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Brandis et al.

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[54] **FERRITIC STAINLESS STEEL**

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Oct. 28, 1971 Germany 2153766

[52] **U.S. Cl.** .... **75/126 C,** 75/125, 75/126 J, 75/126 P, 75/126 Q, 75/128 C, 75/128 F, 75/128 N, 75/128 W

[51] **Int. Cl.**.. **C22c 39/20,** C22c 39/50, C22c 39/54

[58] **Field of Search** ...... 75/126 C, 125, 124, 126 P, 75/126 Q, 126 T, 128 C, 128 F, 128 N, 128 W

[56] **References Cited**

UNITED STATES PATENTS

2,121,590	6/1938	Espe	75/126 C
2,141,016	12/1968	Payson	75/128 W
2,200,545	5/1940	Field	75/126 C
2,624,669	1/1953	Crafts	75/126 C
2,624,671	1/1953	Binder	75/126 R
3,562,781	2/1971	Tanczyn	75/125
3,713,812	1/1973	Brickner	75/126 C
3,726,668	4/1973	Baumel	75/126 C

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Assistant Examiner—Arthur J. Steiner
Attorney, Agent, or Firm—Kenyon & Kenyon Reilly Carr & Chapin

[57] **ABSTRACT**

A ferritic stainless steel containing 18 to 35% chromium and having a very low carbon and nitrogen content, the total of the two preferably being not greater than 0.01%, has a molybdenum content of from at least 0.5% and up to 6.0%. As compared to prior art ferritic high-chromium stainless steels, this new steel gives substantially greater resistance to corrosion by fluids containing chlorides, higher notched bar impact and tensile test values, has in general substantially improved cold formability, and has other advantageous properties which may be increased by the addition of alloying elements.

1 Claim, 4 Drawing Figures

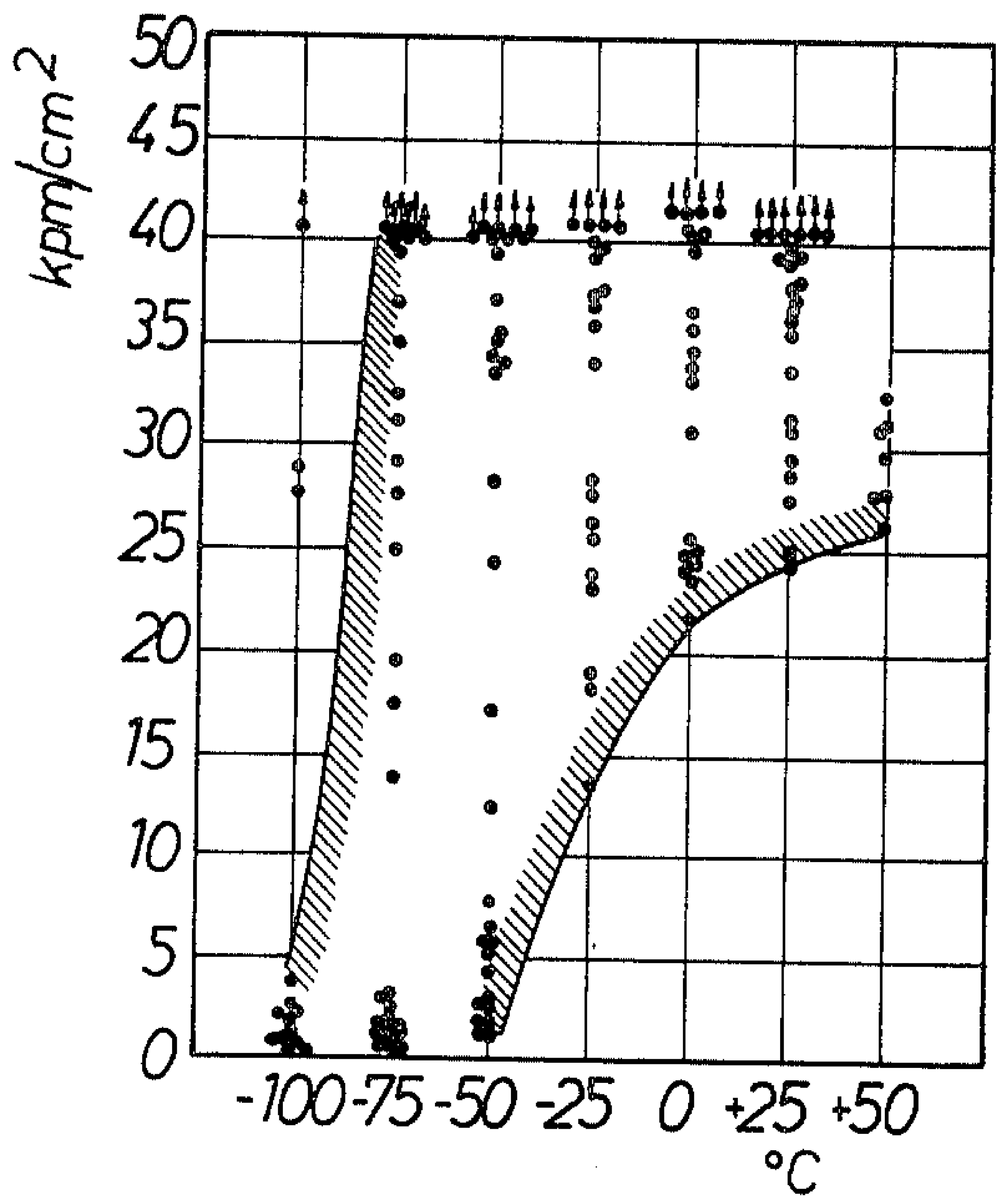

kpm/cm²
50
45
40
35
30
25
20
15
10
5
0
-100 -75 -50 -25 0 +25 +50
°C

Fig.1

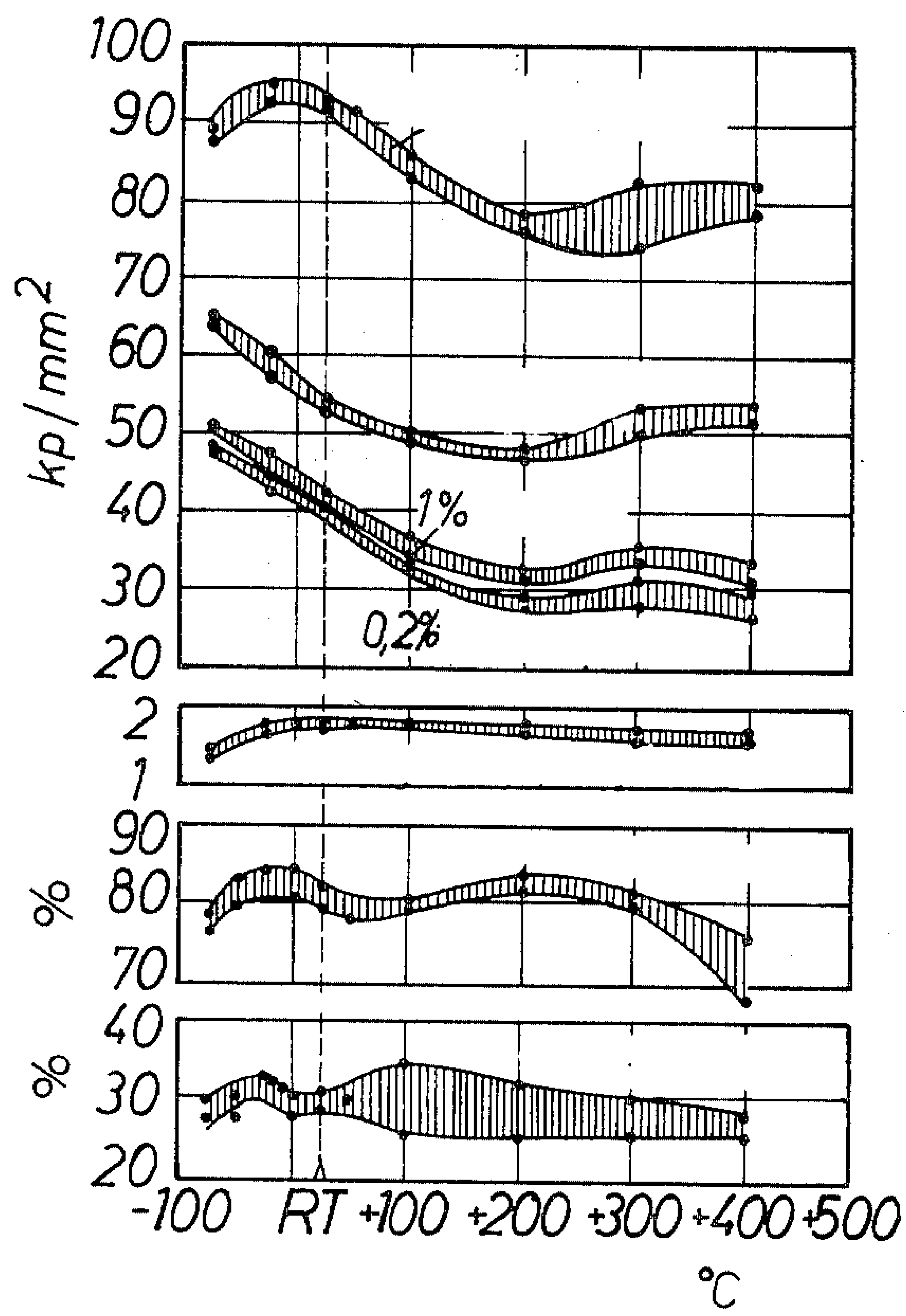

kp/mm²
100
90
80
70
60
50
40
30
20
1%
0,2%
2
1
%
90
80
70
%
40
30
20
-100 RT +100 +200 +300 +400 +500
°C

Fig.2

Fig. 4

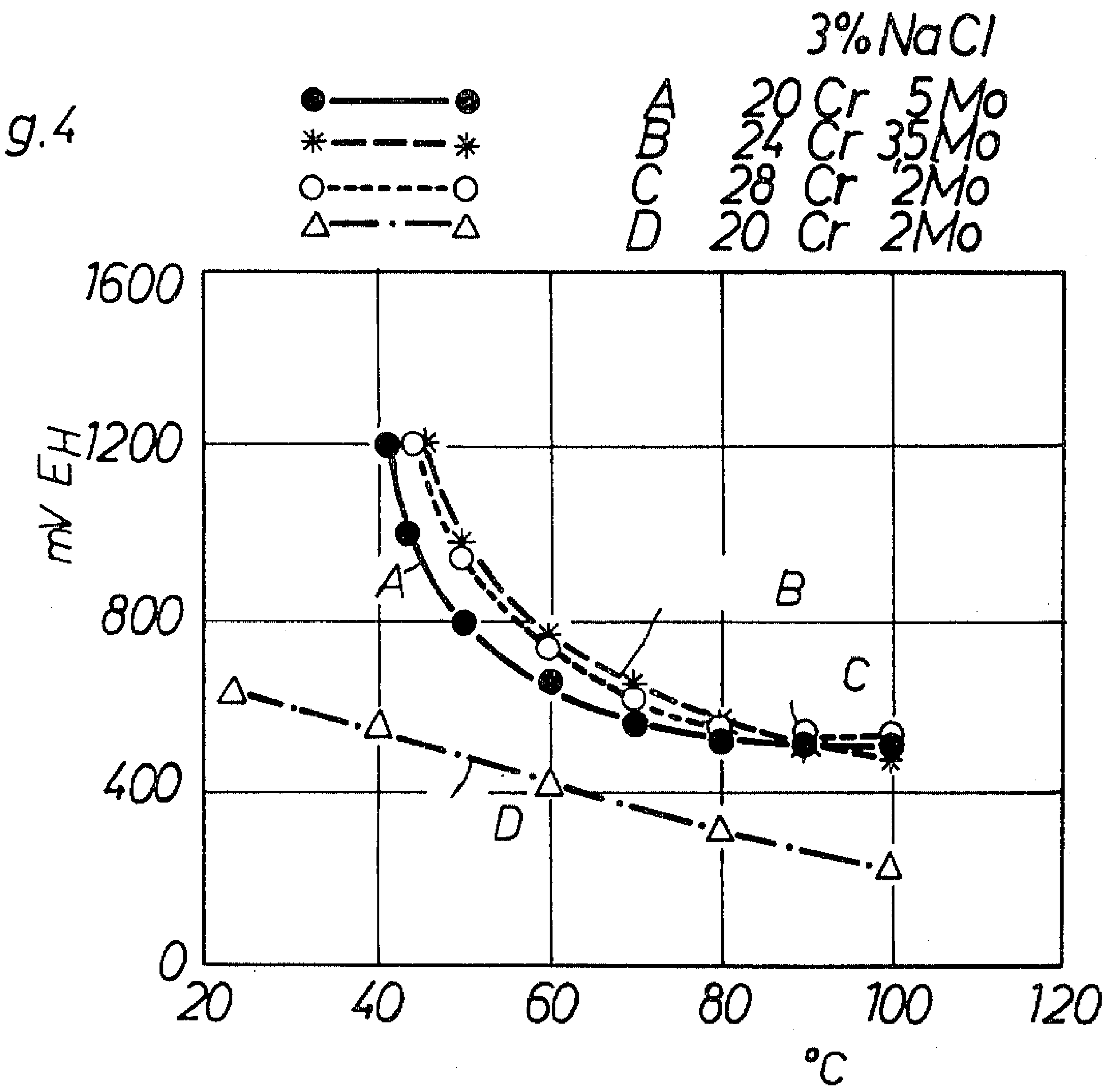
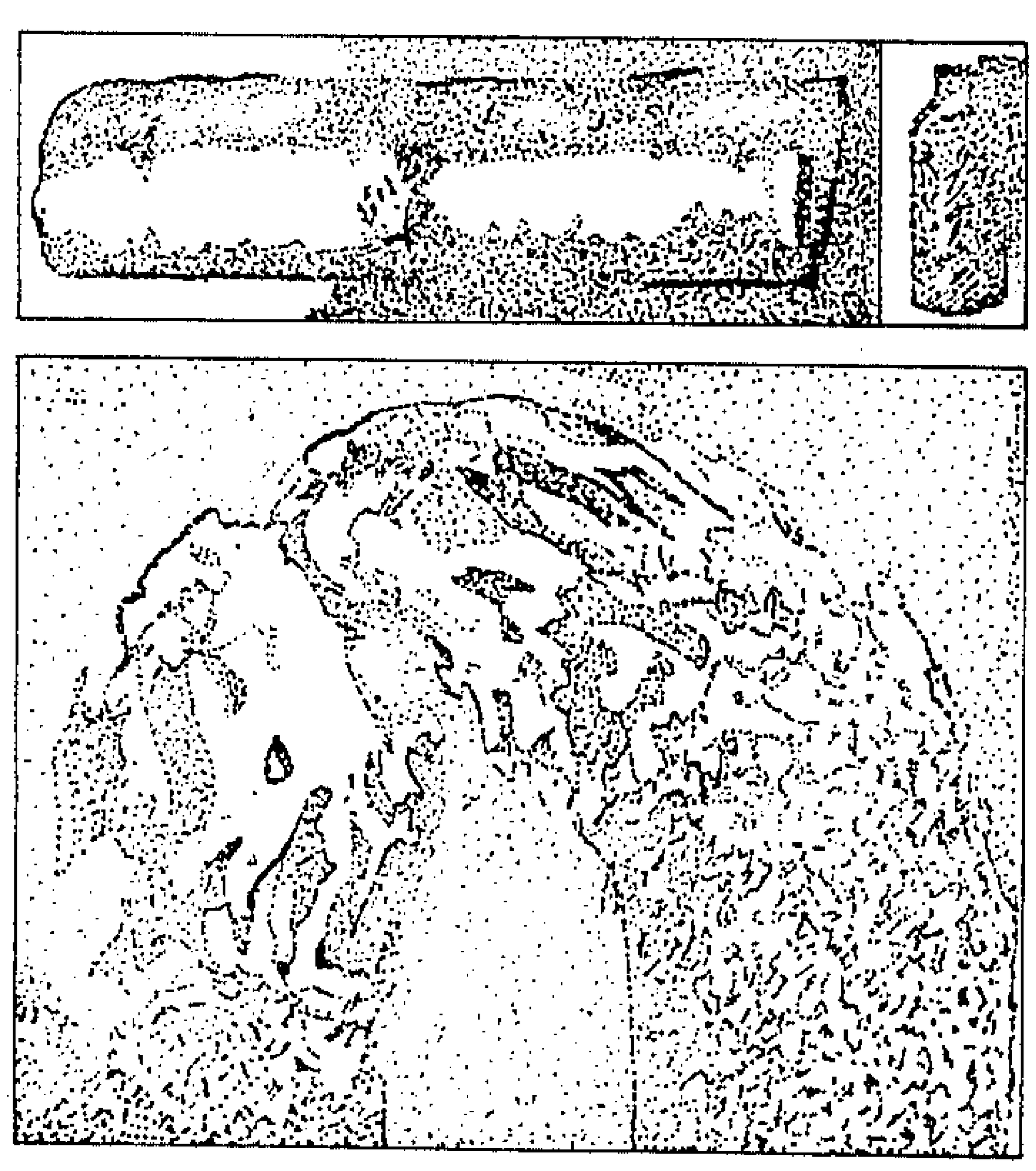

3% NaCl
A 20 Cr 5Mo
B 24 Cr 35Mo
C 28 Cr 2Mo
D 20 Cr 2Mo
mV EH
1600
1200
800
400
0
20
40
60
80
100
120
°C
A
B
C
D

Fig. 3



FERRITIC STAINLESS STEEL

BACKGROUND OF THE INVENTION

The austenitic stainless steels have almost exclusively been specified for the manufacture of chemical processing equipment and in some cases, such as enclosures containing corrosive liquids under pressure, have been considered to be mandatory. Their advantages are well known. However, they do have disadvantages, one being that they are very susceptible to stress-corrosion cracking.

The ferritic stainless steels are fundamentally resistant to stress-corrosion cracking as can be shown by testing them in boiling 42% magnesium-chloride solutions, or in a calcium-chloride solution having a mercury-chloride addition. Such steels contain adequate chromium to develop passivity as required to make them qualify as stainless steels. To meet severe operating conditions, they contain up to from 20 to 30% chromium, an example being Type No. 446 of the American Iron and Steel Institute Standard Type Numbers, this steel containing from 23 to 27% chromium.

However, prior art ferritic stainless steels become brittle when cold-worked; they give low notched bar impact and tensile test values. This brittleness is exhibited not only at subnormal temperatures but also at temperatures up to 100°C. and even somewhat higher. Also, when heated, as during welding, and quickly cooled, they may be brittle.

Another disadvantage suffered by ferritic stainless steels has been that their general resistance to corrosion when subjected to fluids containing chlorides has been insufficient to permit their use when such conditions are encountered. This lack of resistance to such corrosion has prevented the use of ferritic stainless steels in many applications, the austenitic stainless steels being used instead.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a ferritic high-chromium stainless steel which is free from the disadvantages of prior art ferritic high-chromium stainless steels, to a degree permitting it to compete more successfully with the austenitic stainless steels in all fields.

According to the present invention, this object is attained by a steel containing from 18 to 35% chromium and having very low carbon and nitrogen contents, the total of the two preferably being not greater than 0.01%, and having a molybdenum content of from at least 0.5% and up to 6.0%, the balance being iron, the new steel optionally including certain additional alloying elements.

The carbon and nitrogen content in conjunction with the high chromium content is insufficient to result in the formation of chromium carbides or nitrides at the grain boundaries of the steel, this resulting in the steel having adequately high notched bar impact and tensile test values even if the steel is rendered course grained by being heated. The molybdenum provides for adequate corrosion resistance when the steel is subjected to corrosive fluids containing chlorides.

DESCRIPTION OF THE DRAWINGS

FIG. 1 graphically shows notched impact strengths at differing temperatures;

FIG. 2 graphically shows tensile stength characteristics;

FIG. 3 illustrates a bent specimen of a sheet of steel; and

FIG. 4 graphically shows the pitting tendency of four steels.

DESCRIPTION OF THE INVENTION

The ferritic high-chromium stainless steels of this invention have compositions within the following ranges:

18 to 35%	chromium
6 to 0.5%	molybdenum
0 to 5%	nickel
0 to 2%	copper
0 to 3%	silicon
0 to 1%	manganese
0 to 0.5%	apiece of titanium, zirconium, niobium or tantalum, boron, aluminum
0 to 0.015%	carbon
0 to 0.015%	nitrogen

Remainder iron and impurities occasioned by smelting conditions

In the above and throughout this specification and the appended claims, all references to compositional percentages are by weight.

With increasing chromium content, ranging from 18 to 25%, there is an increase in the passivity obtained by these new steels. Chromium contents below 18% do not provide sufficient passivity to be considered acceptable when meeting severe corrosion conditions; more than 35% of chromium does not appear to provide further improvement in passivity.

The low carbon and nitrogen contents prevent the formation of excessive compounds at the grain boundaries with the attendant trouble this might cause. Although the maximum content of carbon and nitrogen are specified at 0.015%, each it is preferable that their total should not exceed 0.01%.

The novel molybdenum content specified for use in these new ferritic stainless steels provides a very substantial and decisive improvement in their resistance to corrosive pitting and passivity. It is surprisingly effective in rendering the new steels generally resistant to corrosion when subject to the attack of fluids containing chlorides, this contrasting with the lack of resistance to such attacks by prior art ferritic high-chromium stainless steels. At the same time their fundamental resistance to stress-corrosion cracking is not deleteriously affected.

With the lower chromium contents, the higher molybdenum contents are used, and with the higher chromium contents, the lower molybdenum contents are used, all while keeping within the specified ranges for the chromium and molybdenum contents.

It can be seen that the new steels essentially consist of the chromium contents, the maintenance of carbon and nitrogen at the low levels specified, and the molybdenum contents specified. The balance, is, of course, mainly iron, the reference to impurities being with the understanding that such impurities must be kept below values that would produce a harmful effect on the properties of the steel. The optional use of the other alloying elements is explained as follows:

The use of up to 5% nickel, preferably 1.5 to 4%, increases both the cold-toughness and the corrosion resistance of the new steels, particularly when they must operate under reducing conditions.

As to the copper specified, its use of up to 2%, preferably from 0.05 to 1.5%, and of silicon up to 3%, preferably from 0.5 to 2%, has the advantage of further improving the resistance to corrosion.

The further optional additions of 0.5%, preferably 0.01 to 0.5% of the elements titanium, zirconium, either niobium or tantalum, improve the cold-toughness and machinability of the new steels. The same advantages are obtained by the optional addition of up to 0.5%, preferably 0.001 to 0.01 of boron. These additions also improve the weldability and the resistance of the steel to intergranular corrosion in the transition zones of welds.

As indicated, it is permissible to have present up to 1% of manganese and up to 0.5% of aluminum.

Because of their high chromium contents, the ferritic stainless steels made in accordance with this invention have great resistance to corrosion under oxidizing conditions as might be expected. In addition, and surprisingly, it has been found that these steels, even under reducing conditions, have excellent resistance to corrosion, far superior to those of known austenitic chromium-nickel steels which also contain molybdenum. In the following Tables 1, 2 and 3, for a ferritic stainless steel of this invention, containing 28% chromium and 2% molybdenum, the remainder being essentially iron, a comparison is made as to resistance to corrosion in boiling formic acid, acetic acid, and mixtures of them (Table 1), in boiling phosphoric acid (Table 2), and in oxalic acid (Table 3), in the latter case at different temperatures and acid concentrations, the steel of the invention being compared with known austenitic chromium-nickel and chromium-nickel-molybdenum steels of the composition given in each case.

Table 1

Resistance to corrosion in boiling formic acid, acetic acid, and their mixtures (test lasted 24 hours) Weight loss in g/m². h

Steel	Material No.	10% CH_3COOH	20% CHOOH	60 % CH_3COOH +10% HCOOH
28% Cr, 2% Mo, Rest Fe	—	0	0.04	0
X5 CrNi 18 9	1.4301	0.14	1.22	1.24
X5 CrNiMo 18 10	1.4401	0	0.91	0.50

Table 2

Resistance to corrosion in boiling phosphoric acid (Test lasted 24 hours) Weight loss in g/m². h

Steel	Material No.	50% P	H_3PO_4 A	60% P	H_3PO_4 A	70% P	H_3PO_4 A
28% Cr, 2% Mo, Rest Fe	—	<0.01	0.01	0.13	0.11	0.50	0.51
X2 CrNiMo 18 10	1.4404	0.35	n.b.	0.88	n.b.	3.5	n.b.
X5 CrNiMoTi 25 25	1.4577	0.01	0.02	0.01/1.2	1.9	2.1	n.b.

P = air-passive use
A = used after activating with zinc
n.b. = not determined

Table 3

Corrosion resistance in oxalic acid. (Test lasted 24 hours) Weight loss in g/m². h

Acid Concentration	Test Temp.	28% Cr, 2% Mo, Rest Fe	X5 CrNiMo 18 12	X5 CrNiMoTi 25 25
	40	<0.01	0.10	<0.01
5%	60	<0.01	0.11	<0.01
	80	<0.01	0.30	0.07

Table 3 – Continued

Corrosion resistance in oxalic acid. (Test lasted 24 hours) Weight loss in g/m². h

Acid Concentration	Test Temp.	28% Cr, 2% Mo, Rest Fe	X5 CrNiMo 18 12	X5 CrNiMoTi 25 25
	Sp	0.01	1.02	0.80
	40	<0.01	0.03	<0.01
10%	60	<0.01	0.16	<0.01
	80	<0.01	0.35	<0.01
	Sp	0.01	1.90	1.10
	40	n.b.	0.11	n.b.
20%	60	n.b.	0.29	0.03
	80	<0.01	0.34	<0.01
	Sp	<0.01	2.0	0.97
35%	Sp	0.01	n.b.	n.b.
50%	Sp	0.01	n.b.	n.b.

n.b. = not determined
Sp = boiling point

From the above Tables 1, 2 and 3, can be seen the superiority of the ferritic stainless steels falling within the previously specified ranges, and containing 28% chromium 2% molybdenum, the remainder substantially all iron, as respects resistance to corrosion, in comparison with the known austenitic chromium-nickel and chromium-nickel-molybdenum steels, the tests being made in various corrosive mediums.

It was not to be expected that ferritic steels of a composition within the ranges specified herein would remain more passive at substantially lower potentials than do the corresponding chromium-nickel and chromium-nickel-molybdenum steels having almost the same chromium content. Reduction mediums, which because of their great negative redox potential lead to activation and thus to dissolving of the high-chromium austenitic steel X5 CrNiMo 25 25, are not capable of activating the new ferritic chromium-steel having about the same chromium content; these mediums are even capable of stabilizing the passive state. Thus for example, in 16% H_2SO_4 at 100°C., the transition from the passive to the active state, for a steel containing 28% chromium and 2% molybdenum, is at −250 mVE_H; whereas this potential, for the high-chromium austenitic chromium-nickel-molybdenum steel X2 CrNiMoN containing 25% chromium, 25% nickel and 2% molybdenum, the remainder being iron, lies at −75 mVE_H,

Numerous chemical syntheses and reactions take place under conditions where the hydrogen potential is determinative. Under such conditions the potential of the passive steel surface adjusts itself to the hydrogen potential. Whereas at such hydrogen potential austenitic/chromium-nickel and chromium-nickel-molybdenum steels become active in aggressive mediums (low pH value), and thus are able to suffer greater attack, the ferritic chromium-steels according to this invention, remain passive.

As has already been stated at the outset, up to the present time the use of ferritic stainless steels for the purposes set forth herein had against them unsatisfactory notch impact stengths.

In a striking way it has now been found that ferritic chromium-steels made in accordance with this invention have excellent mechanical characteristics, and in particular good notch impact strength and notch tensile strength, as is shown by the following Table 4, and FIGS. 1 and 2 of the drawings. In Table 4 below, are shown the notch impact strengths for three steels within the invention's range of composition, at temperatures from −100°C. to room temperature.

Table 4

Notch impact strength in mkp/cm² (DVM specimen)

Measurement Temp. °C	Steel Type: 35/0.5 CrMo 0.002% C, 0.002% N	28/2 CrMo 0.001% C, 0.002% N	20/5 CrMo 0.003% C, 0.001% N
<100	—	0.9/1.0/0.7	—
− 75	28.2/0.7/1.6	35.5/1.3/37.9	2.0/0.7/0.8
− 50	1.2/1.3/2.1	>40/>40/39.8	24.1/20.6/1.9
− 25	33.9/35.8/37.3	>40/>40/40	1.1/31.5/26.0
± 0	34.5/34.6/35.8	>40/>40/>40	33.2/33.9/1.2
+ 20	32.9/37.6/38.9	>40/>40/>40	32.8/31.2/31.8

In this Table 4, which for each temperature for the measurement of each type of steel gives three measured values of notch impact strengths, it is seen that all specimens at room temperature are sure to have notch impact strengths of better than 30 mkp/cm². Therefore it is possible to employ the steels of the invention in a range of temperatures from room temperature to higher temperatures, in cases where ability to withstand corrosion, as well as good mechanical characteristics, and in particular notch impact strength, are important.

For the steel of Type 28/2 CrMo, there are plotted in FIG. 1 the notch impact strengths for temperatures ranging from −100°C to + 50°C, and in FIG. 2 are plotted other mechanical characteristics in a temperature range from −100°C to +400°C. From these graphs it is once more seen that, in the region of room to higher temperatures of about 400°C, ferritic chromium steels of the present invention have excellent strength and toughness characteristics.

FIG. 1 shows, for low temperatures of below −50°C, the transition temperatures of the notch impact strength for 17 melts of this 28/2 CrMo steel containing 0.004 to 0.006% carbon and 0.001 to 0.004 nitrogen, after a heat-treatment for 30 minutes at 850° to 875°C, followed by quenching in water. In the region of room temperature down to at least −25°C no cold-brittleness occurs.

FIG. 2 shows the strength characteristics of two production melts of the steel 28/2 CrMo containing 0.002%C and also 0.0025% N, after a heat-treatment for 30 minutes at 875% C, followed by quenching in water, in the tensile test using smooth and notched specimens (notch number 3.0). Noteworthy is the high tensile strength/notch tensile strength ratio of 1.7, which goes below the value 1 only at −100°C.

FIG. 3 shows the example of a 4 mm thick metal sheet of the 28/2 CrMo steel containing C + N equal to or less than 0.01%, which was welded to other similar material by the electric plasma-arc welding process, and then bent at a sharp 180° angle lengthwise of and transversely of the welded seam, displaying previously unknown bending-toughness behavior for chromium-rich ferritic steels.

In Table 5 are given the compositions of four different steels within the alloying range given herein, their resistance to corrosive pitting, in the range from 20° to 100°C, being shown in FIG. 4

Table 5

Steel	C %	Si %	Mn %	Cr %	Mo %	S %	P %	N %	C+N %
A	0.003	<0.01	<0.01	19.9	4.85	0.008	<0.005	0.001	0.004
B	0.001	<0.01	<0.01	23.8	3.43	0.008	<0.005	0.001	0.002
C	0.002	<0.01	<0.01	28.1	2.11	0.008	<0.005	0.001	0.003
D	0.004	<0.01	<0.01	19.6	2.00	0.006	<0.005	0.001	0.005

According to the general opinion held up to the present time, molybdenum is with respect to resistance to corrosion pitting about three times as efficacious as chromium; that is each 1% of molybdenum has in this respect the same effect as 3% of chromium. Accordingly steel A containing 20% chromium and 5% molybdenum should have about the same and apparently certainly no more resistance to corrosion pitting as steel B which contains 24% chromium and 3.5% molybdenum. This hitherto accepted assumption ought in actuality to be confirmed by FIG. 4 where there are plotted for the four steels A, B, C and D, their liability to pitting in 3% NaC1 in a temperature range from 25° to 100°C. Because of the almost similar pitting potentials, steels A, B and C, should show equally good resistance to pitting, whereas steel D, because of its poorer pitting potential according to FIG. 4, should let us expect poorer resistance to pitting.

It has now turned out in a surprising way that the aforesaid assumption is incorrect, and that in actuality the following findings were made: with the formation of encrustations, forming confined spaces in which corrosive fluids may be trapped, that is in regions of high cloride concentration and/or lowered pH values, steels C and D displayed the same behavior with respect to pitting. Both steels, in boiling sea-water containing from 2% to 10% NaCl, as half-immersed specimens, even after only a few hours, showed below the encrustations forming in a steam space substantial patches of corrosion. Steel B behaved somewhat better showing the first corrosion phenomena only after some days. Steel A on the other hand, in spite of being considerably encrusted, even after 2,000 hours showed no signs of a corrosive attack. Thus it has the best behavior as respects pitting in chloride-containing mediums — an unexpected result.

The proved excellent corrosion-chemical characteristics, and the described excellent mechanical-technological characteristics, in particular the cold-toughness, of the ferritic stainless steels of the range of composition to be used in accordance with this invention, form a secure basis for allowing the use of these steels for the building of pressure-tanks under specified obligations or warranties, and for making possible their use in a wide field of application in the chemical industry, and also in a general way in processes under reducing conditions, and in particular in the field of producing and processing organic chemical substances. The ferritic stainless steel of this invention is moreover suitable for ship building, for building appratus and equipment, such as heat exchangers, e.g., handling sea water, for pumps, piping, and the like.

What is claimed is:

1. A ferritic high-chromium stainless steel operating while stressed at temperatures ranging between −100°C and 100°C and higher while in contact with fluids containing chlorides and consisting by weight of:

18 to 35%	chromium
.5 to 6%	molybdenum
0.001 to 0.01%	boron
0 to 5%	nickel
0 to 2%	copper
0 to 3%	silicon
0 to 1%	manganese
0 to 0.015%	carbon
0 to 0.015%	nitrogen

Remainder iron and impurities occasioned by smelting conditions.

* * * * *