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(54) **Iron-chromium alloy with high corrosion resistance.**

(57) A corrosion-resistant Fe-Cr alloy for use in corrosive atmosphere near a seashore or in a chemical plant has a composition containing approximately not less than 5 wt% of Cr, not more than 100 ppm of C, N, O and S in total, from 0.01 to 1.0 wt% of P and the balance substantially Fe and impurities. The alloy may further contain not more than about 1.0 wt% of Al, not more than about 1.0 wt% of Si and not more than about 1.0 wt% of Mn, and at least one element selected from the group consisting of Ti, Nb, V, Zr, Ta, W and B in an amount which approximately meets the following condition (1). It is also possible to include at least one element selected from the group consisting of Ni, Co and Cu in an approximate amount which meets the following condition (2), and/or at least one element selected from the group consisting of Al, Si and Mn in an approximate amount which meets the following condition (3):

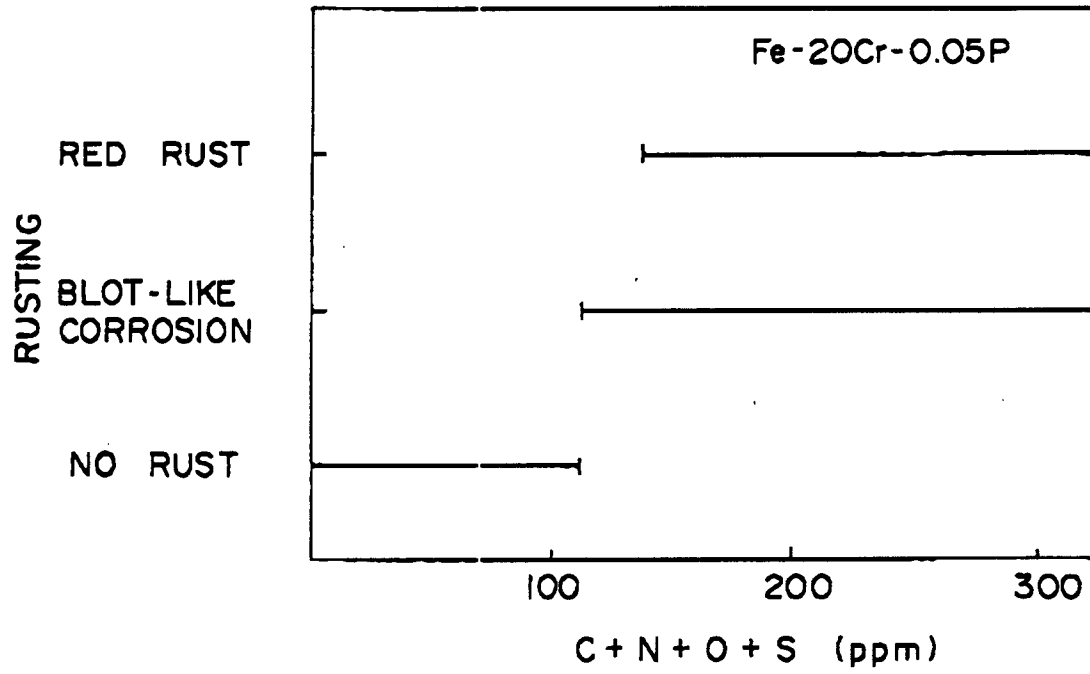
$0.01 \text{ wt}\% \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 20\text{B} \leq 1.0 \text{ wt}\%$ (1)

$0.01 \text{ wt}\% \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt}\%$ (2)

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$1.0 \text{ wt\%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt\%}$ (3)

FIG. 1



BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

5 The present invention relates to an Fe-Cr alloy, more particularly an Fe-Cr stainless steel, which excels in corrosion resistance.

DESCRIPTION OF THE RELATED ARTS

10 In general, Fe-Cr alloys are known as materials which excel in corrosion resistance. It is also known that elements such as C, N, O and S in such an Fe-Cr alloy produce detrimental effects on the corrosion resistance for the reasons stated below.

C and N: Formation of Cr-short layer due to generation of inter-granular Cr carbonitrides.

O and S: Enhancement of rust originating points due to increase in the inclusions.

15 Thus, as already known to those skilled in the art, it is an effective measure for improving corrosion resistance of Fe-Cr alloy to reduce the contents of these inclusions, and attempts have been made for reduction of the contents of C, N, O and S, as well as for elimination of Cr-short layer by addition of carbonitrides of elements such as Ti and Nb. Various proposals which hitherto have been made for the purpose of improving corrosion resistance of Fe-Cr alloys will be described.

20 Japanese Patent Laid-Open No. SHO 61-186451 discloses an Fe-Cr alloy having a Cr content ranging between 25 wt% and 50 wt%, wherein contents of C and N are lowered to specific values and Si, Mn and Mo are added in specified amounts, so as to achieve improved resistance to corrosion.

Japanese Patent Publication No. HEI 2-1902 discloses an Fe-Cr alloy having a Cr content which is above 20.0 wt% but not more than 25.0 wt%, in particular a corrosion-resistant ferrite stainless steel in which contents of C and N are reduced and Mo, Mn and Nb are added in specified amounts so as to improve resistance to high-temperature cracking during welding, as well as to achieve improved toughness of weld.

25 Japanese Patent Laid-Open No. HEI 3-2355 discloses an Fe-Cr alloy having a Cr content of from 16.0 wt% and 25.0 wt%, in particular a ferrite stainless steel in which Nb is added in a specified amount determined in relation to total content of C and N, so as to improve cold workability, toughness and corrosion resistance.

In these proposals, however, there is no hint that ultimate reduction in the contents of C, N and O provides an unexpectedly remarkable improvement in the corrosion resistance.

35 Addition of P for the purpose of improving corrosion resistance has been known and actually carried out in weather-resistant steels and anti-sea-water steels, but is not commonly adopted in Cr-containing stainless steels.

Thus, although various Fe-Cr alloys have been proposed in known arts, these alloys are still unsatisfactory and sometimes fail to meet demands for high corrosion resistance. For instance, further improvement in corrosion resistance is required for the materials of architectural structures near a seashore or a reaction vessel of a chemical plant.

SUMMARY OF THE INVENTION

45 Accordingly, an object of the present invention is to provide an Fe-Cr alloy which exhibits improved corrosion resistance over the known Fe-Cr alloys, more particularly a stainless steel suitable for use in a severe corrosive atmosphere, such as an architectural structure near a seashore or a reaction vessel of a chemical plant.

To achieve this object, the present inventors have made an intense study to find that an Fe-Cr alloy, which has very small contents of C, N and O as compared with known alloys of this kind and which contains a specified amount of P, exhibits remarkably improved weather resistance. The inventors further discovered that the intergranular corrosion resistance of the steel is further improved by addition of at least one element selected from the group consisting of Ti, Nb, V, Zr, Ta, W and B in the above-mentioned P-containing Fe-Cr alloy, and that resistance to pitting corrosion is remarkably improved by the addition of a specific amount of Mo to the same Fe-Cr alloy. It has also been discovered that an anti-acid characteristic is significantly improved by addition of a specific amount of at least one element selected from the group consisting of Ni, Co and Cu, and that an appreciable improvement in oxidation resistance is achieved by addition of a specific amount of at least one element selected from the group consisting of Al, Si and Mn.

The present invention is based upon the above-described discoveries and knowledge.

Thus, according to the present invention, there is provided an Fe-Cr alloy having high corrosion resistance, having a composition containing not less than 5 wt% of Cr, not more than 100 ppm in total of C, N, O and S, from 0.01 to 1.0 wt% of P and the balance substantially Fe and incidental impurities.

The Fe-Cr alloy of the invention can further contain various additional elements in amounts which do not affect the advantage of the invention, so as to develop various additional desirable effects.

The above and other objects, features and advantages of the present invention will become clear from the following description when the same is read in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a chart illustrative of the relationship between weather resistance of Fe-Cr alloys and the total contents of C, N, O and S of the alloys;

Fig. 2 is a chart illustrating the relationship between weather resistance of Fe-Cr alloys and P contents of the alloys;

Fig. 3 is a chart illustrative of the relationship between pitting-corrosion resistance of Fe-Cr alloys and the total contents of C, N, O and S of the alloys;

Fig. 4 is a chart illustrating the relationship between pitting-corrosion resistance of Fe-Cr alloys and P contents of the alloy;

Fig. 5 is a chart illustrative of the relationship between anti-acid characteristics of Fe-Cr alloys and (Ni + Co + 2Cu) values of the alloys; and

Fig. 6 is a chart illustrative of the relationship between anti-oxidation characteristics of Fe-Cr alloys and (3Al + 2Si + Mn) values of the alloys.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will be fully described hereinafter with reference to the accompanying drawings.

Fig. 1 is a graph illustrative of the relationship between the weather resistance of the steel and the total content (ppm) of C, N, O and S components of Fe-20%Cr-0.05%P alloys, as visually evaluated after 6-month exposure of south-oriented (inclination angle 36°) samples of the alloy at a location which is 5 m distant from a seashore.

The ranks or degrees of rusting evaluation are:

Rank 1: No rust observed

Rank 2: Blot-like rust observed

Rank 3: Dot-like red rust observed

It will be seen that no rust was observed when the total content of C, N, O and S was not greater than about 100 ppm. It is thus understood that weather resistance is remarkably improved when the amounts of C, N, O and S are reduced to such a level that the total content of these elements is not more than about 100 ppm.

Fig. 2 illustrates the relationship between the degree of rusting and P content in Fe-18%Cr alloys having total C, N, O and S contents not less than about 100 ppm and not more than about 100 ppm, after 1-year exposure to atmosphere. The degree of rusting was evaluated into the following four ranks:

Rank 1: Slight blot-like corrosion

Rank 2: Blot-like rust over entire area

Rank 3: Blot-like and red spot rust over entire area

Rank 4: Red rust over entire area

From Fig. 2, it will be understood that an Fe-Cr alloy having C, N, S and O total content of about 100 ppm or less exhibits superior weather resistance when the P content is about 0.01 wt% or more.

Fig. 3 shows the relationship between the total contents of C, N, O and S of Fe-18%Cr-0.02%P alloys and the degree of pitting corrosion potential ($V'_{C,10}$ (mV vs SCE)). It will be seen that high resistance to pitting corrosion is obtained when the total content of C, N, O and S is about 100 ppm or less.

As will be understood from the characteristics shown in Figs. 1 to 3, corrosion resistance of Fe-Cr alloy is remarkably improved when the total content of C, N, O and S of the alloy is very small while the P content of the alloy is greater than a predetermined value.

Fig. 4 shows the relationship between Mo content of Fe-18%Cr-0.1%P alloy having the C, N, O and S total content of about 100 ppm or less and the pitting corrosion potential ($V'_{C,10}$ (mV vs SCE)). It will be seen that resistance to pitting corrosion is further enhanced when the Mo content is about 0.05 wt% or greater.

Fig. 5 shows the relationship between the degree of corrosion of Fe-20%Cr-0.03%P alloy having the C, N, O and S total content of about 100 ppm or less and the (Ni + Co + 2Cu) value (wt%) of the alloy, as

observed when the alloy was immersed in boiling 1% HCl aqueous solution for 18 hours. From this Figure, it is clear that the degree of corrosion decreases, i.e., the anti-acid property of the steel is improved, when the above-mentioned value is about 0.01 wt% or greater.

A cyclic oxidation test, each cycle consisting of 30-minute heating at 1075 °C in the air followed by 12-minute cooling, was executed on Fe-20%Cr-0.06P alloy having the total content of C, N, O and S not more than 100 ppm, and change of weight was measured for every 25 cycles. The number of cycles sustained until oxidation weight increment exceeds 5.0 mg/m² was measured and plotted in relation to the (3Al + 2Si + Mn) value (wt%). It will be seen that a remarkable improvement in oxidation resistance was attained when the (3Al + 2Si + Mn) value (wt%) exceeded about 0.1 wt%.

Features and advantages of the present invention will become clear from the following description of the preferred embodiments.

(First Embodiment)

Cr: Cr should be contained in an amount not less than about 5 wt%, preferably not less than about 10 wt%. In order that the alloy of the present invention exhibits the required level of corrosion resistance, it is essential that the Cr content meets the requirement specified above.

C, N, O and S: In conventional Fe-Cr alloy, these elements are contained in a total amount of several hundreds of ppm as inevitable or incidental impurities. In contrast, in the alloy of the present invention, the total content of these elements is limited to not more than about 100 ppm, preferably not more than about 85 ppm. Such reduction of the total content of these elements is essential in the present invention, in order to achieve the improvement in corrosion resistance. As explained before in connection with Figs. 1 to 3, the object of the present invention cannot be achieved when the above-mentioned total content exceeds about 100 ppm.

P: The alloy of the present invention contains P in an amount which falls between about 0.01 wt% and 1.0 wt%, preferably between about 0.015 and 0.3 wt%. The above-specified P content provides excellent corrosion resistance of the alloy. Addition of P in excess of 1.0 wt%, however, is not recommended from the viewpoint of production because such a large P content undesirably reduces not only corrosion resistance but also toughness.

The first embodiment of the Fe-Cr alloy of the present invention, having a Cr content and a total content of C, N, O and S and P which fall within the ranges specified above, exhibits superior corrosion resistance and, therefore, can suitably be used as the material of outer members of architectural structures, outer panels of automobiles and so forth.

(Second Embodiment)

The second embodiment of the Fe-Cr alloy of the present invention contains, in addition to the elements used in the first embodiment, Al, Si and Mn as deoxidation elements. It is possible to achieve the object of the present invention when the alloy composition of the first embodiment further contains Al, Si and Mn in approximate amounts as specified below:

Al: not more than 1.0 wt%, preferably not more than 0.5 wt%

Si: not more than 1.0 wt%, preferably not more than 0.8 wt%

Mn: not more than 1.0 wt%, preferably not more than 0.7 wt%

Addition of each of Al, Si and Mn in excess of the limit mentioned above is not recommended because the deoxidation effect is saturated. The second embodiment of the Fe-Cr alloy meeting the conditions stated above exhibits superior corrosion resistance and can suitably be used for the same purposes as those of the first embodiment.

(Third Embodiment)

The third embodiment of the Fe-Cr alloy of the present invention contains, in addition to the composition of the first or the second embodiment, at least one element selected from the group consisting of Ti, Nb, V, Zr, Ta, W and B, in an approximate amount which meets the following condition (1), preferably the following condition (1'):

Condition (1)

$$0.01 \text{ wt\%} \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 20\text{B} \leq 1.0 \text{ wt\%}$$

Condition (1')

$$0.03 \text{ wt\%} \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 20\text{B} \leq 0.5 \text{ wt\%}$$

Satisfactorily high corrosion resistance can be obtained even when such element or elements are not contained. However, addition of such element or elements in accordance with the condition specified above provides a further improvement of the resistance to intergranular corrosion, as well as corrosion resistance at the weld portion. Addition of such element or elements in excess of the above-specified range is not recommended because such addition causes a reduction of workability due to solid solution strengthening of such element or elements. For the same reason, the content of each of such element independently, when added, should fall within the following approximate range:

Ti: from 0.01 to 0.5 wt%

Nb: from 0.01 to 0.5 wt%

Zr: from 0.01 to 0.5 wt%

V: from 0.01 to 0.5 wt%

Ta: from 0.01 to 0.5 wt%

W: from 0.01 to 0.5 wt%

B: from 0.0003 to 0.01 wt%

The third embodiment of the Fe-Cr alloy of the present invention, meeting the conditions and requirements set forth above, exhibits superior resistance to intergranular corrosion, in addition to the corrosion resistance offered by the preceding embodiments and, therefore, can suitably be used for the same purposes as the preceding embodiments and other purposes where a high corrosion resistance is specifically required for weld parts.

(Fourth Embodiment)

The fourth embodiment of the Fe-Cr alloy of the present invention contains, in addition to the composition of the first or the second embodiment, about 0.05 to 20 wt%, preferably about 0.1 to 6.0 wt%, of Mo. Fe-Cr alloy of the present invention can exhibit sufficiently high resistance to corrosion even when Mo is not present. Addition of Mo in an amount specified above, however, acts to further increase resistance to pitting corrosion, as well as weather resistance. Addition of Mo in excess of about 20 wt% undesirably makes the material hard while reducing the toughness of the base metal. The fourth embodiment of the Fe-Cr alloy of the present invention, which meets the requirements described above, provides superior resistance to pitting corrosion and weather resistance, as well as high corrosion resistance and, therefore, can be used suitably for purposes where high resistance to intergranular corrosion and high weather resistance are required, as well as high corrosion resistance.

(Fifth Embodiment)

A fifth embodiment of the Fe-Cr alloy of the present invention possesses the features of both the third embodiment which excels in the corrosion resistance at weld parts and the fourth embodiment which excels in the resistance to pitting corrosion. Thus, the fifth embodiment contains, in addition to the composition of the first or the second embodiment, about 0.05 to 20 wt%, preferably about 0.1 to 6.0 wt%, of Mo and at least one element selected from the group consisting of Ti, Nb, V, Zr, Ta, W and B, by an amount which meets the approximate condition of the following condition (1), preferably approximately the following condition (1'):

Condition (1)

$$0.01 \text{ wt\%} \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 20\text{B} \leq 1.0 \text{ wt\%}$$

Condition (1')

$$0.03 \text{ wt\%} \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 20\text{B} \leq 0.5 \text{ wt\%}$$

Preferred range of content of each of such elements is not described because it is the same as that in the third embodiment. The reasons of limitation of the contents of the elements also are not described because they are the same as those explained in connection with the third and fourth embodiments. The

fifth embodiment of the Fe-Cr alloy of the present invention, meeting the conditions described above, exhibits superior corrosion resistance at weld parts, in addition to the corrosion resistance of the base metal. This embodiment therefore can suitably be used as the material of structural parts which are to be assembled by welding.

(Sixth Embodiment)

A sixth embodiment of the Fe-Cr alloy of the present invention contains at least one element selected from the group consisting of Ni, Co and Cu in an amount which meets approximately the following condition (2) or condition (2'), in addition to the composition of the first, second, third, fourth or fifth embodiment.

Condition (2)

$$0.01 \text{ wt\%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt\%}$$

Condition (2')

$$0.05 \text{ wt\%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 5 \text{ wt\%}$$

The Fe-Cr alloy of the present invention exhibits rather high corrosion resistance even when such element or elements are not contained. By adding at least one of these elements, however, it is possible to further improve anti-acid property and weather resistance of the alloy. When the content of Ni, Co and/or Cu is below the range specified above, it is not possible to attain appreciable effect in improving the anti-acid property, whereas, when the range specified above is exceeded, production of the alloy is impeded. When at least one element selected from the group consisting of Ni, Co and Cu is added, the approximate content of each element is preferably determined as follows, for the reasons stated before.

Ni: 0.05 to 5.0 wt%

Co: 0.05 to 5.0 wt%

Cu: 0.05 to 2.5 wt%

The sixth embodiment of the Fe-Cr alloy of the present invention, meeting the conditions described above, exhibits superior anti-acid property, as well as high corrosion resistance, and, therefore, can suitably be used as structures in chemical plants.

(Seventh Embodiment)

The seventh embodiment of the Fe-Cr alloy of the present invention contains at least one element selected from the group consisting of Al, Si and Mn in an approximate amount which meets the following condition (3), preferably condition (3'), in addition to the composition of the first, third, fourth or the fifth embodiment.

Condition (3)

$$1.0 \text{ wt\%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt\%}$$

Condition (3')

$$3.0 \text{ wt\%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 20 \text{ wt\%}$$

At least one of Al, Si and Mn is positively added for the purpose of improving oxidation resistance. Thus, the seventh embodiment is directed to a purpose which is different from that of the second embodiment. The Fe-Cr alloy of the present invention can exhibit superior corrosion resistance even when it lacks one or more of Al, Si and Mn. Addition of at least one of Al, Si and Mn, however, offers an additional advantage that the alloy can have further improved oxidation resistance. When the upper limit of about 50 wt% of the above-mentioned condition (3) is exceeded, oxide inclusions are dispersed in the alloy so as to impair producibility and workability, making it difficult to produce the alloy. Preferred range of content of each of Al, Si and Mn when added is shown below, together with the reason why such range is preferred.

Al: about 0.1 to 10.0 wt%

Al content below about 0.1 wt% does not provide appreciable effect, although not ineffective. Addition of Al in excess of about 10.0 wt% makes impairment of producibility noticeable.

Si: about 0.1 to 10.0 wt%

Si content below about 0.1 wt% does not provide appreciable effect, although not ineffective. Addition of Si in excess of about 10.0 wt% makes impairment of producibility noticeable.

Mn: about 0.1 to 20.0 wt%

Mn content below about 0.1 wt% does not provide appreciable effect, although not ineffective. Addition of Mn in excess of about 20.0 wt% makes impairment of producibility noticeable.

The seventh embodiment of the Fe-Cr alloy of the invention meeting the above-described requirements exhibits large resistance to oxidation at high temperature, as well as excellent corrosion resistance, and, therefore, can advantageously be used as a material for the exhaust system of automobiles.

(Eighth Embodiment)

An eighth embodiment of the Fe-Cr alloy of the present invention possesses the advantage of the above-described seventh embodiment, i.e., excellent resistance to oxidation, in addition to the advantage of the sixth embodiment described before, i.e., superior anti-acid property. Thus, the eighth embodiment of the Fe-Cr alloy of the invention contains, in addition to the composition of the first, third, fourth or fifth embodiment, at least one element selected from the group consisting of Ni, Co and Cu in an approximate amount meeting the following condition (2), preferably condition (2'), as well as at least one element selected from the group consisting of Al, Si and Mn by an amount meeting the following condition (3), preferably condition (3').

Condition (2)

$$0.01 \text{ wt\%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt\%}$$

Condition (2')

$$0.05 \text{ wt\%} \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 5 \text{ wt\%}$$

Condition (3)

$$1.0 \text{ wt\%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt\%}$$

Condition (3')

$$3.0 \text{ wt\%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 20 \text{ wt\%}$$

Preferred ranges of the contents of the respective elements, as well as the reasons, are not described in further detail because the ranges and reasons explained before in connection with the sixth and seventh embodiments apply also in this embodiment.

Alloys of the first to eighth embodiments described hereinbefore can be produced through melting and casting from predetermined amounts of high-purity materials prepared by, for example, electrolytic processes. It is possible to use Al, Si and Mn as deoxidizers in this production process. After the melting and casting, the alloy may be subjected to ordinary process such as a process including the steps of hot rolling, annealing, pickling, cold rolling, annealing, (pickling), and temper rolling.

Preferably, in the alloy of the present invention, the balance other than the elements described above is Fe. The effect of the present invention, however, is never impaired even when one or more of elements selected from the group consisting of Ca, Mg, REM (rare earth metal), Pb, Bi, Se and Te is present in an amount below about 1 % in total.

The advantages of the present invention can be achieved regardless whether the alloy is used in the form of a hot-rolled annealed sheet or a cold-rolled annealed sheet, and regardless of the state of finishing of the sheet, e.g., 2D, 2B, BA, HL or polishing.

5 Examples

The invention will be more clearly understood from the following description of Examples.

Small ingots, each being 30 kg in weight, were prepared from various Fe-Cr alloys having compositions as shown in Table 1, using an ultra-high-vacuum 50 kg RF furnace. The melting was conducted by means
10 of the ultra-high-vacuum furnace which can realize the maximum vacuum of 10^{-7} Torr at normal temperature, using materials of high degrees of purity, in order to maintain the total content of S, C, N and O to the level not greater than 100 ppm. Furthermore, in order to minimize migration of impurity elements from the crucible, several charges of ultra-high-purity iron were melted to wash the crucible, before the melting was actually conducted. The melting was conducted while forcible agitation was applied to the melt.

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Table 1 (1)

Invented Alloy	C *	M *	Q *	S *	P	Cr	Mo	Al	Si	Mn	Ochere	α *	β	γ	δ	Embodiment
1	26	26	31	10	0.012	19.6	0.001	0.001	0.01	0.01		93				1
2	18	21	26	5	0.013	20.1	0.001	0.002	0.01	0.01		70				1
3	11	32	19	27	0.019	19.9	0.001	0.001	0.01	0.01		89				1
4	9	15	40	9	0.021	20.0	0.001	0.001	0.01	0.01		73				1
5	13	12	16	11	0.103	19.6	0.001	0.001	0.01	0.01		52				1
6	11	39	18	15	0.629	20.1	0.001	0.003	0.01	0.01		83				1
7	18	23	19	26	0.103	11.1	0.002	0.002	0.01	0.01		86				1
8	20	9	31	13	0.013	41.0	0.003	0.002	0.01	0.01		73				1
9	16	19	23	18	0.105	7.1	0.001	0.001	0.01	0.01		76				1
10	19	23	18	20	0.022	19.9	0.001	0.02	0.83	0.03		80				2
11	21	31	19	15	0.019	20.1	0.002	0.01	0.06	0.76		86				2
12	16	19	31	9	0.020	20.1	0.001	0.60	0.02	0.02		75				2

Unit: wt%; *: ppm; α : C+N+O+S; β : Ti+Nb+Zr+V+W+Ta+20B; γ : Ni+Co+2Cu; δ : 3Al+2Si+Mn

Table 1 (2)

Invented Alloy	C *	W *	O *	S *	P	Cr	Mo	Al	Si	Nb	Others	α *	β	γ	δ	Embodiment
13	13	26	17	16	0.020	20.0	0.001	0.46	0.70	0.61		72				2
14	9	21	16	18	0.083	10.9	0.002	0.001	0.01	0.01	Ti:0.015	64	0.015			3
15	21	15	30	15	0.091	11.1	0.001	0.18	0.40	0.51	Zr:0.036	81	0.036			3
16	13	31	18	9	0.089	11.1	0.001	0.003	0.01	0.01	Nb:0.039	71	0.039			3
17	7	15	34	20	0.106	11.2	0.001	0.002	0.01	0.01	Ti:0.013, Ta:0.052	76	0.065			3
18	18	21	41	15	0.099	11.2	0.001	0.005	0.01	0.01	Ti:0.059, Nb:0.042, B:0.0015	95	0.131			3
19	21	11	29	13	0.101	11.2	0.002	0.10	0.46	0.53	Ti:0.059, Ta:0.061, N:0.10, V:0.066	74	0.286			3
20	16	26	13	17	0.110	11.2	0.001	0.002	0.01	0.01	Ti:0.223, Nb:0.365, Zr:0.164, V:0.121, W:0.03	72	0.913			3
21	16	21	31	15	0.103	20.0	0.06	0.002	0.01	0.01		69				4
22	11	21	18	19	0.190	20.3	0.49	0.019	0.01	0.01		83				4
23	21	19	24	13	0.121	20.0	5.89	0.006	0.01	0.01		77				4
24	13	18	41	9	0.018	20.3	0.41	0.001	0.02	0.01		81				4

Unit: wt%; *: ppm; α : C+N+O+S; β : Ti+Nb+Zr+V+W+Ta+20B; γ : Ni+Co+2Cu; δ : 3Al+2Si+Mn

Table 1 (3)

Invented Alloy	C *	M *	O *	S *	P	Cr	Mo	Al	SL	Mn	Others	α *	β	γ	δ	Embedl-ment
25	18	22	39	10	0.384	20.3	0.39	0.002	0.01	0.01		89				4
26	8	27	28	10	0.113	18.4	6.64	0.001	0.01	0.01	Vi:0.082, Ni:0.090	73	0.172			5
27	8	31	40	10	0.709	19.3	0.55	0.002	0.01	0.02	Ti:0.161, Nb:0.182, Bi:0.022	89	0.783			5
28	13	19	26	23	0.023	20.0	0.001	0.002	0.01	0.01	Co:0.021	81		0.021		6
29	21	15	30	15	0.020	20.1	0.001	0.003	0.01	0.01	Mo:0.037, Cu:0.013	81		0.043		6
30	31	26	18	9	0.021	19.9	0.001	0.001	0.01	0.01	Mo:0.143, Co:0.300, Cu:0.236	84		0.915		6
31	8	28	26	15	0.015	19.6	0.001	0.03	0.43	0.10		72			1.05	7
32	10	10	22	13	0.015	20.1	0.002	0.05	0.73	12.15		55			13.76	7
33	9	15	30	11	0.016	19.3	0.001	7.31	1.03	1.22		65			25.21	7

Unit: wt%; *: ppm; α : C+N+O+S; β : Ti+Nb+Zr+V+W+Ta+20B; γ : Ni+Co+2Cu; δ : 3Al+2Si+Mn

Table 1 (4)

Comparison Alloy	C *	Fe *	O *	S *	P	Cu	Mo	Al	Si	Mn	Others	α *	β	γ	δ	Embodiment
1	35	28	34	13	0.020	20.0	0.002	0.002	0.01	0.01		110				
2	19	21	30	11	0.003	19.6	0.001	0.001	0.01	0.01		81				
3	18	16	20	19	1.069	20.0	0.001	0.002	0.01	0.01		73				
4	36	21	43	23	0.096	11.0	0.002	0.003	0.01	0.01		123				
5	43	23	31	29	0.006	40.1	0.001	0.002	0.01	0.01		126				
6	26	13	15	17	0.093	4.8	0.001	0.001	0.01	0.01		71				
7	31	29	29	32	0.103	19.9	0.001	0.001	0.01	0.01		121				

Unit: wt%; *: ppm; α : C+N+O+S; β : Ti+Nb+Zr+V+W+Ta+20B; γ : Ni+Co+2Cu; δ : 3Al+25Si+Mn

Each sample ingot thus obtained was cut so that surface portions of 1 cm thick was removed therefrom. Then, the ingot was soaked for 1 hour at an appropriate temperature selected to range from about 1100 °C to about 1250 °C and then hot-rolled into sheet 4 mm thick, followed by annealing which was employed for the purpose of recrystallization. Then, after removal of the surface carbo-nitrided surface region by cutting, a cold rolling and a subsequent recrystallizing annealing were conducted once or twice, whereby a cold-

rolled sheet 0.7 mm thick was finally obtained as the test sample. The surface portion of each test sample was removed by polishing as required.

The test samples thus prepared were subjected to various corrosion tests for the purpose of evaluation of various anti-corrosion properties.

(Weather resistance test)

(1) Test samples were exposed to atmosphere at a location in a coastal industrial zone for 1 year. The degrees of rusting of the sample surfaces were visually evaluated into the following five ranks:

- Rank 1: No rusting
- Rank 2: Trace of blot-like rust
- Rank 3: Slight blot-like rust
- Rank 4: Blot-like rust and red spot rust
- Rank 5: Large red-rusting tendency

(2) Gloss was measured by a gloss meter (HG-246) produced by Suga Testing Instrument Manufacturing and gloss retention ratio was determined in terms of the ratio between the gloss before the exposure to the atmosphere and the gloss after the exposure, as shown below.

$$\text{Gloss retention ratio} = \{Gs(20)(\text{After Exposure})/Gs(20)(\text{Before Exposure})\} \times 100$$

(Intergranular Corrosion Test)

A test for examining the samples for resistance to intergranular corrosion was conducted in accordance with sulfuric acid/copper sulfate testing method specified by JIS (Japanese Industrial Standards) G 0575, and resistance to intergranular corrosion was evaluated based on whether cracks exist or not.

(Pitting Corrosion Test)

A test was conducted to examine the samples for resistance to pitting corrosion, using corrosion electrical potentials determined following those specified in JIS G 0577. The potential at which pitting corrosion was caused was recorded in terms of the potential at which a current density of 10 $\mu\text{A}/\text{cm}^2$ was reached.

(Weather Resistance Test)

Test samples were immersed for 18 hours in boiling 0.5 % HCl aqueous solution, and losses of weight due to corrosion were measured for evaluation of anti-acid property into the following four ranks:

- : Corrosion below 0.1 $\text{g}/\text{m}^2 \cdot \text{hr}$
- o: Corrosion 0.1 to 1 $\text{g}/\text{m}^2 \cdot \text{hr}$
- △: Corrosion 1 to 3 $\text{g}/\text{m}^2 \cdot \text{hr}$
- X: Corrosion 3 $\text{g}/\text{m}^2 \cdot \text{hr}$ or greater

(Oxidation Resistance Test)

A cycling test was conducted by repeating cycles each consisting of 30-minute heating at 1075°C in the air and subsequent 12-minute cooling. Change in the weight was measured for every 25 cycles, and the number of cycles sustained until oxidation occur, more specifically until the oxidation weight increment exceeds 5.0 mg/m^2 , was recorded for the purpose of evaluation of oxidation resistance.

The result of the experiment will be described hereinunder.

(Test Result 1)

Tables 2, 3 and 4 respectively show the results of the weather resistance test conducted on the Fe-20%Cr alloy, Fe-11%Cr alloy and Fe-40%Cr alloy.

Table 2

Fe-20%Cr Alloy				
Alloy	Evaluation of Rusting Degree	Gloss Retention Ratio (%)	C + N + O + S (ppm)	P (wt%)
Invented Alloy 1	2	88	93	0.012
Invented Alloy 2	1	90	70	0.013
Invented Alloy 3	2	85	89	0.019
Invented Alloy 4	1	92	73	0.021
Invented Alloy 5	1	95	52	0.103
Invented Alloy 6	2	83	83	0.629
Comparison Alloy 1	4	65	110	0.020
Comparison Alloy 2	3	77	81	0.003
Comparison Alloy 3	5	49	73	1.069

Table 3

Fe-11%Cr Alloy				
Alloy	Evaluation of Rusting Degree	Gloss Retention Ratio (%)	C + N + O + S (ppm)	P (wt%)
Invented Alloy 7	2	81	86	0.103
Comparison Alloy 4	5	29	123	0.096

Table 4

Fe-40%Cr Alloy				
Alloy	Evaluation of Rusting Degree	Gloss Retention Ratio (%)	C + N + O + S (ppm)	P (wt%)
Invented Alloy 8	1	96	73	0.013
Comparison Alloy 5	3	76	126	0.006

From Tables 2, 3 and 4, it will be clearly seen that the alloys in accordance with the present invention exhibited distinguished weather resistance. Superior weather resistance cannot be obtained when the total content of C, N, O and S exceeds about 100 ppm or when the P content does not fall within the range specified by the present invention.

Table 5 shows the results of the weather resistance test on Fe-(4 - 20)%Cr-0.1%P alloys.

Table 5

Fe-(4 to 20)%Cr-0.1%P Alloy				
Alloy	Evaluation of Rusting Degree	Gloss Retention Ratio (%)	C + N + O + S (ppm)	Cr (wt%)
Invented Alloy 5	1	95	52	19.6
Invented Alloy 7	2	82	86	11.1
Invented Alloy 9	3	75	76	7.1
Comparison Alloy 6	5	21	71	4.8

It will be seen from Table 5 that excellent weather resistance is exhibited when the Cr content is 5 wt% or greater. The alloy of Comparative Example 6, having a Cr content of 4.8 wt%, showed heavy red rusting, and seriously impaired gloss, proving that this alloy cannot be weather-resistant.

(Test Result 2)

Table 6 shows the results of the weather resistance test conducted on Fe-20%Cr-0.02%P alloys.

Table 6

Fe-20%Cr-0.02%P Alloy						
Alloy	Evaluation of Rusting Degree	Gloss Retention Ratio (%)	C + N + O + S (ppm)	Al (wt%)	Si (wt%)	Mn (wt%)
Invented Alloy 10	2	84	80	0.02	0.83	0.05
Invented Alloy 11	1	93	86	0.01	0.06	0.76
Invented Alloy 12	1	88	75	0.60	0.02	0.02
Invented Alloy 13	1	91	72	0.46	0.70	0.61
Invented Alloy 3	2	85	89	0.001	0.01	0.01
Invented Alloy 4	1	92	73	0.001	0.01	0.01

From Table 6, it is understood that the alloy exhibited sufficiently high weather resistance even when Al, Si or Mn used as the deoxidation agent was present, contained, provided that the content of each of such deoxidizer is not more than about 1.0 wt% and provided that the requirements for the total content of C, N, O and S and the P content are met.

(Test Result 3)

Table 7 shows the results of weather resistance test and intergranular corrosion test conducted on Fe-11%Cr-0.1%P alloys (C + N + O + S $\leq$ 100 ppm).

Table 7

Fe-11%Cr-0.1%P(C + N + O + S ≤ 100ppm)				
Alloy	Evaluation of Rusting Degree	Gloss Retention Ratio (%)	Sulfur Acid/Copper Sulfate Test	β Value (wt%)
Invented Alloy 14	2	79	No Cracking	0.015
Invented Alloy 15	2	80	No Cracking	0.036
Invented Alloy 16	2	82	No Cracking	0.039
Invented Alloy 17	2	79	No Cracking	0.065
Invented Alloy 18	2	81	No Cracking	0.131
Invented Alloy 19	2	86	No Cracking	0.286
Invented Alloy 20	2	79	No Cracking	0.913
Invented Alloy 7	2	80	Cracked	Tr.
Comparison Alloy 4	5	29	Cracked	Tr.

From Table 7, it will be understood that the alloy exhibited not only high weather resistance but also high resistance to intergranular corrosion, provided that the value ($\beta = \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 20\text{B}$) is about 0.01 wt% or more, when the requirements for the Cr content, total content of C, N, O and S and the P content are met.

(Test Result 4)

Table 8 shows the result of the weather resistance test and pitting corrosion test conducted on Fe-20%Cr-(0.01 - 0.4)%P-(0.001 - 6)%Mo alloys.

Table 8

Fe-20%Cr-(0.01 to 0.4)%P-(0.001 to 6)%Mo Alloy						
Alloy	Evaluation of Rusting Degree	Gloss Retention Ratio (%)	Pitting Corrosion Potential (V _c .10)	C + N + O + S (ppm)	Mo (wt%)	P (wt%)
Invented Alloy 21	2	81	369	69	0.06	0.103
Invented Alloy 22	2	79	455	83	0.49	0.190
Invented Alloy 23	1	92	>1000	77	5.89	0.121
Invented Alloy 24	1	98	450	81	0.41	0.018
Invented Alloy 25	1	84	460	89	0.39	0.384
Invented Alloy 5	1	95	313	52	0.001	0.103
Comparison Alloy 7	4	53	96	121	0.001	0.103

From Table 8, it will be understood that the alloys in accordance with the present invention, containing 0.05 wt% of Mo and meeting the requirements for the Cr content, C, N, O and S total content and P content, exhibited superior resistance to pitting corrosion. The alloy of Comparison Example 7, which contained C, N, O and S in excess of about 100 ppm in total, was inferior not only in weather resistance but also in pitting corrosion.

(Test Result 5)

Table 9 shows the results of the weather resistance test and intergranular corrosion test conducted on the alloys Sample Nos. 26 and 27 of the present invention.

Table 9

Alloy	Evaluation of Rusting Degree	Gloss Retention Ratio (%)	Sulfuric Acid/Copper Sulfate Test	Pitting Corrosion Potential
Invented Alloy 26	2	99	No crack	>1000
Invented Alloy 27	3	78	No crack	450

It will be seen that high levels of resistance to intergranular corrosion and pitting corrosion, in addition to superior weather resistance, were exhibited by the alloys of the present invention which contain Mo in an amount within the specified range and (Ti + Nb + Zr + V + Ta + W + 20B) falling within the specified range and meeting the requirements for the Cr content, C, N, O and S total content and P content.

(Test Result 6)

Table 10 shows the results of weather resistance test and anti-acid test conducted on Fe-20%Cr-0.02P alloys (C + N + O + S < 100 ppm).

Table 10

Fe-20%Cr-0.02P Alloys (C + N + O + S < 100ppm)				
Alloy	Evaluation of Rusting Degree	Gloss Retention Ratio (%)	Evaluation of Anti-Acid Property	Ni + Co + 2Cu Value (wt%)
Invented Alloy 28	2	86	◎	0.021
Invented Alloy 29	1	91	◎	0.063
Invented Alloy 30	1	90	◎	0.915
Invented Alloy 3	2	85	△	Tr.
Invented Alloy 4	1	92	○	Tr.

From Table 10, it is clear that the anti-acid property was improved when the value (Ni + Co + 2Cu) exceeds 0.01 wt%.

(Test Result 7)

Table 11 shows the results of weather resistance test and oxidation resistance tests conducted on Fe-20%Cr-0.015%P alloys (C + N + O + S < 100 ppm).

Table 11

Fe-20%Cr-0.015%P Alloys (C + N + O + S < 100 ppm)				
Alloy	Evaluation of Rusting Degree	Gloss Retention Ratio (%)	No. of Cycles Sustained Until Extraordinary Oxidation	3Al + 2Si + Mn Value (wt%)
Invented Alloy 31	1	93	225	1.05
Invented Alloy 32	1	90	250	13.76
Invented Alloy 33	1	87	250	25.21
Invented Alloy 2	1	90	25	Tr.

From Table 11, it will be seen that oxidation resistance was improved when the value (3Al + 2Si + Mn) exceeded 1.0 wt%.

As will be understood from the foregoing description, the Fe-Cr alloy of the present invention in its various forms provides superior corrosion resistance and, therefore, can suitably be used in various fields in which Fe-Cr alloys have been used conventionally and in which further improvement in corrosion resistance is specifically required.

Claims

1. A corrosion-resistant Fe-Cr alloy having a composition containing not less than about 5 wt% of Cr, not more than about 100 ppm of C, N, O and S in total, from about 0.01 to 1.0 wt% of P and the balance substantially Fe and impurities.

2. A corrosion-resistant Fe-Cr alloy according to Claim 1, further containing not more than about 1.0 wt% of Al, not more than about 1.0 wt% of Si and not more than about 1.0 wt% of Mn.

3. A corrosion-resistant alloy according to either one of Claims 1 and 2, further containing at least one element selected from the group consisting of Ti, Nb, V, Zr, Ta, W and B by an amount which meets approximately the following condition (1):

$$0.01 \text{ wt}\% \leq \text{Ti} + \text{Nb} + \text{Zr} + \text{V} + \text{Ta} + \text{W} + 20\text{B} \leq 1.0 \text{ wt}\% \quad (1)$$

4. A corrosion-resistant alloy according to either one of Claims 1 to 2, further containing from about 0.05 wt% to 20 wt% of Mo.

5. A corrosion-resistant alloy according to either one of Claims 1 or 2, further containing at least one element from the group consisting of Ni, Co and Cu by an amount which meets the following approximate condition (2):

$$0.01 \text{ wt}\% \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt}\% \quad (2)$$

6. A corrosion-resistant Fe-Cr alloy according to Claim 1, further containing at least one element selected from the group consisting of Al, Si and Mn by an amount which meets the following approximate condition (3):

$$1.0 \text{ wt}\% \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt}\% \quad (3)$$

7. A corrosion-resistant Fe-Cr alloy according to Claim 1, further containing at least one element from the group consisting of Ni, Co and Cu by an amount which meets the following condition (2) and at least one element selected from the group consisting of Al, Si and Mn by an amount which meets the following approximate condition (3):

$$0.01 \text{ wt}\% \leq \text{Ni} + \text{Co} + 2\text{Cu} \leq 6 \text{ wt}\% \quad (2)$$

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$$1.0 \text{ wt\%} \leq 3\text{Al} + 2\text{Si} + \text{Mn} \leq 50 \text{ wt\%} \quad (3)$$

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FIG. 1

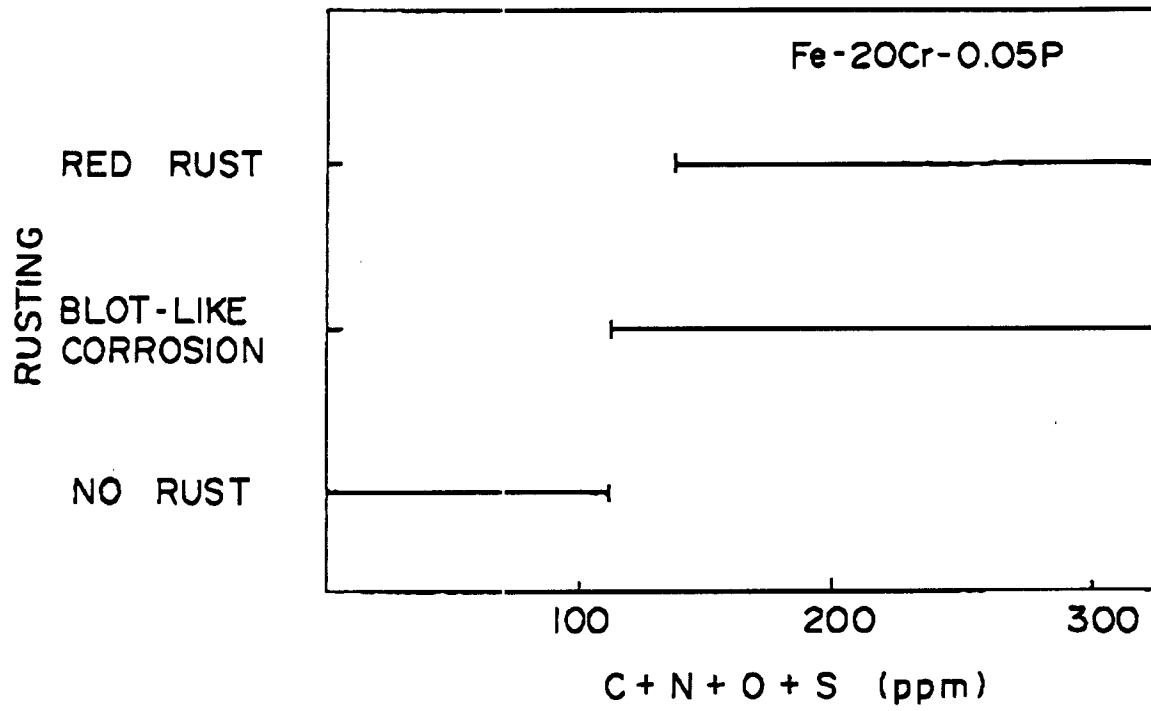


FIG. 2

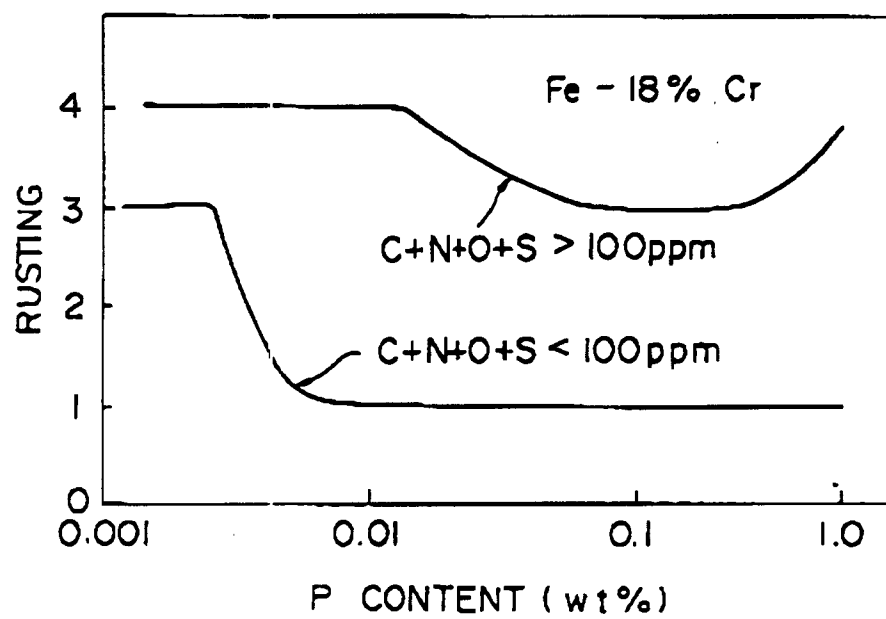


FIG. 3

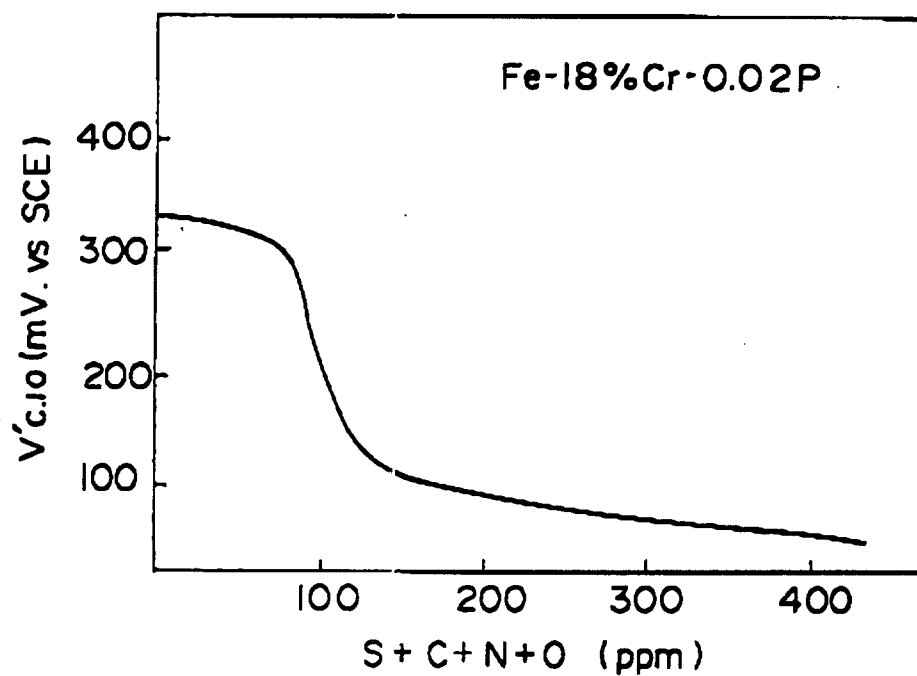


FIG. 4

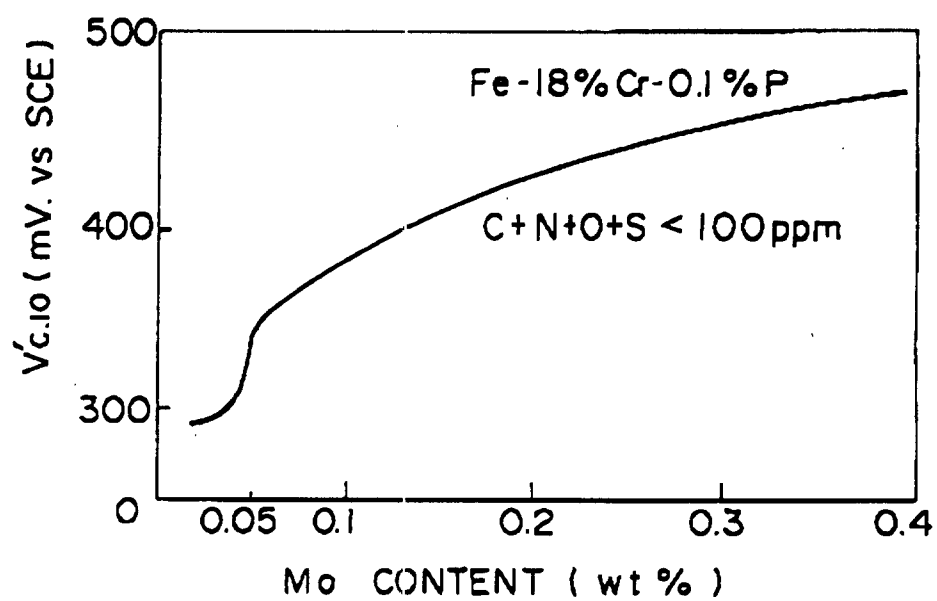


FIG. 5

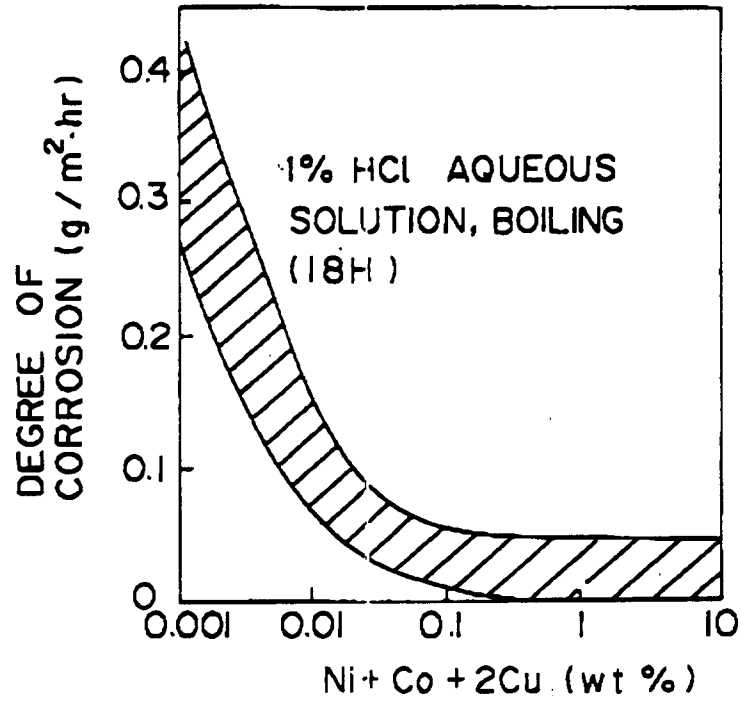
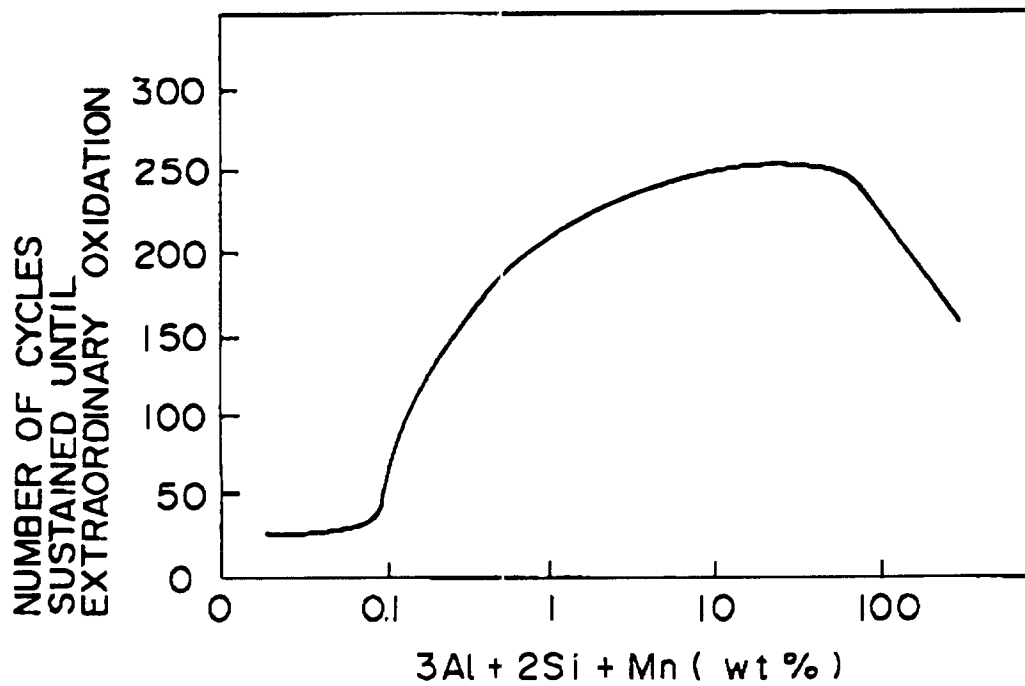


FIG. 6





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 93 10 8298

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 130 220 (NISSHIN STEEL) * the whole document *	1-7	C22C38/18

A	US-A-3 992 198 (DEMO) * the whole document *	1-7	

A	EP-A-0 402 281 (DAIDO TOKUSHUKO K.K.) * the whole document *	1-7	

A	US-A-2 402 424 (MC CAULEY) * the whole document *	1-7	

			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C22C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12 AUGUST 1993	Examiner LIPPENS M.H.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	