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[54] CORROSION RESISTANT LOW CARBON CHROMIUM ALLOY STEEL

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

[51] **Int. Cl.** **C22c 39/14,** C22c 39/20

[58] **Field of Search** .... 75/126 C, 125, 128 W

[56] **References Cited**

UNITED STATES PATENTS

3,231,709	1/1966	Foley	75/126 C
3,235,417	2/1966	Roy	75/126 C
3,368,889	2/1968	Baumel	75/128 W
3,630,723	12/1971	Asada	75/128 W
3,561,953	3/1968	Nimi	75/128 A

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Attorney—Leonard W. Sherman et al.

[57] **ABSTRACT**

A chromium-containing steel having excellent corrosion resistance whose content of calcium is 0.0005 – 0.02 weight percent, content of carbon is not more than 0.02 weight percent and content of chromium is 25 – 38 weight percent. Such a steel can be produced by adding calcium or an alloy thereof to a melt of ferrochromium containing chromium within the foregoing range and thereafter carrying out the refining operations of decarbonization, deoxidation and desulfurization.

3 Claims, 2 Drawing Figures

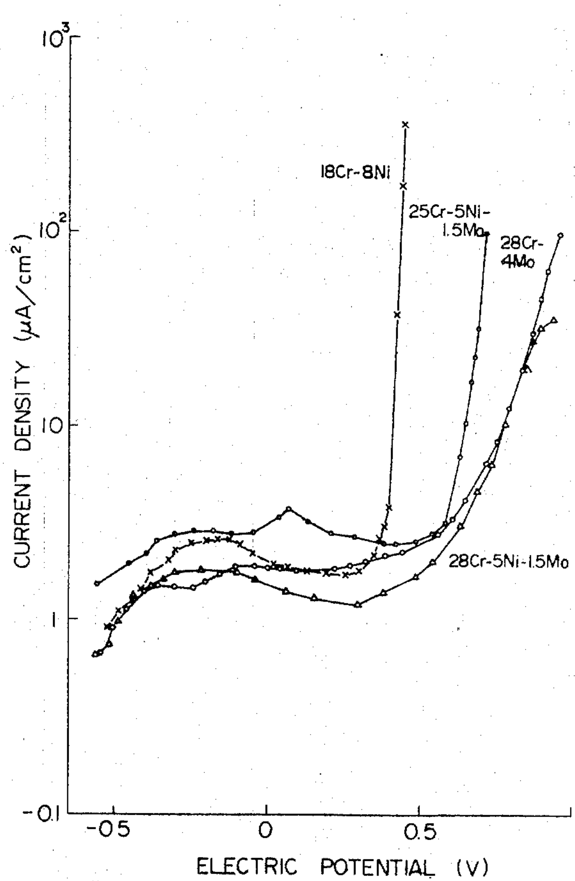


Fig. 1

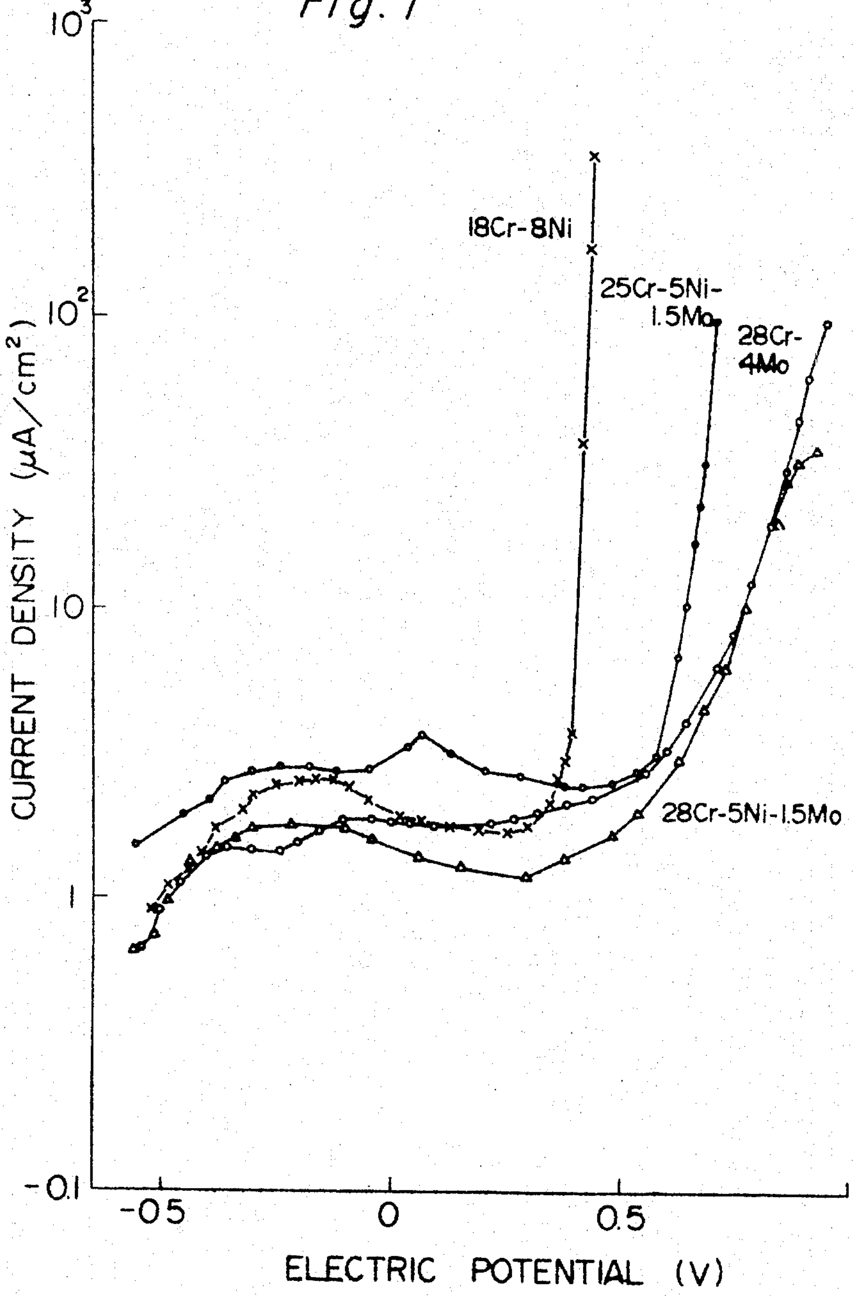
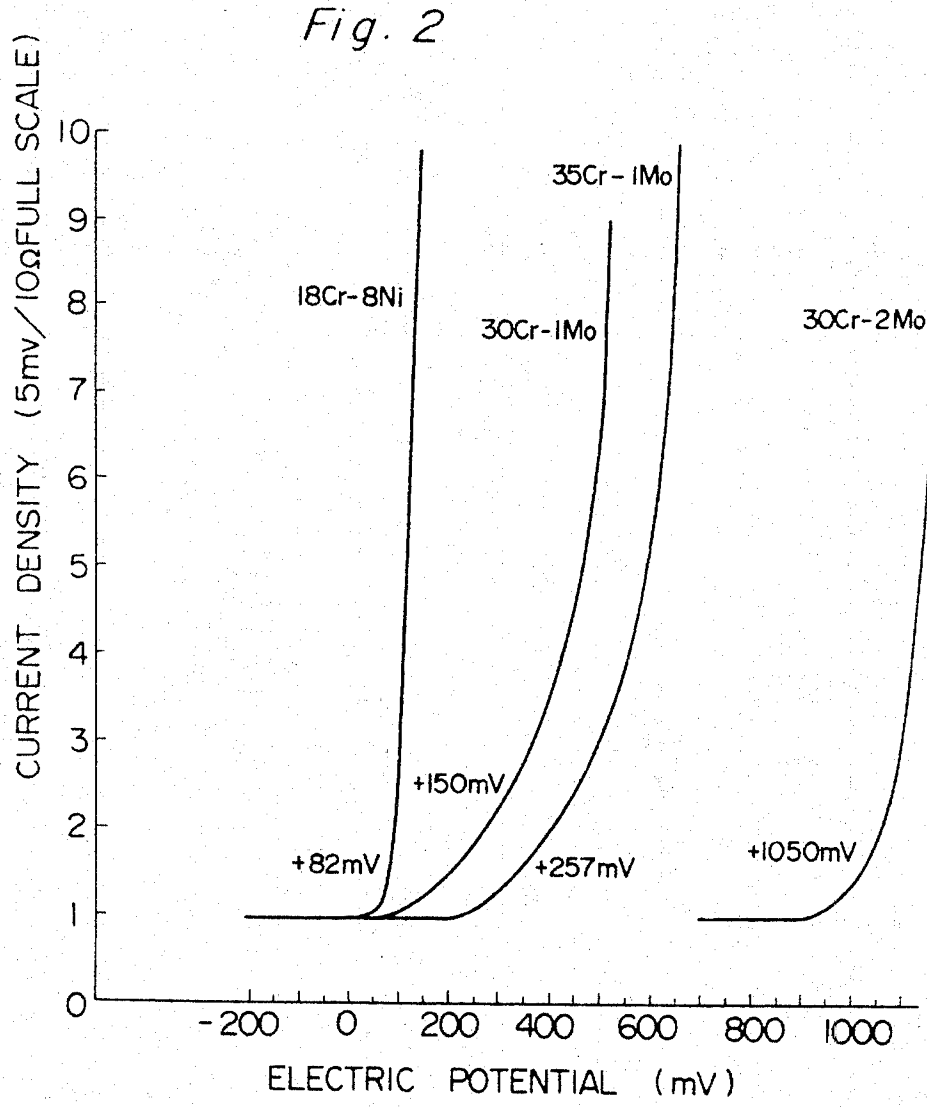

10^3
10^2
10
1
-0.1
CURRENT DENSITY (μA/cm²)
-0.5
0
0.5
ELECTRIC POTENTIAL (V)
18Cr-8Ni
25Cr-5Ni-
1.5Mo
28Cr-
4Mo
28Cr-5Ni-1.5Mo

Fig. 2


CURRENT DENSITY (5mv/10Ω FULL SCALE)
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1
2
3
4
5
6
7
8
9
10
18Cr-8Ni
35Cr-1Mo
30Cr-1Mo
30Cr-2Mo
+150mV
+82mV
+257mV
+1050mV
-200
0
200
400
600
800
1000
ELECTRIC POTENTIAL (mV)

CORROSION RESISTANT LOW CARBON CHROMIUM ALLOY STEEL

This invention relates to low carbon ferrochromium, i.e., a chromium alloy steel, whose corrosion resistance, workability and other properties have been improved.

The ferrochromium of the present invention is a chromium-containing ferrite type alloy steel consisting essentially, by weight, of the following constituents:

Ca . . . 0.0005 – 0.02 percent, preferably 0.001 – 0.005
C . . . up to 0.02 percent
O_2 . . . up to 0.015 percent
S . . . up to 0.015 percent
With the limitation that the sum of O_2 and S does not exceed 0.025 percent.
N_2 . . . up to 0.025 percent
Cr . . . 25 – 38 percent, preferably 27 – 35 percent
Mo . . . 0.5 – 5 percent
Ni . . . 0 – 5 percent
Cu . . . 0 – 3 percent
Nonmetallic inclusions — up to 0.1 percent
Fe . . . remainder.

The term "nonmetallic inclusions," as here used, are those nonmetallic ingredients that become inevitably included in the product as constituents of the slag formed during the refining of the iron chromium alloy. These nonmetallic inclusions are composed on a weight basis of 3–20% CaO, 5–80% Al_2O_3, 5–80% SiO_2 and trace amounts of Cr_2O_3, MnO, FeO and CaS.

The chromium alloy steel of the invention can be produced by refining a melt of iron chromium alloy whose content of chromium comes within the range specified herein above, the operation being carried out in either a vacuum furnace or a vacuum degassed apparatus, in vacuo or under an inert atmosphere such as argon, by the addition of decarbonization, deoxidation and desulfurization agents.

The austenite stainless steel based on the 18 – 8 stainless steel has been used chiefly in the past for applications requiring especially great resistance to corrosion as in the chemical industry and for other areas requiring corrosion resistance. However, the austenite stainless steel are deficient in its resistance to corrosion, especially crystal grain boundary corrosion and stress corrosion cracks.

On the other hand, the ferrite type stainless steel is valuable also as an industrial material, and extensive researches have been made with a view to providing a steel which would possess the resistance to corrosion required to overcome the foregoing deficiency. However, none has been found as yet that is entirely satisfactory.

The new stainless steel E-Brite 26-1 (trade name of Airco Company, U.S.A.), which is produced by a method developed by Airco Company, i.e., an arrangement consisting of combination of the steps of vacuum induction melting, electron beam vacuum skull refining and continuous casting operations, is a chromium-containing ferrite stainless steel. Nevertheless, it has a resistance to corrosion that is comparably superior, to that of such austenite type stainless steel containing nickel and chromium, e.g., No. 304 (18 Cr - 8 Ni) and No. 316 (18 Cr - 10 Ni - 3 Mo). It has the drawback that the equipment required in its production process is expensive.

In the case of the chromium-containing ferrite type alloy steel of the present invention, there is no need for costly melting equipment, and its production can be carried out readily in either a vacuum furnace or a vacuum degassed apparatus in which the refining operations of decarbonization, deoxidation and desulfurization are carried out by adding either metallic calcium or a calcium alloy. As the metallic constituents other than calcium in the calcium alloy, mentioned can be made of such as Al, Mn, Si, Fe and combinations of these metals.

The invention steel is decarbonized and desulfured with calcium and the like under vacuum conditions. Hence, it was found that the carbon content was reduced to below 0.02 percent, e.g., about 0.005 percent, and the content of sulfur was reduced to below 0.025 percent, e.g., about 0.007 percent, with the consequence that the corrosion resistance, workability, resistance to stress corrosion cracks and other properties could be improved.

The decarbonization and desulfurization mechanism of the present invention in the case of the alloys of low carbon range will be described by means of the following Experiments 1 and 2.

EXPERIMENT 1

Iron chromium alloy containing 30 percent chromium was refined in an alumina crucible, using calcium or a calcium alloy. By way of comparison, the refining operation was also carried out in like manner but using carbon as the reducing agent. The constituents other than Fe of the so obtained products are shown on a weight percentage basis in Table 1. In Table 1, Melt No. 1 is the composition of the starting iron chromium alloy, while Melts Nos. 2 – 5 are the examples where either calcium or the calcium alloy was used as the deoxidant, and Melt No. 7 is the example where carbon was used.

TABLE 1

Melt No.	Deoxidant	Cr	O_2	C	N_2	Si	Mn	Al	S	Ca
1		31.2	0.030	0.005	0.010	0.01	0.02	0.002	0.010	Trace
2	0.5% Ca alloy	31.0	.0041	.003	.007	.1	.05	.098	.010	0.003
3	1.0% Ca alloy	30.6	.0038	.003	.007	.24	.07	.23	.011	.005
4	0.5% metallic Ca	30.8	.0039	.003	.007	.01	.01	.082	.010	.004
5	1.0% metallic Ca	31.0	.0024	.004	.006	.01	.01	.21	.006	.005
7	0.05% C	31.2	.0046	.025	.007	.01	.01	.016	.010	Trace

In the case of the Melt No. 1 of Table 1, about 1 kilogram of iron chromium alloy consisting of electrolytic Cr and electrolytic Fe, in which Cr accounted for about 30 percent, was vacuum-melted in an alumina crucible, the experiment being repeated several times. When the same starting material was used, the product obtained had on the average a carbon content of 0.005 percent, an oxygen content of 0.03 percent and a nitrogen content of 0.01 percent. Further, when the nonmetallic inclusions contained in the composition were examined with a microscope in this case, the principal constituent was in all cases oxides of Cr.

It became clear from these results that since the content of C was a small quantity of such as 0.005 percent in the case of Melt No. 1, the oxides of Cr were stable even though vacuum-melting was carried out, and hence the reduction by means of carbon did not make any progress. On the other hand, in the case of the Melt No. 7, as a comparing experiment, the vacuum-melting was carried out as in the case with Melt No. 1, after which 0.05 percent of carbon was added to reduce the oxides of Cr, with the results shown. In this case, C increased from 0.005 to 0.025 percent while the oxygen decreased from 0.03 to 0.0046 percent. It is believed that the oxide of Cr in the case of Melt No. 1 was reduced.

While the form of the oxide of Cr will vary depending upon the process of production employed, it is believed to be either Cr_2O_3 or Cr_3O_4. Hence, the direct reduction by means of carbon can be shown by the following equations:

$$Cr_2O_3 + C \rightarrow CO\uparrow + Cr_3C_2 \tag{1}$$

or

$$Cr_3O_4 + C \rightarrow CO\uparrow + Cr_7C_3 \tag{1'}$$

From the fact that O_2 decreased from 0.03 to 0.0046 percent, as hereinabove indicated, it is apparent from these results that the oxide of chromium is decomposed and deoxidation takes place.

On the other hand, in the case of Melts Nos. 2 and 3, the vacuum-melting was carried out in the same alumina crucible as employed in the case of Melt No. 1 (the composition was identical to that of Melt No. 1), after which a calcium alloy consisting of 20.5% Ca, 23.8% Si, 19.65% Al, 18.73% Mn and the remainder Fe was added in amounts respectively of 0.5 percent and 1 percent in an atmosphere of argon gas. As a result, carbon decreased from 0.005 to 0.003 percent, and nitrogen decreased from 0.01 to 0.007 percent.

Melt Nos. 4 and 5 are those in which metallic calcium in amounts of respectively of 0.5 percent and 1 percent were added to the composition of Melt No. 1.

Thus it is seen that in the case of Melts Nos. 2 – 5 the carbon content decreased from 0.005 percent to 0.003 – 0.004 percent (corresponding to a decrease of 20 – 40 percent from the original carbon content), the O_2 content decreased from 0.03 percent to 0.0024 – 0.0039 percent (corresponding to a decrease of 80 – 90 percent from the original O_2 content), and the N_2 content decreased from 0.01 percent to 0.006 – 0.007 percent (a decrease of 30 – 40 percent from the original N_2 content).

The mechanism of reduction of the oxide of Cr by the metallic calcium is believed to proceed in the following manner.

$$Cr_2O_3 + 3Ca \rightarrow 3CaO + 2Cr \tag{2}$$

$$Cr_3O_4 + 4Ca \rightarrow 4CaO + 3Cr \tag{3}$$

$$CaO + C \rightleftarrows Ca\uparrow + CO\uparrow \tag{4}$$

As is apparent from these reaction equations, when the reactions are conducted in vacuo or in argon atmosphere, the decarbonization and deoxidation take place as a result of the C and CaO being eliminated from the reaction system as CO and Ca. In addition, while the matter of denitrogenation in the present invention is not fully known, it is believed that at the time of the elimination of CO and Ca from the reaction system nitrogen escapes by being entrained with the CO and Ca. It is not conceivable that CaN forms during denitrogenation. Further, in the case of Melts Nos. 4 and 5 there is an increase in both cases of Al of 0.082 percent and 0.21 percent although metallic calcium has been added. However, it is believed that the aluminum in the molten steel has increased as a result of the reduction of the alumina by means of the metallic calcium, the material of which the crucible is made.

EXPERIMENT 2

The experiment was carried out as in Experiment 1 but employing a magnesia crucible instead of an alumina crucible. The starting iron chromium alloy contains about 35 percent of chromium and about 1 percent of molybdenum, the contents of the other constituents being otherwise practically the same as in the case of Experiment 1. The refining was carried out, using metallic calcium and carbon as the deoxidant. The results obtained are shown in Table 2.

In the case of Melt No. 8, carbon was used, while in the cases of Melts Nos. 9 – 11, metallic calcium was used.

TABLE 2

Melt No.	Deoxidant	Cr	O_2	C	N_2	Si	Mn	Al	S	Ca	Mo
8	0.05% C	35.35	0.0053	0.017	0.008	0.01	0.01	0.005	0.012	Trace	1.00
9	1.0% Ca	33.70	.008	.001	.007	.01	.01	.008	.012	.004	1.01
10	1.0% Ca	31.20	.005	.001	.007	.01	.01	.006	.010	.003	1.00
11	1.0% Ca	27.35	.007	.002	.007	.01	.01	.007	.010	.004	1.00

In the case of the Melts Nos. 8 – 11, a magnesia crucible was employed instead of the alumina crucible of Experiment 1, and, instead of using argon gas, in vacuo either 0.05 percent of C or 1 percent of Ca was added to an alloy containing about 35 percent of Cr and 1 percent of Mo. The steel ingots, as in the case of Experiment 1, was about 1 kilogram, and the starting material was in all instances the same as that of Experiment 1.

Hence, the composition of Melt No. 8 does not differ greatly from that of Melt No. 7 of Table 1, but the Al content of Melt No. 7 using the alumina crucible is 0.016 percent, a higher value. In the case of Melts Nos. 9, 10 and 11 metallic calcium was added in vacuo in each instance. While the oxygen decreased from 0.03 percent to 0.005 – 0.008 percent, the carbon content decreased to an extremely low value of 0.001 – 0.002 percent from its original value of 0.005 percent. This phenomenon is believed to be due to an increase in the calcium that participates in the decarbonization reaction as a result of the lesser consumption of calcium by the crucible. This is also explainable from the fact that there is hardly any increase in Al in each of the instance of Melts Nos. 9, 10 and 11 of Experiment 2. On the other hand, there is no great difference in the content of nitrogen between Experiment 1 and Experiment 2.

Next, the importance of the range of contents of the various constituents, as defined for the invention chromium alloy steel, will be explained.

1. Ca 0.0005 – 0.02 percent

The fact that the Ca content that is detected after the vacuum treatment is from 0.0005 to 0.02 percent is very effective in improving the corrosion resistance and other properties of the product. A content of Ca in excess of 0.02 percent impairs the corrosion resistance as well as mechanical workability. On the other hand, when the Ca content is less than 0.0005 percent, this also impairs the properties, of the product, since its decarbonization is not complete. Preferable content of Ca is 0.001 – 0.005 percent.

2. O_2 not in excess of 0.015 percent, S not in excess of 0.015 percent, and the sum of S and O_2 not in excess of 0.025 percent

When the oxygen content exceeds 0.015 percent, the amount of oxides remaining as impurities increases to result in impairment of the corrosion resistance and mechanical workability. On the other hand, when S remains in excess of 0.015 percent, the mechanical workability of the product becomes poor. For the same reason, the sum of S and O_2 must be held to a value not in excess of 0.025 percent, or else the corrosion resistance as well as mechanical properties are impaired.

3. C not in excess of 0.02 percent

While C is an element that becomes included during the process of producing the ferrochromium, its presence in a great quantity is not desirable, since the corrosion resistance of the product is impaired.

From this standpoint, the previously mentioned E-Brite 26-1 has been proposed, as having reduced the C content. In the present invention the content of C is reduced to below 0.02 percent, and preferably to about 0.001 percent thus achieving a great improvement of the corrosion resistance.

Further, if the C content is of the order of 0.02 percent, the resistance to stress corrosion cracks is not impaired and, at the same time, C does not separate out into the crystal grain boundary. Hence, from this standpoint the invention alloy also possesses good resistance to brine water.

4. Cr 25 – 38 percent

Cr is an indispensable element for enhancing the resistance to corrosion. Hence, it is desirable that the content of Cr is as great as possible. However, when Cr exceeds 38 percent, the hot workability of the product suffers. On the other hand, when the content of Cr falls to below 25 percent, not only is it not possible to achieve an improvement in the corrosion resistance of the product, but also the properties possessed as a ferrite type stainless steel are sacrificed. Preferable content of Cr is 27 – 35 percent.

5. Mo 0.5 – 5 percent

Mo is an element which not only improves the resistance to corrosion but also has the ability of forming ferrite. Hence, the lower limit of Mo has been set at 0.5 percent, so as to enable it to demonstrate these effects. On the other hand, the upper limit of Mo was set at 5 percent, since an amount exceeding this value was not necessary in view of its relationship with the other constituents such as the contents of Cr, C and O_2, as well as its high cost.

6. Ni 0 – 5 percent

Ni is added chiefly for improving the impact value at low temperatures. However, since Ni not only is expensive but also is a powerful austenite-forming element, the addition of Ni in excess impairs the properties of the product as a ferrite steel. Hence, the upper limit was set at 5 percent.

7. Cu 0 – 3 percent

Some Cu becomes included during the production process, but this is effective in improving the corrosion resistance, resistance to stress corrosion cracks and resistance to crystal grain boundary corrosion. Hence, the presence of Cu up to 3 percent is permissible.

8. Nonmetallic inclusions not exceeding 0.1 percent, the composition of the inclusions being as follows: CaO 3–20 percent, Al_2O_3 5–80 percent, and traces of Cr_2O_3, MnO, FeO and CaS

This value has been established on the basis of measurements of the upper and lower limits experimentally of the changes of the composition of the nonmetallic inclusions, i.e., the slag, that varies depending upon the composition of of the metallic Ca or Ca alloy that is added in vacuo or in an atmosphere of argon gas to the chromium-containing molten steel in the vacuum furnace or vacuum degassed apparatus in producing the chromium alloy steel of the present invention. If slag in an amount in excess of 0.1 percent remains, the corrosion resistance and mechanical properties of the product are impaired.

The superior corrosion resistance of the low carbon chromium alloy steel of the invention will now be illustrated by reference to the accompanying drawings; in which FIGS. **1** and **2** are graphs showing comparisons of the corrosion resistance of the invention steels with that of the conventional 18–8 austenite type stainless steel. The corrosion resistance was tested by immersing the steel samples in an aqueous sodium chloride solution and measuring the polarization properties.

FIG. **1** shows the results obtained when measurements were made under the conditions of 0.1N aqueous solution of NaCl, 25°C., absence of oxygen, and rate of potential raise of V/27.5 minute. On the other hand, the results in the case of FIG. **2** were obtained by measurements made using a 3 percent aqueous solution of NaCl solution at room temperature.

The invention steels that were tested were 25Cr-5Ni-1.5Mo, 28Cr-4Mo, 28Cr-5Ni-1.5Mo, 30Cr-1Mo, 35Cr-1Mo and 30Cr-2Mo steels. All of these steels were products that were refined with either calcium or a calcium alloy, as described in the foregoing Experiments 1 and 2, and the compositions in all cases fall within the range as defined by the present invention. On the other hand, the 18–8 austenite type stainless steel used as the comparative sample was a commercially available product.

In the comparative test, first, as shown in FIG. **1**, the invention steels demonstrate a better anti-pitting property in all cases than the 18Cr-8Ni austenite type stainless steel. The anti-pitting property of the invention steels becomes better as the pitting potential is raised. In FIG. **1** the pitting potential becomes higher in the order of 18Cr-8Ni, 25Cr-5Ni-1.5Mo, 28Cr-4Mo and 28Cr-5Ni-1.5Mo.

A similar tendency is also seen in the case of the results of FIG. **2**, the pitting potential becoming higher in the order of 18Cr-8Ni, 30Cr-1Mo, 35Cr-1Mo and 30Cr-2Mo. It is thus obvious that the invention steels are superior in their resistance to corrosion.

What is claimed:

1. A corrosion-resistant low carbon chromium alloy steel consisting essentially, percent by weight, of 0.0005 – 0.02 of Ca, up to 0.02 of C, up to 0.015 of O_2, up to 0.015 of S, with the limitation that the sum of O_2 and S does not exceed 0.025, up to 0.025 of N_2, 25 – 38 of Cr, 0.5 – 5 of Mo, 0 – 5 of Ni, 0 – 3 of Cu, up to 0.1 of nonmetallic inclusions, and the remainder being Fe; said nonmetallic inclusions being the nonmetallic ingredients that become inevitably included in the product as constituents of the slag that is formed during the refining process and consist, on a weight basis, of 3 – 20% CaO, 5 – 80% Al_2O_3, 5 – 80% SiO_2, and traces of Cr_2O_3, MnO, FeO and CaS.

2. The chromium alloy steel according to claim **1** wherein the content of Ca is 0.001 – 0.005 percent by weight.

3. The chromium alloy steel according to claim **1** wherein the content of Cr is 27 – 35 percent by weight.

* * * * *