

[54] **HIGH CORROSION FATIGUE STRENGTH STAINLESS STEEL**
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[22] Filed: **May 31, 1973**
[21] Appl. No.: **365,714**

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[52] **U.S. Cl.**..... **75/128 A; 75/128 C; 75/128 G; 75/128 T; 75/128 W; 148/38**
[51] **Int. Cl.²**..... **C22C 38/44; C22C 38/48; C22C 38/58**
[58] **Field of Search**..... **75/128 W, 128 A, 128 C, 75/128 G, 128 T; 148/38**

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[57] **ABSTRACT**
A high corrosion fatigue strength stainless steel is formed by combining less than 0.07 wt% carbon, less than 0.05 wt% nitrogen, from 0.1 to 2 wt% silicon, from 0.1 to 4 wt% manganese, from 10 to 15 wt% chromium, from 2 to 7 wt% nickel, from 0.1 to 3 wt% molybdenum, and a total of from 0.01 to 1 wt% of at least one element from the group of titanium, niobium and tantalum with the balance being iron, impurities and other incidental constituents.

1 Claim, 5 Drawing Figures

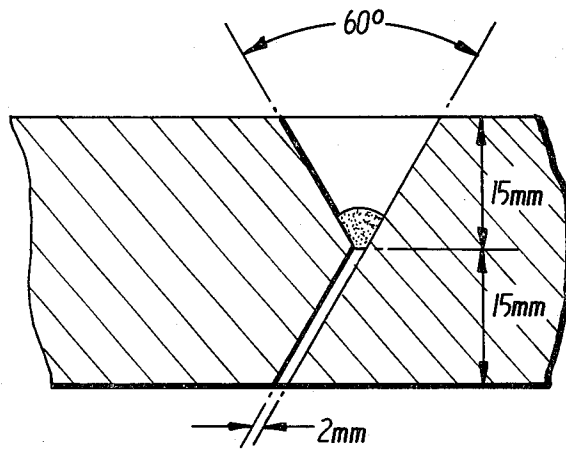


FIG. 1

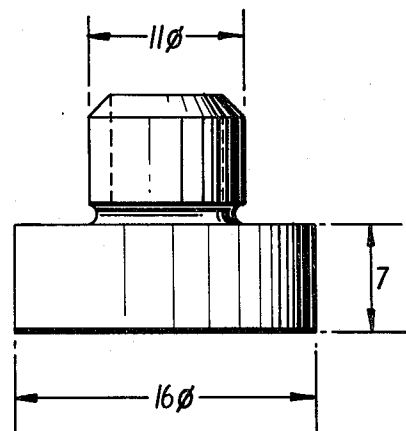


FIG. 3

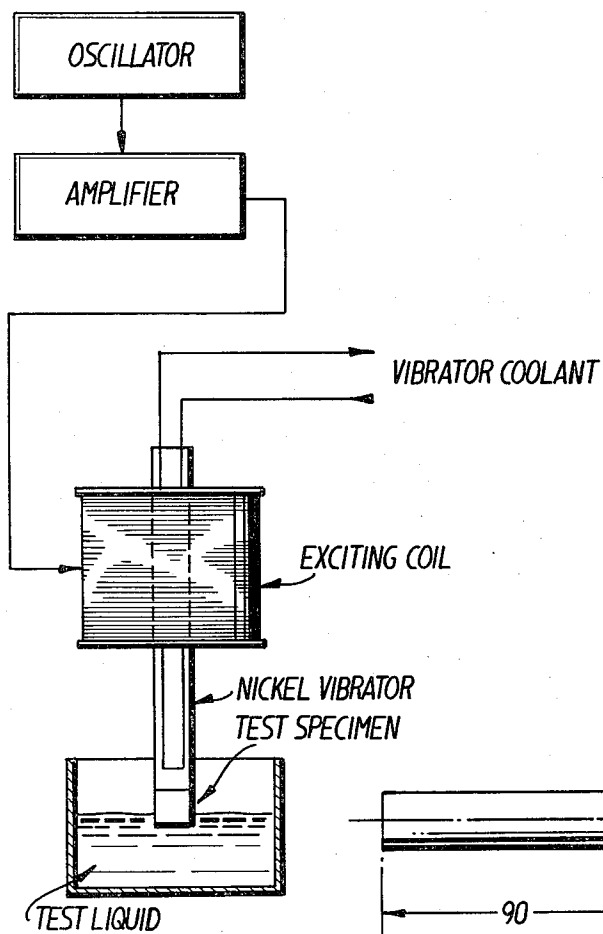


FIG. 2

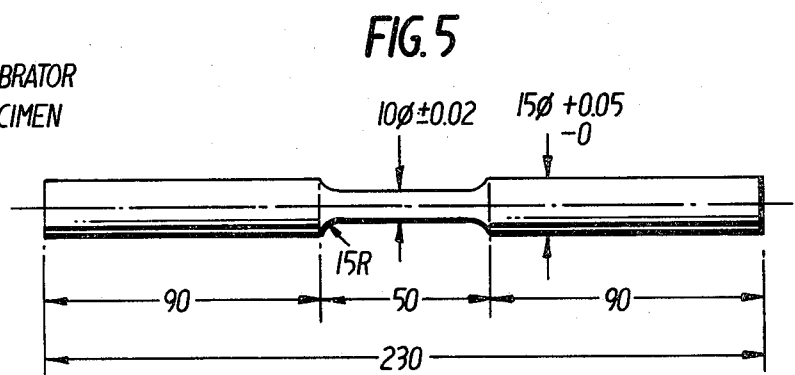


FIG. 5

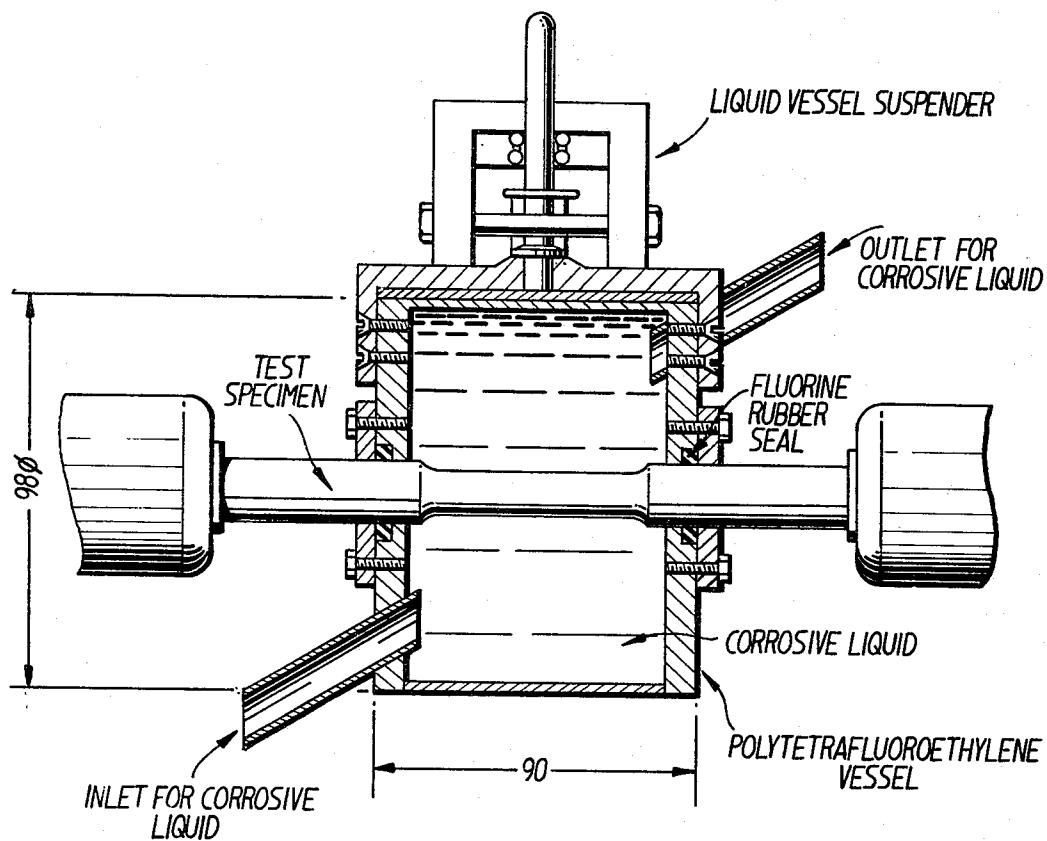


FIG. 4

HIGH CORROSION FATIGUE STRENGTH STAINLESS STEEL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a stainless steel especially suited for casting and which has high corrosion fatigue resistance and excellent weldability. More particularly, this invention relates to a stainless steel suited for casting and which is useful as a casting material for purposes such as ship engine propellers or water turbine runners.

2. Description of the Prior Art:

Recently, the production of large, high speed ships has imposed increasingly stringent requirements on the material design of ship propellers. For instance, such factors as corrosion resistance, resistance to cavitation damage and fatigue strength in the corrosive sea water environment, especially under sustained stress conditions, have become of substantial importance. Furthermore, from the repair or maintenance standpoint, very good weldability of propellers is required, particularly for water turbine runners. Previously, 13%-Cr martensitic stainless steel had been used for this application. However, whenever it became necessary to weld repair, austenitic welding electrodes had to be used because of the poor weldability of such steels. To some extent, the strength of the base metal was thereby sacrificed.

It has also been known to use manganese bronze or nickel-aluminum bronze alloys for sea water ship propellers in order to provide good castability, corrosion resistance and machineability. However, these types of alloys are no longer used because of the aforementioned severe material requirements imposed on ship propellers and water turbine runners.

A need, therefore, exists for a stainless steel which is suitable for use as a ship propeller, a hydrofoil or water turbine runner, and yet which has high corrosion fatigue strength and good weldability.

SUMMARY OF THE INVENTION

Accordingly, one object of the present invention is to provide a stainless steel having high corrosion fatigue strength, high resistance to cavitation damage and good weldability as well as good mechanical properties, which is suitable for use as a casting material for ship propellers and water turbine runners.

Briefly, these objects and other objects of the invention as hereinafter will become readily apparent can be attained by a highly corrosion resistant and high fatigue strength stainless steel which contains less than 0.07 wt% carbon, less than 0.05 wt% nitrogen, from 0.1 to 2 wt% silicon, from 0.1 to 4 wt% manganese, from 10 to 15 wt% chromium, from 2 to 7 wt% nickel, from 0.1 to 3% molybdenum and a total of from 0.01 to 1 wt% of at least one of titanium, niobium and tantalum with the balance of the composition being iron together with impurities or incidental constituents.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention and many of the attendant advantages thereof will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings, wherein:

FIG. 1 is a diagram of a welding test device;

FIG. 2 is an illustration of a steel specimen for use in a magnetostriction oscillation cavitation test device;

FIG. 3 is a diagram of a magnetostriction oscillation cavitation device;

FIG. 4 is a diagram of a corrosion fatigue test device showing the construction of a liquid vessel; and

FIG. 5 is an illustration of a steel specimen for use in a corrosion fatigue test device (mm).

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Progress toward the development of the stainless steel of this invention has been made possible by the following discoveries:

The addition of a certain amount of at least one of the elements Ti, Nb and Ta in the presence of Mo in a steel eliminates embrittlement of the steel which is caused by the presence of C and N compounds in the steel.

The corrosion fatigue strength of the steel is improved by minimizing the amount of C and N.

Appropriate concentrations of Cr and Ni also improve the corrosion fatigue strength and weldability of the steel.

Certain amounts of Mo also improve these characteristics.

Certain amounts of Si promote embrittlement of the steel.

The addition of manganese in certain concentrations not only provides considerable savings by limiting the consumption of Ni as an alloy element, but also improves the toughness of the steel.

The stainless steels of the present invention are subjected to normalization at temperatures of from 900° to 1100°C, or, after the normalization treatment, to tempering at temperatures of from 550° to 750°C (stress relieving annealing). It is important, especially when the steel is cast that it be annealed one to three times at temperatures from 550° to 850°C. The structure of a stainless steel treated in this manner consists essentially of a martensitic and austenitic structure. The concentration levels of the alloying elements and the heat treatments of the steel should be adjusted so that the retained austenitic level is in the range of from 10 to 45%, and the ferrite level remains below 20%.

The present invention thus provides a high corrosion fatigue strength stainless steel especially suited for casting, which comprises less than 0.07wt% carbon, less than 0.05 wt% nitrogen, from 0.1 to 2 wt% silicon, from 0.1 to 4 wt% manganese, from 10 to 15 wt% chromium, from 2 to 7 wt% nickel, from 0.1 to 3 wt% molybdenum and a total of from 0.01 to 1 wt% of at least one of the elements titanium, niobium and tantalum with the balance being substantially iron and impurities.

The amount of carbon in the steel should be limited to less than 0.07 wt% because a carbon level exceeding the upper limit reduces the toughness of large products made from the steel, such as cast and slow cooled castings of stainless steels which may be prepared according to the procedure of the present invention. Furthermore, concentration levels of carbon above the limit indicated have adverse effects on the corrosion fatigue strength, corrosion resistance and weldability. These properties are optimized when the carbon level is maintained below 0.05%.

The amount of nitrogen in the steel should also be limited to less than 0.05% because it forms nitrides

which cause embrittlement and thus lower the corrosion fatigue strength. The desired properties of the steel are optimized when the nitrogen level is below 0.03 %.

The amount of Si in the steel can vary between 0.1 and 2%. Silicon is included in the steel melt in concentrations over 0.1% to act as a deoxidizer. However, if the concentration exceeds 2%, embrittlement of the steel is promoted.

Manganese should be present in the steel in amounts ranging from 0.1 to 4%. A minimum of about 0.1% of manganese is necessary as an austenizing element which improves the toughness of the steel and also serves as a deoxidizer. Manganese contents in excess of 4% are too high and do not provide any further improvement in the desired properties of the steel.

Chromium should be limited to within the range of from 10 to 15%. Chromium is an essential component in this type of stainless steel, since its presence greatly improves the corrosion resistance of the steel. To achieve the objects of the invention, that is, to make a steel which possesses the desired degree of corrosion resistance in sea water and fresh water, it is necessary that the chromium be present in concentrations which exceed 10%. The corrosion resistance of the alloy increases with increasing chromium levels. Chromium contents in excess of 15%, are, however, detrimental as that high a percent increases the likelihood of formation of delta-ferrite steel which causes embrittlement and lowers the corrosion fatigue strength. The desired properties can be optimized when the chromium level is from 12 to 14%.

Nickel contents should be within the range of from 2 to 7%. The presence of nickel in the alloy serves as an outstanding austenite forming element. At least 2% nickel is necessary in order to improve the toughness and weldability of the steel. However, nickel contents in excess of 7% increase the proportions of retained austenitic character so that the required corrosion fatigue strength is not obtained. Nickel contents within the range defined above meet the requirement of a steel having from 10 to 45% retained austenite character and having less than 20% delta-ferrite character after suitable heat treatments and thus provides the desired mechanical properties. The optimum nickel content, which increases the corrosion fatigue strength of the steel without decreasing toughness, is interdependent with the chromium and molybdenum contents. For example, if from 12 to 14% Cr is used, from 4 to 6% nickel is a suitable amount.

Molybdenum is present in amounts ranging from 0.1 to 3%. Molybdenum contents of at least 0.1% are necessary to substantially increase the corrosion fatigue strength as well as to increase the resistance to corrosive environments such as sea water, in co-operation with carbide forming elements such as titanium, niobium and tantalum. If the molybdenum content exceeds 3%, however, no appreciable improvement is observed in these properties, but rather embrittlement is promoted and poor corrosion fatigue strength results.

At least one of the elements titanium, niobium and tantalum should be present in the steel in amounts so that the total content of these elements is within the range of from 0.01 to 1%. Titanium, niobium or tantalum in the presence of molybdenum suppresses the precipitation of carbides or nitrides of chromium, and thus increases the corrosion fatigue strength. Further, they are effective in improving erosion and intergranular corrosion resistance. For these purposes, the titanium, niobium and/or tantalum content as single elements or in combination in the presence of molybdenum should be at least 0.01%. If the content of these elements is in excess of 1% the alloy will be susceptible to deleterious segregation, which lessens the toughness of the steel.

Having generally described this invention, a further understanding can be obtained by reference to certain specific examples which are provided herein for purpose of illustration only and are not intended to be limiting unless otherwise specified.

EXAMPLES

Table I shows the compositions of various samples of steel and Table II gives the mechanical properties, resistance to cavitation damage and corrosion fatigue strength of these samples.

Samples 1 to 5 and 13 to 17 represent various stainless steel compositions according to the present invention. Samples 6 to 12 are various comparative examples whose compositions are outside the scope of the present invention. These samples were prepared by heating a 20 kg cast material to 1150°C, then cooling the cast material at a rate of 15°C/hr to room temperature. By this procedure were obtained large size castings having a heat history which corresponds to the history of a casting which has been cast, slowly cooled and then subjected to a heat treatment at a residual stress relieving annealing temperature.

As shown in Table II, the results obtained from the steels of this invention show considerable improvement in properties over the steels of the comparative examples.

TABLE I

		CHEMICAL COMPOSITION OF STAINLESS STEEL SAMPLES (WT%)											
Sample No.		C	Si	Mn	P	S	Cr	Ni	Mo	Ti	Nb	Ta	N
1	Present Invention	0.03	0.25	0.53	0.019	0.008	12.68	5.10	1.05	—	0.24	—	0.02
2		0.03	0.29	0.51	0.019	0.009	14.72	5.40	1.04	—	0.26	—	0.02
3		0.03	0.25	0.52	0.019	0.010	12.87	5.30	0.98	0.15	—	—	0.02
4		0.03	0.23	0.49	0.019	0.011	12.91	5.23	1.01	—	0.19	0.03	0.02
5		0.03	0.26	0.51	0.018	0.010	12.96	5.18	1.00	—	—	0.43	0.02
6	Comparative Examples	0.12	0.45	0.55	0.022	0.009	12.57	0.51	—	—	—	—	0.02
7		0.03	0.20	0.51	0.020	0.008	12.77	5.08	—	—	—	—	0.02
8		0.08	0.42	0.79	0.022	0.007	12.45	5.95	1.47	—	—	—	0.02
9		0.03	0.23	0.49	0.017	0.009	12.91	5.11	—	—	0.25	—	0.02
10		0.06	0.27	0.47	0.026	0.009	15.18	4.50	2.87	—	0.43	—	0.02
11		0.05	0.37	0.42	0.027	0.009	15.93	4.63	1.04	—	0.29	—	0.02
12		0.04	0.40	0.67	0.022	0.010	14.57	4.58	1.04	—	0.25	—	0.10
13	Present Invention	0.02	0.21	0.48	0.018	0.009	13.20	6.71	1.01	—	0.25	—	0.02
14		0.03	0.28	0.53	0.019	0.010	12.98	3.33	0.97	—	0.27	—	0.02
15		0.03	0.22	0.47	0.019	0.008	10.74	5.03	1.08	—	0.26	—	0.02
16		0.06	0.27	0.48	0.021	0.011	13.01	5.10	1.00	—	0.25	—	0.04
17		0.03	0.28	0.53	0.020	0.011	12.99	4.97	0.97	—	0.25	—	0.04

TABLE II

Sample No.		PROPERTIES OF SAMPLES				Weight loss due to cavitation erosion (mg)*	Fatigue Strength in 3% NaCl (kg/mm ²)**
		0.2 ρ Field Strength (kg/mm ²)	Tensile Strength (kg/mm ²)	Elongation (%)	Charpy impact value (2mm V 0°C.) (kg.m/cm ²)		
1	Present Invention	70.2	95.3	16	3.5	6.5	>30
2		64.7	91.3	21	3.0	6.8	>30
3		69.3	94.8	16	3.7	6.8	>30
4		70.5	95.1	16	3.5	6.7	>30
5		69.9	95.7	16	3.6	6.9	>30
6	Comparative Examples	30.2	52.5	19	0.6	13.4	10
7		62.8	85.3	18	9.5	9.0	14
8		75.3	95.7	17	8.5	6.2	13
9		71.1	88.3	16	3.7	7.1	18
10		60.2	90.0	8	0.8	7.5	17
11		61.5	90.2	16	2.0	8.2	20
12		59.2	91.4	18	1.1	7.8	18
13	Present Invention	45.2	94.2	25	5.7	7.7	27
14		63.7	92.1	15	2.7	6.8	>30
15		72.6	98.3	14	3.2	6.4	>30
16		70.7	95.8	16	3.6	6.8	23
17		70.1	95.3	16	3.5	6.9	25

Remarks:

(*)denotes the weight loss of the steels due to cavitation erosion as determined by a vibratory test. (Test conditions: frequency 6.5 kc, amplitude, 6 microns, 3% NaCl, 25°C, 3 hours).

(**)denotes a rotation bending test (10⁷ cycles).

Table III is a comparison of the properties of two stainless steels both having the composition of sample 1 wherein one steel was tested in an as cast condition and the other was tested after the casted metal had been subjected to an annealing treatment. As is apparent from this table the stainless steels of the present invention have impact values comparable to the comparative stainless steels and yet have a higher corrosion fatigue strength.

FIGS. 2 to 5 are illustrations of other test devices used for testing the steels and samples of steel suitable for testing.

TABLE IV

Sample No.	WELDING TEST RESULTS	
	Cracks after welding test	
from 1 to 5	Absent	
from 6 to 12	Present	
from 13 to 17	Absent	

TABLE III

Sample No.	Heat History	HEAT HISTORY OF SAMPLES AND PROPERTIES THEREOF					
		0.2% Yield Strength (kg/mm ²)	Tensile Strength (kg/mm ²)	Elongation (%)	Charpy impact value (2mm V notch 0°C.) (kg.m/cm ²)	Weight loss due to cavitation erosion* (mg)	Fatigue Strength in 3% NaCl** (kg/mm ²)
1	As cast (Slow Cooling)	50.2	82.2	5	1.0	—	—
	As cast :1050°C. × 5 hours Furnace Cooling :650°C. × 5 hours	53.5	86.4	22	4.6	6.9	>30

(*) and (**) have the same meaning as described in Table II.

Tables IV and V give the welding test results of the samples of the present invention and the comparative samples. The welding tests were conducted according to the procedures of the so-called Y type weld Cracking test which by nature is kind of a binding test. The particular test procedures themselves are of little significance as this test is intended only for a comparison of the samples. In order to obtain a better understanding of the test, an illustration of the test device is shown in FIG. 1. In this test, the root spacing is 2mm and the ambient temperature is room temperature.

Table V gives the mechanical properties and the corrosion fatigue strength of the welding specimens.

TABLE V

MECHANICAL PROPERTIES & CORROSION FATIGUE STRENGTH OF THE WELDING SPECIMENS			
0.2% Yield Strength (kg/mm ²)	Tensile Strength (kg/mm ²)	Elongation (%)	Broken portion
67.3	89.2	18	Base metal
Charpy impact value (2mm V, 0°C.)		Bending	Fatigue

TABLE V-continued

MECHANICAL PROPERTIES & CORROSION FATIGUE STRENGTH OF THE WELDING SPECIMENS				
0.2% Yield Strength (kg/mm ²)	Tensile Strength (kg/mm ²)	Elongation (%)	Broken portion	
	(kg.m/cm ²)	R=2T 130°	Strength in 3% NaCl (kg/mm ²)	
Base metal	Heat affected zone	Deposit	No Cracks	30
3.5	4.6	5.4		

The test results shown in Table I to V show the data obtained for the various corrosion fatigue strength, resistance to cavitation damage and weldability tests conducted. The results show the superior properties which the steels of the present invention possess compared to those of the prior art alloys.

The stainless steels of the present invention can be used as forged, rolled and/or rod materials. The properties of these materials are the same as those of the casted metal. For example, Tables VI and VII show the chemical composition and the properties of a forged rod (20mm diameter) according to the present invention.

TABLE VI

CHEMICAL COMPOSITION OF THE FORGED MATERIAL									
C	Si	Mn	P	S	Cr	Ni	Mo	Nb	N
0.03	0.31	0.56	0.011	0.010	12.81	4.98	0.97	0.27	0.02

Heat treatment: 1050°C × 3 hours air cooling followed by 650°C × 5 hours air cooling.

TABLE VII

MECHANICAL PROPERTIES OF THE FORGED MATERIAL				
0.2% Yield Strength (kg/mm ²)	Tensile Strength (kg/mm ²)	Elonga- tion (%)	Charpy impact value (2mmV,0°C.) (kg.m/cm ²)	Fatigue Strength in 3% NaCl (kg/mm ²)
69.5	93.5	21	15.2	>30

10 The stainless steels according to the present invention can be readily made in a conventional electric arc furnace or in a high frequency induction furnace, and necessitate no particular casting process. They are well suited, especially, for use as materials for ship propellers, hydrofoils and water turbine runners which require steels having high corrosion fatigue strength and good weldability.

15 Having now fully described this invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit or scope of the invention as set forth herein.

20 What is claimed as new and intended to be covered by Letters Patent is:

25 1. A high corrosion fatigue strength stainless steel which consists essentially of less than 0.05 wt% carbon, less than 0.03 wt% nitrogen, from 0.1 to 2 wt% silicon, from 0.1 to 4 wt% manganese, from 12 to 14 wt% chromium, from 4 to 6 wt% nickel, from 0.1 to 3 wt% molybdenum and a total of from 0.01 to 1 wt% of at least one element selected from the group consisting of titanium, niobium and tantalum with the balance being essentially iron such that said steel has from 10 - 45% retained austenite.

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