as the main components added in the range from 0.05 to 0.5 percent and the balance substantially iron, the percents all being by weight.

15. An austenitic heat-resisting cast steel consisting essentially of C in the range from 0.35 to 0.48 percent, Si in the range from 0.5 to 1.2 percent, Mn in the range from 0.7 to 2.0 percent, Ni in the range from 18 to 38 percent, Cr in the range from 23 to 28 percent, Ti in the range from 0.15 to 0.35 percent, Nb in the range from 0.1 to 0.4 percent, Misch metal containing Ce and La as the main components added in the range from 0.20 to 0.45 percent and the balance substantially iron, the cast steel containing not more than 50 p.p.m. of oxygen and 400 p.p.m. of nitrogen, respectively, the percents all being by weight, said cast steel possessing high creep rupture strength and excellent ductility at temperatures higher than about 700° C.

16. An austenitic heat-resisting cast steel of high creep rupture strength and excellent ductility at temperatures higher than about 850° C. for use in chemical apparatus consisting essentially of C in the range of from 0.30 to 0.55 percent, Si in the range from 0.2 to 2 percent, Mn in the range from 0.5 to 3 percent, Ni in the range from 18 to 38 percent, Cr in the range from 23 to 28 percent, Ti in the range from 0.05 to 0.6 percent, Nb in the range from 0.07 to 0.7 percent, a rare earth metal alloy containing Ce and La as the main components added in the range from 0.2 to 0.45 percent and the balance substantially iron, the cast steel containing not more than 50 p.p.m. of oxygen and 400 p.p.m. of nitrogen, respectively, the percents all being by weight.

17. A welding wire composed of an austenitic heat resisting steel material consisting essentially of C in the range from 0.3 to 0.55 percent, Si in the range from 0.2 to 2 percent, Mn in the range from 0.5 to 3 percent, Ti in the range from 0.05 to 0.6 percent, Nb in the range from 0.07 to 0.7 percent, a rare earth metal alloy containing Ce and La as the main components and the balance substantially iron, the amount of oxygen contained in the steel being less than 50 p.p.m., the percents all being by weight.

18. The austenitic cast steel of claim **10**, wherein the amount of oxygen contained as impurities in the steel is not greater than 50 p.p.m.

19. The austenitic cast steel of claim **10**, wherein the amount of nitrogen contained in the steel is not greater than 1,000 p.p.m.

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