⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 109 350**
**A2**

# ⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: **83730106.8**

㉒ Date of filing: **09.11.83**

(51) Int. Cl.$^3$: **C 22 C 19/05, C 22 F 1/10**

㉚ Priority: **10.11.82 JP 197362/82**
**13.06.83 JP 104094/83**
**13.06.83 JP 104095/83**
**29.08.83 JP 156427/83**

(43) Date of publication of application: **23.05.84**
**Bulletin 84/21**

(84) Designated Contracting States: **DE FR SE**

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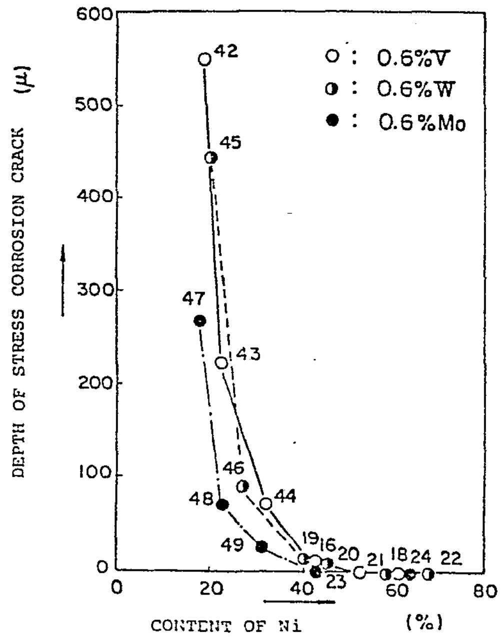
## (54) Nickel-chromium alloy.

(57) The present invention provides a nickel-chromium alloy in which it has an excellent mechanical character and improves a pitting corrosion resistance, a stress corrosion cracking resistance and a crystal boundary etching resistance, and the Ni-Cr alloy is obtained by carrying out an annealing treatment under required conditions, said alloy having the following composition:

in therms of % by weight,
40 - 70% of Ni;
0.015% or less of C;
1.0% or less of Si;
25 - 35% of Cr;
1.0% or less of Mn;
0.030% or less of P;
0.020% or less of S and
the residue comprising Fe and impurities.



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The present invention relates to a non-deposition hardening type nickel based alloy which will be subjected to a high-temperature and high-pressure water or vapor and which has a remarkably improved crystal boundary etching resistance, mechanical properties and pitting corrosion resistance, in addition to the maintenance of a stress corrosion cracking resistance, and further has a bettered stress corrosion resistance in an aqueous NaOH solution.

The present invention relates to a nickel-chromium alloy excellent in a stress corrosion cracking resistance, more specifically, to a nickel-chromium alloy in which the stress corrosion cracking resistance is noticeably improved by depositing an insolubilized carbide in grains thereof and by strengthening a coating on the surface thereof.

The present invention also relates to an alloy for a heat transfer pipe, particularly to an alloy for a heat transfer pipe on the secondary side of a nuclear reactor.

Heretofore, as materials, for a container for giving off vapor in a nuclear reactor, which will be exposed to the high-temperature and high-pressure water or vapor, for example, at 200 to 400°C and at 50 to 200 atm, and as materials used under a cooling system environment in a nuclear reactor, there are nickel based alloys such as

INCOROI 800 (trade name), and INCONEL 600 (trade name) and INCONEL 690 (trade name) set forth in Table 1 below. In recent years, these alloys have further been treated by heating them at a rather lower temperature than a level (hereinafter referred to as T°C), at which a carbide is thoroughly solubilized, alternatively by further additionally specifically heating and retaining them at a temperature of 650 to 750°C, in order to improve the crystal boundary etching resistance and stress corrosion cracking resistance.

However, the nickel based alloys which have undergone such a conventional thermal treatment are still poor in the pitting corrosion resistance and stress corrosion cracking resistance.

In view of the above-mentioned conventional techniques, an object of the present invention is to provide a method for a thermal treatment of a nickel based alloy without such drawbacks above, i.e. a method for a thermal treatment of a nickel based alloy by which its mechanical properties, pitting corrosion resistance, stress corrosion cracking resistance and crystal boundary etching resistance can be improved.

For the aforesaid object, the summary of the present invention is directed to a nickel based alloy, characterized in that said nickel based alloy for a material which will be subjected to a high-temperature and high-pressure water or vapor comprises, in terms of % by weight, 58% or more of Ni, 25 to 35% of Cr, 0.003% or less of B, 0.012 to 0.035% of C, 1% or less of Mn, 0.5% or less of Si, 0.015% or less of P, 0.015% or less of S, and the residue of Fe and usual impurities; in a first thermal treatment process, said nickel based alloy is heated and retained at a temperature of T°C to (T + 100)°C and is cooled at a greater cooling rate than a furnace cooling rate; and in a second thermal treatment process, said nickel based alloy is then retained at a temperature of 600 to 750°C and a temperature within a sensitization recovery range for a period of 0.1 to 100 hours and is cooled at a greater cooling rate than said furnace cooling rate.

Heretofore, for tubes, containers and their fittings used in stress corrosion cracking environments including $Cl^-$ ions in nuclear reactors, chemical plants and the like, many nickel based alloys which are considered to be excellent in the stress corrosion cracking resistance have been used. However, it has been reported that even in the case of a 30% Cr-60% Ni system alloy which has generally been used, the occurrence of the stress corrosion cracking cannot be avoided in certain environments.

Thus, an object of the present invention is to provide an alloy which can overcome such a drawback inherent in the 30% Cr-60% Ni system alloy and which is excellent in a corrosion resistance, especially the stress corrosion cracking resistance so that it may be used for the tubes, the containers and their fittings in the nuclear reactors, the chemical plants and the like in the form of thick-walled plates, round rods or pipes.

The inventors of the present case have paid much attention to the fact that the aforesaid 30% Cr-60% Ni based alloy is finally annealed at a relatively high temperature of 980 to 1150°C in compliance with a carbon content and is used in a state of including no insolubilized carbide, and they have researched into a relation between a morphology of the carbide in the alloy system and its corrosiveness. As a result, it has been found that an active deposition of the carbide, if in the grains thereof, is rather effective for the improvement in the stress corrosion cracking resistance. Further, in view of the report that in environments of a high-temperature water including $Cl^-$ ions, stress corrosion cracks would occur starting from pitting corrosions, the addition of Mo, W and V, which are known as elements effective for the improvement in the pitting corrosion resistance, has been attempted with the intention of strengthening the coating. In consequence, it has been found that the corrosion resistance, i.e. the stress corrosion cracking resistance of the obtained alloy is noticeably improved in cooperation with the aforementioned deposition effect of the carbide, and the present invention has now been achieved.

The gist of the present invention is directed to a nickel-chromium alloy excellent in a stress corrosion cracking resistance which is obtained by carrying out an annealing treatment under required conditions, said alloy having the following composition:

in terms of % by weight,

| | |
|---|---|
| 0.04% or less of C; | 1.0% or less of Si; |
| 1.0% or less of Mn; | 0.030% or less of P; |
| 0.02% or less of S; | 40 to 70% of Ni; |
| 25 to 35% of Cr; | 0.1 to 0.5 % of Al; |
| 0.05 to 1.0% of Ti; | |

0.5 to 5.0% in all of one or more of Mo, W and V; and the residue comprising substantially Fe.

The above-mentioned required conditions mean annealing conditions within a range (Y) surrounded by points A, B, C, D and E in Figure 4 attached hereto or an annealing operation at a temperature of 900 to 975°C. However, in the case of the latter, 0.2 to 5.0% of Nb is further added to the above-mentioned composition on condition that the content of Ti-is 0.2 to 1.0% and Nb/C is 10 to 125.

The aforesaid range (Y) is determined by A (C = 0%, 910°C), B (C = 0%, 850°C), C (C = 0.02%, 850°C), D (C = 0.04%, 900°C) and E (C = 0.04%, 1000°C).

If the operation is made under the annealing conditions in the range (Y), the stress corrosion cracking resistance of the Ni-Cr alloy, which is heretofore insufficient, can be remarkably improved. Such an unexpected effect would be considered to be due to a synergistic effect of (i) the requirement that the C content is limited to 0.04% or less and a final annealing is carried out at a relatively low temperature in compliance with the C content, and (ii) the requirement that at least one of Mo, W and V is added as an element for reinforcing the coating.

When the annealing operation is carried out at the aforesaid temperature of 900 to 975°C according to the present invention, the stress corrosion cracking resistance of the Ni-Cr alloy, which is heretofore insufficient, can also be remarkably improved. Such an effect would be considered to be due to a synergistic effect of (i) the fact that when the C content is limited to 0.04% or less and the final annealing operation is carried out at a relatively low temperature of 900 to 975°C, in the case of the Ni based alloy including 40% or more of Ni, Nb has a greater carbon-fixing effect than Ti, therefore a less amount of Cr carbide will deposit on crystal boundaries, and (ii) the intention that at least one of Mo, W and V is added for the reinforcement of the coatings.

Presently, a heat transfer pipe of a steam generator in a nuclear reactor such as a pressurized water reactor is made of an only annealed alloy or Alloy 600 (trade name, 75%Ni-15%Cr-8%Fe) which has further been subjected to a specific thermal treatment (700°C x 15 hr). However, recent researches have revealed that Alloy 600 which is the alloy for the heat transfer pipe has the following problems. That is to say, a stress corrosion cracking sometimes occurs owing to an alkaline concentrate in the gap between the heat transfer pipe and a pipe-supporting plate in envrironments (alkaline environments including ammonia and hydrazine and having a pH of 9.2 to 9.5 and a temperature of 280°C) on the secondary side of the nuclear reactor, and a pitting corrosion tends to take place owing to $Cl^-$ ions in leaked seawater in the same environments on the secondary side of the nuclear reactor. Further, this pitting corrosion will deeply penetrate and the number of the pitting corrosions will augment with the increase in a concentration of the $Cl^-$ ions.

Heretofore, it is known that the spefific thermal treatment is given to a nickel based alloy for the sake of the improvement in a stress corrosion cracking resistance (hereinafter referred to as the SCC resistance). For example, Japanese Patent Disclosure No. 25216/1979 discloses a method in which after a final annealing treatment, the alloy is successively heated and retained at a temperature of 550 to 850°C for a period of 1 to 100 hours in order to deposit a carbide on crystal boundaries, thereby heightening the SCC resistance. Even by such a conventional technique, however, a resistance to the stress corrosion cracking caused by the alkaline concentrate, i.e. an alkali stress corrosion cracking resistance and the pitting corrosion resistance cannot be improved. Further, in fact, the nickel based alloy obtained by such a conventional method cannot always provide a satisfactory combination of the alkali stress corrosion cracking resistance and the pitting corrosion resistance.

Thus, an object of the present invention is to provide an alloy for a heat transfer pipe excellent in the corrosion resistance, especially an alloy for a heat transfer pipe excellent in the alkali stress corrosion cracking resistance and the pitting corrosion resistance.

Another object of the present invention is to provide an alloy for a heat transfer pipe which can be used particularly advantageously under alkali environments in a steam generator of a pressurized water reactor.

The inventors of the present case have intensively carried on researches for the achievement of such objects, and they have acquired the following knowledges:

(1) The addition of one or more of elements Mo, W and V which are effective for the pitting corrosion resistance permits heightening a passive coating on the alloy in order to improve the pitting corrosion resistance.

(2) The alkali stress corrosion cracking resistance can be remarkably improved by first heating and retaining the alloy for 1 minute or more at a temperature not less than a level at which a carbide in the alloy is thoroughly solubilized, in order to carry out an annealing treatment; cooling it to a temperature of 200°C or less; and accomplishing the specific thermal treatment for it at a temperature of 600 to 750°C for a period of 0.1 to 100 hours.

(3) Such an alkali stress corrosion cracking resistance can be improved, together with the aforesaid betterment in the pitting corrosion resistance, by virtue of the addition of one or more of Mo, W and V.

Since the nickel based alloy, inter alia the high Cr-Ni based alloy including 25 to 35% of Cr is small in the solubility of C therein, Cr carbide deposits on crystal boundaries during the cooling process or practical use after the annealing step in order to form Cr-poor layers thereon, so that the stress corrosion cracking will take place thereon. Therefore, when carbon is enough solubilized during the annealing step and the alloy is once cooled to a temperature of 200°C or less and the thermal treatment is then carried out by heating it again at a temperature within the range of 600 to 750°C for at most 100 hours, the deposition of Cr carbide ($Cr_{23}C_6$) will be accelerated, but the formation of the Cr-poor layers will positively be inhibited owing to the facilitation of a Cr diffusion from its interior which is brought about by doing the treatment at a heating temperature for a retention time in Figure 2. Such an effect will lead to the improvement in the stress corrosion cracking resistance, particularly the alkali stress corrosion cracking resistance and the pitting corrosion resistance in combination with the aforesaid effect based on the addition of one or more of Mo, W and V. In this connection, the inventors have known that after the final annealing, by once cooling the alloy to a temperature of 200°C or less at which no diffusion of Cr substantially occurs in the alloy, the deposition rate of the carbide at the time of the subsequent thermal treatment is unexpectedly remarkably accelerated, as compared with the case where the thermal treatment is successively carried out after the final annealing.

Accordingly, the present invention is characterized by an alloy for heat transfer pipes excellent in an alkali stress corrosion cracking resistance which is obtained by heating and retaining said alloy at a temperature within the range of a temperature (T°C), at which a carbide in said alloy is thoroughly solubilized, to T + 100°C for 1 minute or more; cooling it once to a level of 200°C or less; and carrying out a thermal treatment under conditions within a hatched range Z in Figure 15, said alloy comprising:

in terms of % by weight,

| | |
|---|---|
| 0.15% or less of C; | 1.0% or less of Si; |
| 1.0% or less of Mn; | 25 to 35% of Cr; |
| 40 to 70% of Ni; | 0.5% or less of Al; |
| 0.01 to 1.0% of Ti; | |

0.5 to 5.0%, in all, of one or more of Mo, W and V;

| | |
|---|---|
| 0.030% or less of P; | 0.020% or less of S; |

and the residue of Fe and impurities.

As definite from the foregoing, the present invention is directed to the alloy for a heat transfer pipe which is excellent in the alkali stress corrosion cracking resistance and the pitting corrosion resistance in the alkaline environments, but in a preferred embodiment, it is directed to the alloy for a heat transfer pipe on the secondary side of a nuclear reactor, for example a heat transfer pipe of a steam generator in a pressurized water reactor.

Brief Description of the Drawings:

Figure 1 is a schematic diagram illustrating a solution temperature of a carbide in a nickel based alloy and a temperature range in a first thermal treatment process;

Figure 2 is a diagram illustrating an influence of conditions of a second thermal treatment process regarding the present invention upon a crystal boundary ectching resistance; and

Figure 3 is a diagram illustrating influences of a cooling rate of the first thermal treatment process and a temperature retaining time of the second thermal treatment process regarding the present invention upon the crystal boundary etching resistance.

Figures 4 to 8 illustrate the case where annealing conditions are in a range (Y), Figure 4 shows a graph of an annealing temperature with respect to a carbon content in the present invention;

Figures 5 to 7 are graphs showing test results of a crystal boundary etching resistance in Examples according to the present invention; Figure 8 is a graph likewise showing test results of a stress corrosion cracking resistance;

Figures 9 to 13 illustrate the case where 0.2 to 5.0% of Nb is additionally added subject to Ti = 0.2 to 1.0%

and Nb/C = 10 to 125 and an annealing temperature is 900 to 975°C, and they are graphs showing test results of Examples according to the present invention.

Figure 14 is a graph showing a temperature range of an annealing treatment regarding the present invention with respect to a content of carbon;

Figure 15 is a graph drawn by plotting alkali stress corrosion cracking resistances with respect to heating temperatures and retention times of thermal treatment conditions; and

Figure 16 is a graph showing relations between contents of Mo, V and W and corrosion amounts.

## Detailed Description of the Invention:

Now, referring to FIGS. 1 to 3, the detailed description will be made to an alloy to be treated.

Alloy to be treated:

The content of Ni is 58% or more, since when it is below 58%, the alloy will be poor in an alkali stress corrosion cracking resistance.

When the content of Cr is less than 25%, the alloy will have a less crystal boundary etching resistance and stress corrosion cracking resistance; when it is more than 35%, abnormal substances will deposit in the second thermal treatment process, which fact will lead to the deterioration in ductility. Therefore, the content of

Cr is within the range of 25 to 35%.

With regard to the element B, when its content is above 0.003%, the alloy will be poor in the crystal boundary etching resistance. Therefore, the content of B is 0.003% or less.

When the content of C is less than 0.012%, the alloy will have an insufficient strength; when it is in excess of 0.035%, it will be poor in the stress corrosion cracking resistance. Therefore, the content of C is within the range of 0.012 to 0.035%.

Elements P, S and the like are incorporated into the product as impurities during a process of a usual iron manufacture or steel manufacture, but too much impurities have bad influence upon the corrosion resistance. Therefore, the content of P is 0.015% or less and that of S is also 0.015% or less.

Further, Mn and Si are added for the sake of a deoxidation, a reinforcement of a matrix and a reinforcement of grain boundaries, but when the content of Mn is more than 1%, the alloy will be hard to melt, and when the content of Si is more than 0.5%, the alloy will be poor in welding properties. Therefore, the content of Mn is 1% or less, and that of Si is limited to 0.5% or less.

First thermal treatment process:

A temperature T°C at which the carbide of the nickel based alloy is thoroughly solubilized varies with the content of C,as elucidated by the schematic view in Figure 1. If this thermal treatment process is carried out at a temperature less than T°C, the carbide will deposit, thereby unreasonably increasing a tensile strength, 0.2% yield point and hardness, and thus deteriorating the stress corrosion cracking resistant. On the contrary, if at a temperature more than (T + 100)°C, a grain size of crystals will become remarkably coarse, thereby deteriorating the crystal boundary etching resistance, and merely providing the insufficient tensile strenght, 0.2% yeld point and hardness.

Further, it is natural that the retention time is prolonged with the increase in the wall thickness of the material, hence it is impossible to uniformly define the retention time. However,generally speaking, the retention time takes 30 minutes or so per 2.54 cm (1 inch) of the material thickness, and in the case that the material thickness is 2.54 cm or less, 1 to 30 minutes will be usually taken. Furhter, since an abnormally prolonged time will produce coarse crystals on the surface of the material and its strength will thus be lowered, it is preferred that the retention time is within the range of 1 minute to 2 hours.

Then, the alloy is cooled, for example, from a level of 200°C to room temperature.

With regard to a cooling rate of the alloy, the cooling rate less than a furnace cooling rate is not advantageous, but any rate of the furnace cooling rate or more is in fact satisfactory. The cooling rate of the furnace cooling rate or more can be obtained by, for example, the furnace cooling, an air cooling, gas cooling, oil cooling, water cooling and the like.

Second thermal treatment process:

After retained at a temperature of T°C to (T + 100)°C for a period of 30 minutes and water cooled in the first thermal treatment process, specimens of Table 2 below were retained at various heating temperatures for various periods of time and were cooled in the same manner as in the aforesaid first process. Then, they were immersed in a boiling solution of 65% $HNO_3$ and 0.1-N HF for a period of 4 hours. Obtained test results are shown in Figure 2 below. In a sensitization range in Figure 2, Cr-free layers are formed on crystal boundaries, and a crystal boundary etching and pitting corrosion thus tend to occur. Further, in the case of the alloys in an unsensitization range therein, there is a probability of their being sensitized during their use as the real materials at a high temperature, therefore they are also liable to bring about the crystal boundary etching. In consequence, the retention temperature in the second thermal treatment process must be in a sensitization recovery range in which the Cr-free layers recover. Furthermore, when the retention temperature is more than 750°C, a solubility of C will be great and a solubility difference will result from a temperature difference between such a temperature and a temperature at the time of a cooling or a practical use. As a result, a carbide tends to deposit on the crystal boundaries. When the retention temperature is less than 600°C, the retention time more than 100 hours will be required, which fact is not economical. Therefore, the retention temperature is limited to the range of 600 to 750°C. Moreover, when the retention time is less than $10^{-1}$ hour, the sensitization recovery range cannot be prepared at the aforesaid temperature; the retention time more than 100 hours is not economical. Therefore, it should be within the range of $10^{-1}$ to 100 hours. With regard to the cooling rate in this case, any rate of the furnace cooling rate or more is satisfactory, as in the first thermal treatment process.

After retained at a temperature of T°C to (T + 100)°C for a period of 30 minutes in the first thermal treatment process, specimens were heated and retained at a temperature of 700°C and were air cooled, and they were then immersed in a boiling solution of 65% $HNO_3$ and 0.2 g of $Cr^{6+}$/liter for a period of 24 hours. Obtained results of crystal boundary etching resistance tests are exhibited in Figure 3 below. As the same drawing indicates, the sensitization range in the second thermal treatment process varies with the cooling rate in the first thermal treatment process, and it has been found that any case gets into the sensitization recovery range within 100 hours.

In Table 3, results of a variety of tests for the specimens in Table 2 are summarized. According to the results, it can be understood that present invention permits providing the nickel based alloy having the remarkably improved crystal boundary etching resistance, pitting corrosion resistance, mechanical properties and alkali stress corrosion cracking resistance, in contrast with the conventional.

As described in detail in the foregoing, the nickel based alloy according to the present invention can noticeably improve the crystal boundary etching resistance, pitting corrosion resistance, mechanical properties and stress corrosion cracking resistance, therefore this invention is most suitable for the thermal treatment for materials which will be subjected to a high-temperature and high-pressure water of 200 to 400°C, for example, materials for a container for giving off vapor in a nuclear reactor and materials for a cooling system in the nuclear reactor.

Table 1

Chemical components of alloys (%)

| | C | Si | Mn | P | S | Ni | Cr | Fe | Ti | Al | Cu |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Inconel 600 | ≤ 0.015 | ≤0.5 | ≤1.0 | ≤0.03 | ≤ 0.015 | ≤72.0 | 14.0 ~17.0 | 6.0 ~10.0 | - | - | ≤0.5 |
| Inconel 690 | ≤0.05 | ≤0.50 | ≤0.50 | - | ≤ 0.015 | ≤58.0 | 27 ~31 | 7~11 | - | - | ≤0.5 |

Table 2

Chemical components of specimens (%)

| | C | Si | Mn | P | S | Ni | Cr | Ti | Al | Fe | B | N |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alloy 1 | 0.013 | 0.24 | 0.18 | 0.013 | 0.001 | 61.16 | 28.82 | 0.31 | 0.30 | 8.98 | 0.0026 | - |
| Alloy 2 | 0.017 | 0.26 | 0.33 | 0.008 | 0.002 | 59.35 | 30.80 | 0.25 | 0.15 | 8.80 | 0.0002 | 0.0196 |
| Alloy 3 | 0.023 | 0.36 | 0.33 | 0.002 | 0.003 | 60.87 | 30.05 | 0.26 | 0.25 | Bal | 0.003 or less | - |
| Alloy 4 | 0.034 | 0.33 | 0.33 | 0.002 | 0.003 | 60.75 | 29.96 | 0.26 | 0.27 | Bal | 0.003 or less | - |

Table 3 Influence of thermal treatment conditions upon crystal boundary etching resistance, stress corrosion cracking resistance, pitting corrosion resistance and mechanical properties of nickel based alloy

| | Thermal Treatment | | Crystal Boundary Etching Resistance | | | Stress Corrosion Cracking Resistance | | | Pitting Corrosion Resistance | Mechanical Properties | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | First Thermal Treatment | Second Thermal Treatment | Fluorine Nitrate | $Cr^{6+}$ Addition Nitric Acid Test | *1 EPR | *2 Neutral | *3 Acid | *4 Alkali | *5 Acid | Tensile Strength | 0.2% Yield Point | Hardness |
| Conventional Method | 900°C (T-130°C) | - | 0 | 0 | 0 | 0 | 0 | x | Δ | 0 | x | x |
| | 900°C (T-130°C) | 700°Cx15h | 0 | 0 | 0 | 0 | 0 | Δ | 0 | 0 | x | x |
| Reference Method | 1100°C (T+ 70°C) | - | 0 | 0 | 0 | 0 | 0 | x | x | 0 | 0 | 0 |
| Present Invention | 1100°C (T+ 70°C) | 700°Cx15h | ◎ | ◎ | ◎ | 0 | 0 | ◎ | ◎ | 0 | 0 | 0 |

◎ : Very good

0 : Good

Δ : Slightly good

x : Bad

*1) Electro Potentiokinetic Reactivation: A method for estimating the crystal boundary etching resistance in a potential-current diagram from a peak current generated when a voltage which has been raised up to a level of a passive state range is dropped.

*2) Retention was made at 360°C for 1000 hours in a running degassed water.

*3) Retention was made at 300°C for 1000 hours in a high-temperature non-degassed water including 500 ppm of Cl.

*4) Retention was made at 325°C for 1000 hours in a degassed water including 10% of NaOH.

*5) Retention was made at 288°C for 1000 hours in a high-temperature non-degassed water including 100 ppm of Cl.

Then, the present invention, referring to FIGS. 4 to 8, will be described below.

The reason why a composition of the alloy according to the present invention is defined as mentioned above is as follows:

C:

Since C is an element harmful to the SCC resistance, its content is limited to 0.04% or less.

Si, Mn and Al:

These elements all are deoxidizers, and they are added in a suitable amount in accordance with melting conditions. However, when the contents of Si, Mn and Al exceed upper limits of 1.0%, 1.0% and 0.5%, respectively, the formed alloy will be deteriorated in cleanness. Further, when being less than 0.1%, Al is not effective.

Ni:

This element is effective to improve a corrosion resistance, particularly it serves to improve an acid resistance and the SCC resistance in a high-temperature water including $Cl^-$ ions. For the achievement of these effects, the content of Ni is required to be 40% or more, and its upper limit is set to 70%, taking addition proportions of alloy elements of Cr, Mo, W, V and the like into consideration.

Cr:

The element Cr is essential for the improvement in the corrosion resistance, but its amount less than 25% is insufficient to enhance the SCC resistance. On the contrary, when it is more than 35%, a hot workability will remarkably deteriorate. Therefore, the content of Cr is limited to the range of 25 to 35% in the present invention.

P:

The element P is present in the alloy as an impurity. If its content is above 0.030%, it will exert a harmful influence upon the acid resistance and the hot workability.

S:

The element S is also one of the impurities. If being present in an amount more than 0.02%, it will be deleterious to the acid resistance and hot workability, as in the case of P.

Ti:

This element Ti is added as a stabilizing agent. That is to say, even if the contents of P and S are controlled below the above-mentioned levels, a remarkable effect cannot be obtained. Therefore, in the present invention, Ti is added in an amount of 0.05% or more to assure the desired hot workability. On the contrary, when the content of Ti is more than 1.0%, its effect will reach a ceiling level. Therefore, the upper limit of this element is to be set to 1.0%.

Mo, W and V:

These elements are effective to heighten the pitting corrosion resistance especially in a high-temperature water including $Cl^-$ ions. When the content of at least one of these elements is less than 0.5% in all, the passive coating on the surface will not be heightened and a pitting corrosion will occur, thereby deteriorating the stress corrosion cracking resistance. On the contrary, when the content of at least one of them is more than 5.0% in all, the effect of the improvment in the pitting corrosion resistance will reach a ceiling level, and the hot workability will noticeably be deteriorated. Therefore, in the present invention, the amount of one or more of Mo, W and V to be added is limited to the range of 0.5 to 5.0% in all.

Nb:

In the nickel based alloy (which includes 40% or more of Ni), Nb is greater in the effect of a carbon fixation than Ti. In the present invention, the content of Nb is set to the range of 0.2 to 5.0%. In this range, the ratio of Nb/C will become 10 to 125. In the case of its amount being 0.2% or less, the effect of fixing carbon is small and a sensitization will thus occur, thereby generating the SCC (stress corrosion cracking). On the contrary, when the content of Nb is more than 5%, the effect (carbon fixation) will reach a ceiling level, and additionally the hot workability will noticeably be deteriorated. Therefore, its upper limit is set to 5.0%.

I. Now, reference will be made to the annealing treatment under annealing conditions in the above-mentioned range (Y).

Referring first to Figure 4, lines BC and CD represent recrystallization lines of the alloy according to the present invention. If the annealing treatment is carried out at a temperature below the levels of the lines BC and CD, no recrystallization will occur, so that the strength of the annealed alloy will be high and its corrosion resistance will be bad. Therefore, the annealing treatment is required to be carried out at a temperature above the levels of the lines BC and CD in accordance with a C content in the alloy. On the other hand, a line AE in the same drawing means an upper limit of temperatures at which the carbon in the alloy is not thoroughly solubilized. Accordingly, so long as the annealing treatment is carried out at a temperature below this upper limit, a carbide will be present in the grains. However, if the annealing operation is done at a temperature above a level of the line AE, all the carbide will be deposited on crystal boundaries in the case that a sensitization treatment is accomplished at at a temperature of 600°C for a period of 3 hours. This will lead to the deterioration in the crystal boundary etching resistance. Therefore, the final annealing is required to be carried out at a temperature below the level of the line AE.

Now, the present invention will further be described in detail in accordance with examples below.

Examples 1 to 29

Alloys (Alloy Nos. of the present invention 1 to 29, conventional alloys Nos. 30 to 37 and comparative alloys Nos. 38 to 41) of compositions comprising chemical components exhibited in Table 1 below were dissolvingly formed in a 17-kg vacuum furnace and subjected to a forging, hot rolling and thermal treatment under usual conditions, and they were then cold rolled as much as 30%, followed by annealing at a variety of temperatures. Further, a thermal treatment, i.e. a sensitization treatment on conditions, 600°C x 3 hours, which were set on the basis of a supposed life in practical use was carried out, and 3-mm-thick x 10-mm-wide x 40-mm-long speciments for crystal boundary etching tests and 2-mm-thick x 10-mm-wide x 75-mm-long specimens for stress corrosion cracking tests were then prepared. These speciments were polished by the use of emery paper No. 320 and were then employed for the tests below.

First, the specimens for the stress corrosion cracking tests were, after polished, caused to overlap each other every 2 specimens and each pair of them was bent into a U-shape to prepare double U-bent specimens. The thus prepared specimens were immersed in a solution including 1000 ppm of $Cl^-$ (as NaCl) at 325°C for 1500 hours by the use of an autoclave (a high-temperature and high-pressure container). After the completion of the tests, cracks on inside surfaces of the specimens were measured for their depth by a microscope.

On the other hand, the specimens for the crystal boundary etching tests were immersed in a boiling solution including 60% of $HNO_3$ and 0.1% of HF for 4 hours, and a weight loss caused by the corrosion was measured.

Obtained test results are shown by graphs in Figures 5 to 8. Reference numerals in the graphs represent the numbers of the specimen alloys in Table 4.

A variety of amounts of Ni was added to each fundamental composition comprising 0.02 to 0.03% of C, 25% of Cr and 0.6% of Mo according to the present invention to prepare alloy specimens, and an annealing treatment was then carried out by heating the specimens at 1150°C for 30 minutes. After water cooling, a sensitization treatment was carried out by heating them at 600°C for 3 hours and they were then cooled. The aforesaid crystal boundary etching tests were accomplished on the specimens to prepare data. Figure 5 exhibits the thus obtained data. The aforesaid annealing temperature was higher than that of the present invention.

Even in the case of the allow having the same composition as the alloy according to the present invention, if the annealing temperature is high and when 3 hours' heating at 600°C (the sensitization treatment) and an air cooling operation are carried out, the carbide of Cr will all deposit on the crystal boundaries and Cr-free layers will be formed in the vicinity of the crystal boundaries, so that corrosion will occur. Therefore, it is necessary to lower the annealing temperature.

The graphs in Figure 6 show the crystal boundary etching resistances of the alloys comprising the compositions regarding the present invention and conventional allohs. The alloys in both the groups which had the composition of 0.02 to 0.03% of C and 0.6% of Mo were heated at 900°C for 30 minutes to accomplish the annealing treatment. After water cooling, they were heated at 600°C for 3 hours to accomplish the sensitization treatment, followed by air cooling. In Figure 6, white and black circles represent the alloys including more than 30% of Cr and those including 25 to 30% of Cr, respectively. As understood from the graphs in this drawing, the alloys including an Ni amount below 40% are all great in a corrosion rate; the alloys including an Ni amount of 40% or more have an improved crystal boundary etching resistance. Therefore, the Ni content of 40% or more is necessary.

One or more of Mo, V and W were added to each fundamental composition comprising 0.02% of C, 25% of Cr and 50% of Ni in order to prepare alloy specimens, and an annealing treatment was then carried out by heating the prepared specimens at 900°C for 30 minutes. After water cooling, the sensitization treatment was carried out by heating them at 600°C for 3 hours and they was then air cooled. Thus obtained results of the crystal boundary etching tests are exhibited in Figure 7. This drawing indicates that when the total amount of at least one of Mo, V and W is less than 0.5%, any improvement in corrosion resistance is not seen, but when its content is 0.5% or more, the crystal boundary etching resistance is built up. This would be considered to allow a $Cr_2O_3$ coating formed on the alloy surface to stably exist, because the added Mo, V and W strengthen the passive coating. Hence, the total amount of one or more of the added Mo, V and W is required to be 0.5% or more.

The graphs in Figure 8 show influences of an Ni content(%) and Cr content (%) upon the SCC resistance. Used alloy specimens were prepared through the annealing treatment of 30 minutes' heating at 900°C, water cooling, sensitization treatment of 3 hours' heating at 600°C, and air cooling. In this drawing, white and black circles represent the alloys without stress corrosion cracks and those with some cracks of 20 μ or more.

It is apparent that even if the Cr content is 20% or more as in the present invention, when the Ni content is less than 40%, crystal boundary type stress corrosion cracks will occur. Therefore, the Ni content is required to be 40% or more.

Table 4

(% by weight)

| | Alloy No. | C | Si | Mn | P | S | Ni | Cr | Ti | Mo | W | V | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alloys of the Present Invention | 1 | 0.017 | 0.41 | 0.41 | 0.011 | 0.008 | 40.05 | 25.37 | 0.18 | 0.65 | - | - | Residue |
| | 2 | 0.019 | 0.42 | 0.43 | 0.010 | 0.005 | 45.00 | 27.50 | 0.25 | 0.63 | - | - | " |
| | 3 | 0.018 | 0.41 | 0.41 | 0.011 | 0.006 | 53.50 | 26.50 | 0.27 | 0.64 | - | - | " |
| | 4 | 0.016 | 0.40 | 0.42 | 0.012 | 0.007 | 70.67 | 25.75 | 0.26 | 0.66 | - | - | " |
| | 5 | 0.018 | 0.40 | 0.43 | 0.009 | 0.006 | 25.20 | 31.37 | 0.35 | 0.62 | - | - | " |
| | 6 | 0.019 | 0.51 | 0.42 | 0.018 | 0.011 | 40.08 | 31.30 | 0.23 | 0.58 | - | - | " |
| | 7 | 0.017 | 0.42 | 0.41 | 0.018 | 0.013 | 49.80 | 33.45 | 0.24 | 0.65 | - | - | " |
| | 8 | 0.021 | 0.49 | 0.48 | 0.017 | 0.010 | 60.05 | 31.45 | 0.23 | 0.67 | - | - | " |
| | 9 | 0.020 | 0.48 | 0.48 | 0.015 | 0.010 | 64.35 | 33.25 | 0.23 | 0.63 | - | - | " |
| | 10 | 0.025 | 0.48 | 0.47 | 0.013 | 0.011 | 50.35 | 25.47 | 0.27 | 1.00 | - | - | " |
| | 11 | 0.026 | 0.49 | 0.48 | 0.014 | 0.010 | 50.45 | 25.75 | 0.37 | 3.05 | - | - | " |
| | 12 | 0.009 | 0.41 | 0.43 | 0.012 | 0.009 | 50.35 | 26.45 | 0.27 | 4.50 | - | - | " |
| | 13 | 0.021 | 0.43 | 0.43 | 0.012 | 0.008 | 50.25 | 26.25 | 0.20 | - | 0.63 | - | " |
| | 14 | 0.025 | 0.42 | 0.42 | 0.013 | 0.009 | 51.25 | 25.35 | 0.21 | - | 1.10 | - | " |
| | 15 | 0.027 | 0.44 | 0.43 | 0.012 | 0.008 | 50.37 | 25.36 | 0.19 | - | 2.90 | - | " |

(To be continued)

(Continued from page 33)

(% by weight)

| | Alloy No. | C | Si | Mn | P | S | Ni | Cr | Ti | Mo | W | V | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alloys of the Present Invention | 16 | 0.032 | 0.49 | 0.44 | 0.009 | 0.009 | 51.37 | 26.26 | 0.25 | - | 4.40 | - | Residue |
| | 17 | 0.021 | 0.43 | 0.42 | 0.012 | 0.012 | 50.45 | 25.58 | 0.27 | - | - | 0.65 | " |
| | 18 | 0.023 | 0.42 | 0.41 | 0.011 | 0.008 | 50.46 | 26.45 | 0.36 | - | - | 1.15 | " |
| | 19 | 0.028 | 0.41 | 0.42 | 0.012 | 0.012 | 51.36 | 25.36 | 0.35 | - | - | 3.05 | " |
| | 20 | 0.029 | 0.43 | 0.44 | 0.011 | 0.009 | 51.38 | 25.47 | 0.34 | - | - | 4.60 | " |
| | 21 | 0.019 | 0.42 | 0.43 | 0.013 | 0.008 | 51.46 | 26.80 | 0.45 | 1.2 | 0.8 | - | " |
| | 22 | 0.023 | 0.43 | 0.44 | 0.015 | 0.009 | 52.16 | 25.60 | 0.37 | 2.3 | 1.7 | - | " |
| | 23 | 0.025 | 0.44 | 0.46 | 0.012 | 0.010 | 51.65 | 26.37 | 0.25 | 1.6 | 0.4 | - | " |
| | 24 | 0.009 | 0.43 | 0.45 | 0.011 | 0.009 | 51.75 | 27.46 | 0.16 | 2.85 | 1.1 | - | " |
| | 25 | 0.016 | 0.48 | 0.36 | 0.012 | 0.008 | 50.36 | 26.36 | 0.47 | 1.0 | - | 1.15 | " |
| | 26 | 0.037 | 0.47 | 0.35 | 0.011 | 0.003 | 51.39 | 26.07 | 0.36 | 2.25 | - | 2.0 | " |
| | 27 | 0.026 | 0.46 | 0.36 | 0.009 | 0.006 | 51.46 | 26.34 | 0.46 | 0.4 | 0.2 | 0.20 | " |
| | 28 | 0.025 | 0.47 | 0.37 | 0.010 | 0.008 | 50.36 | 25.98 | 0.26 | 0.8 | 0.2 | 0.35 | " |
| | 29 | 0.018 | 0.49 | 0.43 | 0.011 | 0.007 | 51.05 | 25.46 | 0.36 | 0.8 | 0.8 | 0.95 | " |

(To be continued)

(Continued from page 34)

(% by weight)

| | Alloy No. | C | Si | Mn | P | S | Ni | Cr | Ti | Mo | W | V | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Conventional Alloys | 30 | 0.030 | 0.49 | 0.43 | 0.016 | 0.011 | 50.46 | 25.35 | 0.26 | - | - | - | Re-sidue |
| | 31 | 0.030 | 0.43 | 0.44 | 0.012 | 0.013 | 50.48 | 25.45 | 0.25 | 0.25 | - | - | " |
| | 32 | 0.026 | 0.46 | 0.44 | 0.011 | 0.009 | 50.36 | 25.95 | 0.27 | 0.4 | - | - | " |
| | 33 | 0.038 | 0.43 | 0.43 | 0.018 | 0.010 | 50.37 | 25.86 | 0.25 | - | - | - | " |
| | 34 | 0.025 | 0.46 | 0.47 | 0.025 | 0.012 | 51.36 | 25.74 | 0.24 | - | 0.2 | - | " |
| | 35 | 0.024 | 0.47 | 0.47 | 0.020 | 0.011 | 50.41 | 25.36 | 0.26 | - | - | 0.25 | " |
| | 36 | 0.023 | 0.48 | 0.48 | 0.018 | 0.009 | 50.36 | 25.47 | 0.26 | 0.10 | 0.05 | - | " |
| | 37 | 0.020 | 0.48 | 0.47 | 0.020 | 0.010 | 50.41 | 25.36 | 0.25 | 0.05 | 0.05 | 0.10 | " |
| Alloys for Comparison | 38 | 0.023 | 0.51 | 0.37 | 0.014 | 0.009 | 25.30* | 25.10 | 0.15 | 0.60 | - | - | " |
| | 39 | 0.028 | 0.50 | 0.41 | 0.013 | 0.009 | 33.2* | 25.00 | 0.16 | 0.70 | - | - | " |
| | 40 | 0.024 | 0.36 | 0.48 | 0.012 | 0.008 | 25.15* | 31.50 | 0.36 | 0.65 | - | - | " |
| | 41 | 0.020 | 0.42 | 0.36 | 0.016 | 0.009 | 32.45* | 32.56 | 0.25 | 0.67 | - | - | " |

Note: *Outside the present invention. The conventional alloys all did not include Mo, W and V in amounts required in the present invention.

II. Next, the following will be made to the annealing treatment at a temperature of 900 to 975°C.

In the present invention, the annealing treatment is carried out at a temperature of 900 to 975°C. However, when this annealing temperature is less than 900°C, recrystallization cannot be effected. Therefore, the treated alloy has a high strength and is insufficient in the corrosion resistance. On the contrary, when the annealing temperature is more than 975°C, the carbon in the alloy will be thoroughly solubilized during the annealing operation, so that no carbide will exist in the grains any more. Therefore, when a temperature above 975°C is employed for the annealing operation and when the conditions of 600°C x 5 hours are taken for the sensitization treatment, the carbide will all deposit on crystal boundaries and the crystal boundary etching resistance will thus be deteriorated. Accordingly, the final annealing operation in the present invention is carried out at a temperature of 900 to 975°C.

Referring to FIGS 9 to 13, the present invention will be described below.

Examples 30 to 65

Alloys (Alloy Nos. of the present invention 1 to 36 and comprative alloys Nos. 37 to 63) of compositions comprising chemical components exhibited in Table 5 below were dissolvingly formed in a 17-kg vacuum furnace and subjected to a forging, hot rolling and thermal treatment under usual conditions, and they were then cold rolled as much as 30%, followed by annealing at a variety of temperatures. Further, a thermal treatment, i.e. a sensitization treatment on conditions, 600°C x 5 hours, which were set on the basis of a supposed life in practical use was carried out, and 3-mm-thick x 10-mm-wide x 40-mm-long specimens for crystal boundary etching tests and 2-mm-thick x 10-mm-wide x 75-mm-long specimens for stress corrosion cracking tests were then prepared. These specimens were polished by the use of emery paper No. 320 and were then employed in tests below.

First, the specimens for the stress corrosion cracking tests were, after polished, caused to overlap each other every 2 specimens and were bent into a U-shape to prepare double U-bent specimens. The thus prepared specimens were immersed in a solution including 1000 ppm of $Cl^-$ (as NaCl) at 330°C for 1500 hours by the use of an autoclave (a high-temperature and high-pressure container). After the completion of the tests, cracks on inside surfaces of the specimens were measured for their depth by a microscope.

On the other hand, the specimens for the crystal boundary etching tests were immersed in a boiling solution including 60% of $HNO_3$ and 0.1% of HF for 4 hours, and a weight loss caused by the corrosion was measured.

Graphs in Figure 9 show crystal boundary etching test results of the alloys in which about 0.6% of Mo, W and V was respectively added to the 25% Cr-55% Ni system alloy and various amounts of Nb were added thereto varying the ratio of Nb/C. In each case, an annealing treatment was carried out by heating the alloy specimens at 950°C for 30 minutes. After water cooling, the sensitization treatment was carried out by heating them at 600°C for 5 hours and they were then air cooled. Figure 9 indicates that the alloys in which the ratio of Nb/C is less than 10 is very bad in the crystal boundary etching resistance, but when this ratio is 10 or more, the crystal boundary etching resistance is sharply improved. This phenomenon would be pressumed as follows: If Nb is not added to the alloy in a plenty amount, the sensitization treatment will bring about the deposition of Cr carbide on crystal boundaries, and Cr-free layers will thus be formed in the vicinity of the crystal boundaries, which will lead to the deterioration in the corrosion resistance. In order to accomplish the fixation of carbon, therefore, an enough amount of Nb, i.e. the great ratio of Nb/C is necessary, and a value of this ratio is required to be 10 or more.

Figure 10 shows SCC test results of the alloys in which the Nb/C was 15 to 20; a Cr content was 25%; Mo, W and V were respectively included in an amount of 0.6%; and an Ni content was caused to vary within the range of 18 to 75%. The used alloy specimens were prepared by heating them at 950°C for 30 minutes to accomplish the annealing treatment, followed by water cooling.

The drawing above indicates that if the Ni content is less than 40%, even the 25% Cr alloy in which the Nb/C is 10 or more and Mo, V and W are each contained in an amount of 0.6% will bring about some stress corrosion cracks. Therefore, it is definite that when the Ni content is 40% or more, a responsiveness to the SCC will be high.

Graphs in Figure 11 indicate the presence of a pitting corrosion on the Cr-V-W alloys in a high-temperature and high-pressure solution including 1000 ppm of $Cl^-$ ions, in which alloy the Nb/C was 12 or more and the Ni content was 40% or more. The alloy specimens were used which were prepared by heating them at 950°C for 30 minutes in order to accomplish the annealing treatment, followed by water cooling. In Figure 11, circle and triangle marks represent the alloy specimens including V and the alloy specimens including W, respectively. As seen from the drawing, if the Cr content is less than 25%, the pitting corrosion will occur, even though the contents of V and W each are 0.6% or more and the ratio of the Nb/C is 12 or more. Further, if the contents of V and W each are less than 0.5%, the pitting corrosion will occur even if the Cr content is more than 25%. Therefore, it is necessary for the inhibition of the pitting corrosion that the Cr content is 25% or more and the V or W content is 0.5%, preferably 0.6%. It can be considered from the foregoing that the passive coating only including 25% of Cr is insufficient to prevent the occurrence of the pitting corrosion and the addition of at least one of V and W in the total amount of 0.5% or more permits strengthening the passive coating and withstanding an attack of $Cl^-$ ions. Thus, it is apparent that the pitting corrosion resistance can be improved by the synergistic effect resulting from the addition of Cr, V and/or W.

Figure 12 shows, as in Figure 11, data regarding the pitting corrosion resistance of the alloys each in which Mo or a group of Mo, W and V is further included in addition to such a synergistic effect. The alloy specimens were used which were prepared by heating them at 950°C for 30 minutes in order to accomplish the annealing treatment, followed by water cooling. In Figure 9, circle and rhomb marks represent the alloy specimens including Mo and the group of Mo, W and V, respectively.

It can be understood from the graphs in this drawing that the improvement in the pitting corrosion resistance is accomplished under the requirements that the content of Cr is 25% or more and the content of Mo or the group of

Mo, V and W is 0.5% or more, preferably 0.6% or more.

The graphs in Figure 13 show influence of the annealing temperatures upon the stress corrosion cracking. In this case, the specimens of alloy Nos. 1 and 12 exhibited in Table 5 were employed, and the annealing operation was carried out variously changing the annealing temperatures within the range of 850 to 1050°C. Then, the sensitization treatment was carried out by heating them at 600°C for 5 hours and they were then air cooled. Stress corrosion cracking tests were effected on the thus obtained specimens to measure a depth of cracks. As be definite from the illustrated data, the alloy specimens which were annealed at a temperature of 900 to 975°C are excellent in the stress corrosion cracking resistance. This reason would be that NbC deposits in order to fix the solubilized carbon.

Table 5

(% by weight)

| | Alloy No. | C | Si | Mn | P | S | Ni | Cr | Ti | Nb | V | W | Mo | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alloys of the Present Invention | 1 | 0.025 | 0.41 | 0.36 | 0.009 | 0.003 | 55.21 | 25.45 | 0.25 | 0.40 | 0.61 | - | - | Re-sidue |
| | 2 | 0.013 | 0.47 | 0.37 | 0.012 | 0.009 | 55.01 | 25.36 | 0.21 | 0.40 | 0.62 | - | - | " |
| | 3 | 0.012 | 0.45 | 0.36 | 0.011 | 0.011 | 55.31 | 25.46 | 0.36 | 0.80 | 0.60 | - | - | " |
| | 4 | 0.011 | 0.44 | 0.38 | 0.014 | 0.010 | 55.21 | 25.36 | 0.25 | 1.05 | 0.65 | - | - | " |
| | 5 | 0.020 | 0.43 | 0.37 | 0.012 | 0.010 | 55.46 | 25.45 | 0.21 | 0.24 | - | 0.63 | - | " |
| | 6 | 0.015 | 0.47 | 0.42 | 0.016 | 0.009 | 55.12 | 25.46 | 0.24 | 0.30 | - | 0.61 | - | " |
| | 7 | 0.018 | 0.47 | 0.42 | 0.012 | 0.010 | 55.18 | 25.86 | 0.27 | 0.67 | - | 0.68 | - | " |
| | 8 | 0.026 | 0.46 | 0.41 | 0.011 | 0.009 | 55.36 | 25.76 | 0.26 | 1.30 | - | 0.68 | - | " |
| | 9 | 0.034 | 0.50 | 0.41 | 0.012 | 0.008 | 55.46 | 25.43 | 0.27 | 2.51 | - | 0.63 | - | " |
| | 10 | 0.030 | 0.51 | 0.40 | 0.009 | 0.005 | 55.76 | 25.37 | 0.27 | 3.30 | - | 0.66 | - | " |
| | 11 | 0.025 | 0.50 | 0.41 | 0.009 | 0.006 | 55.86 | 25.48 | 0.26 | 0.30 | - | - | 0.60 | " |
| | 12 | 0.021 | 0.46 | 0.46 | 0.009 | 0.007 | 55.36 | 25.49 | 0.27 | 0.63 | - | - | 0.61 | " |
| | 13 | 0.031 | 0.46 | 0.42 | 0.009 | 0.008 | 55.47 | 25.37 | 0.27 | 1.98 | - | - | 0.65 | " |

(To be continued)

(Continued from page 42)

(% by weight)

| | Alloy No. | C | Si | Mn | P | S | Ni | Cr | Ti | Nb | V | W | Mo | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alloys of the Present Invention | 14 | 0.030 | 0.47 | 0.41 | 0.009 | 0.006 | 55.67 | 25.47 | 0.31 | 2.70 | - | - | 0.62 | Re-sidue |
| | 15 | 0.036 | 0.43 | 0.42 | 0.010 | 0.007 | 55.86 | 25.36 | 0.21 | 4.32 | - | - | 0.69 | " |
| | 16 | 0.021 | 0.42 | 0.41 | 0.011 | 0.008 | 42.01 | 25.36 | 0.19* | 0.42 | 0.62 | - | - | " |
| | 17 | 0.020 | 0.43 | 0.42 | 0.009 | 0.006 | 52.00 | 25.36 | 0.18* | 0.40 | 0.63 | - | - | " |
| | 18 | 0.022 | 0.48 | 0.43 | 0.010 | 0.006 | 60.85 | 25.46 | 0.21 | 0.44 | 0.63 | - | - | " |
| | 19 | 0.021 | 0.46 | 0.46 | 0.009 | 0.006 | 40.37 | 25.36 | 0.22 | 0.42 | - | 0.64 | - | " |
| | 20 | 0.036 | 0.47 | 0.42 | 0.010 | 0.007 | 45.00 | 25.37 | 0.21 | 0.72 | - | 0.66 | - | " |
| | 21 | 0.026 | 0.51 | 0.52 | 0.010 | 0.007 | 58.20 | 25.37 | 0.20 | 0.52 | - | 0.63 | - | " |
| | 22 | 0.026 | 0.50 | 0.51 | 0.009 | 0.008 | 67.20 | 25.47 | 0.21 | 0.52 | - | 0.66 | - | " |
| | 23 | 0.020 | 0.50 | 0.52 | 0.009 | 0.006 | 42.56 | 25.06 | 0.19* | 0.40 | - | - | 0.68 | " |
| | 24 | 0.019 | 0.51 | 0.50 | 0.011 | 0.007 | 62.50 | 25.37 | 0.18* | 0.38 | - | - | 0.69 | " |
| | 25 | 0.018 | 0.49 | 0.46 | 0.012 | 0.006 | 58.36 | 25.34 | 0.12* | 0.36 | 3.01 | - | - | " |
| | 26 | 0.019 | 0.48 | 0.47 | 0.011 | 0.007 | 59.47 | 25.75 | 0.13* | 0.38 | - | 3.25 | - | " |

(To be continued)

(Continued from page 43)

(% by weight)

| | Alloy No. | C | Si | Mn | P | S | Ni | Cr | Ti | Nb | V | W | Mo | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alloys of the Present Invention | 27 | 0.022 | 0.43 | 0.46 | 0.009 | 0.006 | 62.36 | 31.25 | 0.26 | 0.44 | 2.35 | - | - | Residue |
| | 28 | 0.028 | 0.46 | 0.47 | 0.009 | 0.006 | 57.85 | 26.36 | 0.24 | 0.56 | - | 2.35 | - | " |
| | 29 | 0.027 | 0.47 | 0.48 | 0.008 | 0.005 | 53.45 | 34.60 | 0.21 | 0.54 | 1.00 | - | - | " |
| | 30 | 0.031 | 0.50 | 0.49 | 0.009 | 0.006 | 53.21 | 33.85 | 0.23 | 0.62 | - | 2.40 | - | " |
| | 31 | 0.032 | 0.51 | 0.51 | 0.010 | 0.007 | 54.36 | 25.18 | 0.18* | 0.64 | 0.20 | 0.30 | 0.40 | " |
| | 32 | 0.027 | 0.52 | 0.52 | 0.009 | 0.008 | 62.46 | 34.26 | 0.23 | 0.81 | - | - | 1.02 | " |
| | 33 | 0.012 | 0.53 | 0.51 | 0.008 | 0.009 | 49.36 | 27.21 | 0.28 | 0.45 | - | - | 4.25 | " |
| | 34 | 0.013 | 0.48 | 0.49 | 0.009 | 0.008 | 52.36 | 25.36 | 0.18* | 0.42 | 0.3 | 0.4 | 1.25 | " |
| | 35 | 0.015 | 0.47 | 0.47 | 0.012 | 0.008 | 51.38 | 32.36 | 0.25 | 0.46 | 1.36 | 0.52 | 0.85 | " |
| | 36 | 0.025 | 0.47 | 0.47 | 0.012 | 0.007 | 55.49 | 33.29 | 0.25 | 0.56 | 0.21 | 0.11 | 0.42 | " |
| Alloys for comparison | 37 | 0.026 | 0.51 | 0.48 | 0.016 | 0.006 | 55.27 | 25.36 | 0.19* | 0.078* | 0.61 | - | - | " |
| | 38 | 0.038 | 0.52 | 0.47 | 0.009 | 0.005 | 55.16 | 25.46 | 0.16* | 0.19* | 0.62 | - | - | " |
| | 39 | 0.029 | 0.51 | 0.46 | 0.009 | 0.006 | 55.27 | 25.36 | 0.11* | - | - | 0.63 | - | " |

(To be continued)

(Continued from page 44)

(% by weight)

| | Alloy No. | C | Si | Mn | P | S | Ni | Cr | Ti | Nb | V | W | Mo | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alloys for Comparison | 40 | 0.022 | 0.50 | 0.51 | 0.012 | 0.008 | 55.37 | 25.46 | 0.12* | 0.11* | - | 0.64 | - | Re-sidue |
| | 41 | 0.023 | 0.52 | 0.49 | 0.012 | 0.007 | 55.42 | 25.36 | 0.12* | 0.069* | - | - | 0.62 | " |
| | 42 | 0.021 | 0.47 | 0.48 | 0.016 | 0.009 | 18.50* | 25.36 | 0.09* | 0.30* | 0.61 | - | - | " |
| | 43 | 0.025 | 0.46 | 0.48 | 0.016 | 0.010 | 22.51* | 25.36 | 0.05* | 0.30 | 0.63 | - | - | " |
| | 44 | 0.037 | 0.48 | 0.49 | 0.014 | 0.009 | 32.50* | 25.36 | 0.06* | 0.44 | 0.62 | - | - | " |
| | 45 | 0.029 | 0.49 | 0.51 | 0.016 | 0.010 | 20.02* | 25.36 | 0.07* | 0.35 | - | 0.62 | - | " |
| | 46 | 0.035 | 0.37 | 0.46 | 0.012 | 0.010 | 26.75* | 25.47 | 0.06* | 0.42 | - | 0.61 | - | " |
| | 47 | 0.034 | 0.38 | 0.46 | 0.014 | 0.010 | 18.02* | 25.36 | 0.07* | 0.41 | - | - | 0.62 | " |
| | 48 | 0.035 | 0.37 | 0.46 | 0.014 | 0.009 | 22.86* | 25.10 | 0.07* | 0.39 | - | - | 0.61 | " |
| | 49 | 0.037 | 0.41 | 0.41 | 0.016 | 0.010 | 31.67* | 25.27 | 0.07* | 0.41 | - | - | 0.63 | " |
| | 50 | 0.032 | 0.42 | 0.43 | 0.012 | 0.009 | 42.74 | 25.37 | 0.09* | 0.42 | 0.25* | - | - | " |
| | 51 | 0.026 | 0.43 | 0.44 | 0.011 | 0.010 | 43.16 | 20.02* | 0.08* | 0.34 | 0.25* | - | - | " |
| | 52 | 0.029 | 0.47 | 0.46 | 0.009 | 0.012 | 43.26 | 20.12* | 0.09* | 0.34 | 0.85 | - | - | " |

(To be continued)

(Continued from page 45)

(% by weight)

| | Alloy No. | C | Si | Mn | P | S | Ni | Cr | Ti | Nb | V | W | Mo | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alloys for Comparison | 53 | 0.028 | 0.46 | 0.47 | 0.009 | 0.011 | 43.26 | 25.17 | 0.09* | 0.34 | - | 0.35* | - | Re-sidue |
| | 54 | 0.036 | 0.46 | 0.45 | 0.013 | 0.012 | 41.28 | 20.85* | 0.09* | 0.43 | - | 0.41* | - | " |
| | 55 | 0.029 | 0.46 | 0.45 | 0.016 | 0.013 | 42.36 | 20.23* | 0.10* | 0.35 | - | 1.10 | - | " |
| | 56 | 0.031 | 0.39 | 0.38 | 0.013 | 0.010 | 42.85 | 32.50 | 0.09* | 0.37 | - | - | - | " |
| | 57 | 0.028 | 0.40 | 0.41 | 0.015 | 0.009 | 45.26 | 25.06 | 0.09* | 0.34 | - | - | - | " |
| | 58 | 0.036 | 0.40 | 0.40 | 0.014 | 0.008 | 41.27 | 30.01 | 0.08* | 0.40 | - | - | 0.25* | " |
| | 59 | 0.027 | 0.41 | 0.39 | 0.012 | 0.009 | 40.36 | 20.02* | 0.07* | 0.30 | - | - | 0.25* | " |
| | 60 | 0.031 | 0.42 | 0.39 | 0.012 | 0.009 | 41.36 | 20.16* | 0.10* | 0.34 | - | - | 0.80 | " |
| | 61 | 0.032 | 0.42 | 0.41 | 0.014 | 0.007 | 41.27 | 25.98 | 0.11* | 0.35 | 0.06* | 0.11* | 0.08* | " |
| | 62 | 0.036 | 0.40 | 0.40 | 0.016 | 0.008 | 41.37 | 20.09* | 0.10* | 0.40 | 0.08* | 0.16* | 0.18* | " |
| | 63 | 0.037 | 0.39 | 0.41 | 0.015 | 0.009 | 41.67 | 20.36* | 0.12* | 0.41 | 0.45* | 0.21 | 0.36 | " |

Note: *Outside the present invention.

Furthermore, referring to Figures 14 to 16, the present invention will be described below.

The reason why the composition of the alloy and the conditions of the thermal treatment are restricted as mentioned above in the present invention is as follows:

Carbon (C):

The element C is harmful to the SCC resistance, therefore its content in the present invention is 0.15% or less.

Silicon (Si) and manganese (Mn):

Si and Mn both are deoxidizers, and each amount of them is required to be 1.0% or less. However, when each amount of the elements is above 1.0%, the alloy will have deteriorated welding properties and cleanness.

Chromium (Cr):

The element Cr is an essential component for the maintenance of the corrosion resistance of the alloy according to the present invention. When the content of Cr is less than 25%, it will be impossible to obtain such a corrosion resistance as the present invention requires. On the contrary, when it is above 35%, a hot workability of the alloy will remarkably deteriorate. Therefore, the content of Cr is limited to the range of 25 to 35% in the present invention.

Aluminum (Al):

Al is also necessary as a deoxidizer, but when it is above 0.5%, the cleanness of the alloy will be poor. Therefore, its content is limited to 0.5% or less.

Titanium (Ti):

When 0.01% or more of Ti is added to the alloy, its hot workability will be enhanced; when it is added thereto in an amount above 1.0%, its effect will reach a ceiling level. Therefore, its upper limit is 1.0%.

Phosphorus (P):

The element P is included as an impurity in the alloy. If its content is in excess of 0.030%, it will be harmful to the SCC resistance and the hot workability.

Sulfur (S):

This element is also included as an impurity in the alloy. If its content is above 0.020%, it will be harmful to the crystal boundary etching resistance and the hot workability.

Molybdnum (Mo), tungsten (W) and vanadium (V):

These elements all are effective to heighten the pitting corrosion resistance especially in a high-temperature water including $Cl^-$ ions. When the content of at least one of these elements is 0.5% or less in all, a passive coating on the alloy surface will not be heightened and the pitting corrosion will thus occur. On the contrary, when the total content thereof is more than 5.0%, its effect will reach a ceiling level, and additionally the hot workability will noticeably be deteriorated. Therefore, it is preferred that these elements are added to the alloy in an amount of 1.0% or more in all.

Annealing treatment:

When the annealing operation is carried out below a temperature (hereinafter referred to as T°C) at which the carbide in the alloy is thoroughly solubilized, a tensile strength, 0.2% yield point and hardness of the alloy will become unreasonably great. On the contrary, when it is done at a temperature above T + 100°C, the alloy will have remarkably coarse crystal grains, which fact will lead to the deterioration in the corrosion resistance, i.e. the crystal boundary etching resistance and the crystal boundary stress etching resistance, and the tensile strength, 0.2% yield point and hardness cannot be obtained at predetermined levels. Therefore, the annealing temperature in the present invention are from T°C to T + 100°C. For example, in an embodiment of the alloy including 0.02% of C, an annealing temperature of 1050 to 1150°C is preferable. Further, with regard to a retention time, for example, a period of 1 to 120 minutes or 1 to 30 minutes is necessary, though it varies with a wall thickness of the pipe to be formed. With regard to a cooling rate, a high cooling rate as in the case of a water cooling is suitable, but other rates in cases of air cooling and oil cooling as well as a low rate in the case of furnace cooling are also acceptable. Special restriction is not imposed on this point. By such a cooling means, the alloy is cooled to, e.g. 200°C to room temperature.

The above-mentioned temperature at which the carbide in the alloy is thoroughly solubilized varies with a carbon content as exhibited in Figure 14, but it is, e.g. 950°C at 0.01% carbon content, 1050°C at 0.02% content and 1100°C at 0.03% content.

Thermal treatment

After the aforesaid annealing treatment, the specific thermal treatment is carried out by retaining a temperature of 600 to 750°C for 0.1 to 100 hours as shown in Figure 15, whereby the carbide will semicontinuously deposit on the crystal boundaries and the Cr-poor layers in the vicinity of positions where the carbide exists will recover, thereby increasing the crystal boundary stress corrosion cracking resistance. The reason why such specific thermal treatment conditions are restricted to the hatched range (Z) in Figure 15 is as follows: On the left side of the hatched range (Z) in Figure 15, the retention time is lacking. As a result, the Cr carbide will deposit on the crystal boundaries and the Cr-poor layers formed therearound will not enough recover, so that the SCC resistance cannot be obtained to a satisfactory degree. On the right side in Figure 15, the hatched range (Z) terminates at a position corresponding to 100 hours. Such a restriction is for an economical reason, though the farther prolonged heating treatment is good for the SCC resistance. Moreover, with regard to temperature, when it is less than 600°C, diffusion rates of Cr and C will be low. Hence, in order to cause the Cr-poor layers to recover and to improve the SCC resistance at such a temperature, the very longtime heating operation will be required, which fact is not practical. Therefore, the lower limit of the temperature is set to 600°C.

On the other hand, when the temperature is above 750°C, the recovery of the Cr-poor layers and the betterment in the SCC resistance will be achieved in an extremely short period of time. However, since a difference between this specific heating temperature and a practically used temperature (300°C or so) is great, the solubilized carbon will deposit in large quantities in the form of the carbide in accordance with a dimension of the difference at the time of a practical use, so that the crystal boundaries tend to be remarkably sensitized. However, if the specific heating temperature is 750°C or less, the sensitization will be lowered to a negligible degree at the practical use, because the absolute quantity of the solubilized carbon will be small. Therefore, the thermal treatment conditions in the present invention are restricted to the hatched range (Z) surrounded by points A ($10^1$ hours, 750°C), B ($10^2$ hours, 750°C) and C ($10^2$ hours, 600°C) in Figure 15.

Now, the present invention will be described in accordance with examples, but they are merely exemplary and do not intend to limit the present invention at all.

Examples 1 to 18

By a vacuum solubilization, 60%Ni-30%Cr alloys (Alloy Nos.1to 18 and comparative Alloys Nos. 19 to 26) chemical compositions of which were set forth in Table 6 were manufactured. The thus manufactured alloys were forged at a temperature of 950 to 800°C to form them into plates of 25 mm in thickness and were then hot rolled at 1100°C up to a thickness of 7 mm. Next, they were cold rolled up to a thickness of 4.9 mm and were retained at a final annealing temperature of 1100°C for 20 minutes. Subsequently, water cooling was carried out to cool them to room temperature and 3 hours' thermal treatment at 600°C followed (under conditions based on a supposed life in practical environments in use).

From these materials, there were prepared 2-mm-thick x 10-mm-wide x 75-mm-long specimens for an alkali stress corrosion cracking test and 3-mm-thick x 10-mm-wide x 40-mm-long specimens for a corrosion test.

The alkali stress corrosion cracking test was accomplished by polishing the specimens with emery paper No. 320; bending them into a U-shape and holding them with bolts and nuts; immersing them in a solution including 30% of NaOH in an autoclave container (a high-temperature and high-pressure container) at 325°C for 2000 hours; and, after the completion of the immersion process, measuring a depth of cracks by a microscope.

On the other hand, the corrosion test was accomplished by polishing the specimens with emery paper No. 320; immersing them in a solution including 100 ppm of $Cl^-$ ions and having a pH of 4.5 in an autoclave container at 288°C for 2000 hours; and measuring a corrosion amount.

Obtained results are shown in Figures 15 and 16 in the form of summary graphs. Numerals in Figure 16 correspond to the alloy numbers in Table 6.

Figure 15 presents the stress corrosion cracking test results of the specimens of alloy No. 1 under the above-mentioned alkaline conditions. In this drawing, white circles and black circles represent specimens having cracks less than 25 μ in depth and those having cracks more than 25 μ in depth, respectively. As be apparent from the drawing, the specimens in the hatched range (Z) surrounded by points A, B and C have good alkali stress corrosion cracking resistance. In this connection, it was confirmed that the alloys according to the present invention other than alloy No. 1 also had substantially similar results.

The data regarding the corrosion resistance in Figure 16 indicate that when the total content of at least one of Mo, V and W is less than 0.5%, the effect of the corrosion resistance will not be seen, but if its content is 0.5% or more, the corrosion resistance will be improved. This reason would be that the elements of Mo, V and W permit forming the fine and stable passive coating comprising $Cr_2O_3$.

Table 7 summarizes the results of the corrosion resistance under the same conditions as in Figure 16. In this table, circles, triangles and crosses represent specimens not having any pitting corrosion, those having the slight pitting corrosions and those having the pitting corrosions. It can be understood from these results that the alloys according to the present invention are more excellent in the pitting corrosion resistance, as compared with the conventional alloys. Particularly, when the total amount of Mo, V and W to be added is 1.0% or more , the alloy can have the extremely excellent pitting corrosion resistance.

As be definite from the foregoing, the alloy according to the present invention is excellent in the pitting corrosion resistance, the stress corrosion cracking resistance and the alkali stress corrosion cracking resistance, and, in place of the conventional Alloy 600, the alloy according to the present invention can be thus used, for example, particularly for a heat transfer pipe of a steam generator in a pressurized water reactor.

Table 6

(% by weight)

|  | Alloy No. | C | Si | Mn | P | S | Ni | Cr | Ti | Al | Mo | W | V | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alloys of the Present Invention | 1 | 0.023 | 0.41 | 0.39 | 0.011 | 0.006 | 60.01 | 30.32 | 0.27 | 0.13 | 0.63 | - | - | Re-sidue |
|  | 2 | 0.025 | 0.43 | 0.41 | 0.013 | 0.009 | 60.15 | 30.17 | 0.25 | 0.15 | 1.04 | - | - | " |
|  | 3 | 0.026 | 0.49 | 0.41 | 0.013 | 0.009 | 60.44 | 30.19 | 0.27 | 0.13 | 3.03 | - | - | " |
|  | 4 | 0.022 | 0.41 | 0.38 | 0.012 | 0.009 | 60.35 | 30.45 | 0.23 | 0.14 | 4.50 | - | - | " |
|  | 5 | 0.021 | 0.43 | 0.43 | 0.012 | 0.008 | 60.15 | 29.89 | 0.20 | 0.15 | - | 0.63 | - | " |
|  | 6 | 0.025 | 0.42 | 0.38 | 0.013 | 0.009 | 60.25 | 30.35 | 0.21 | 0.15 | - | 1.09 | - | " |
|  | 7 | 0.025 | 0.42 | 0.41 | 0.012 | 0.008 | 60.37 | 30.11 | 0.19 | 0.15 | - | 2.86 | - | " |
|  | 8 | 0.028 | 0.41 | 0.43 | 0.009 | 0.007 | 61.21 | 30.23 | 0.25 | 0.14 | - | 4.40 | - | " |
|  | 9 | 0.021 | 0.43 | 0.42 | 0.012 | 0.010 | 60.28 | 30.16 | 0.27 | 0.15 | - | - | 0.65 | " |
|  | 10 | 0.023 | 0.42 | 0.37 | 0.011 | 0.008 | 60.19 | 30.01 | 0.30 | 0.13 | - | - | 1.12 | " |
|  | 11 | 0.027 | 0.40 | 0.38 | 0.011 | 0.010 | 61.26 | 30.46 | 0.29 | 0.14 | - | - | 3.07 | " |
|  | 12 | 0.029 | 0.43 | 0.40 | 0.011 | 0.009 | 60.39 | 30.47 | 0.33 | 0.13 | - | - | 4.62 | " |
|  | 13 | 0.026 | 0.38 | 0.40 | 0.009 | 0.009 | 61.03 | 30.69 | 0.22 | 0.13 | - | 0.33 | 0.30 | " |
|  | 14 | 0.029 | 0.40 | 0.43 | 0.013 | 0.007 | 61.29 | 30.03 | 0.26 | 0.14 | - | 1.10 | 0.8 | " |

(To be continued)

(Continued from page 56)

(% by weight)

| | Alloy No. | C | Si | Mn | P | S | Ni | Cr | Ti | Al | Mo | W | V | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Alloys of the Present Invention | 15 | 0.026 | 0.38 | 0.41 | 0.014 | 0.009 | 60.66 | 31.22 | 0.26 | 0.14 | - | 2.30 | 1.66 | Re-sidue |
| | 16 | 0.029 | 0.44 | 0.36 | 0.011 | 0.010 | 61.09 | 30.68 | 0.21 | 0.13 | 0.29 | 0.30 | - | " |
| | 17 | 0.025 | 0.44 | 0.40 | 0.012 | 0.010 | 61.22 | 30.16 | 0.23 | 0.15 | 1.6 | 0.3 | - | " |
| | 18 | 0.019 | 0.40 | 0.43 | 0.012 | 0.009 | 60.46 | 31.08 | 0.28 | 0.13 | 2.81 | 1.16 | - | " |
| Alloys for Comparison | 19 | 0.029 | 0.38 | 0.41 | 0.012 | 0.009 | 60.38 | 30.76 | 0.22 | 0.14 | - | - | - | " |
| | 20 | 0.030 | 0.43 | 0.42 | 0.010 | 0.008 | 61.13 | 31.09 | 0.30 | 0.15 | 0.24 | - | - | " |
| | 21 | 0.036 | 0.40 | 0.41 | 0.012 | 0.010 | 60.37 | 31.12 | 0.20 | 0.14 | 0.42 | - | - | " |
| | 22 | 0.026 | 0.38 | 0.40 | 0.012 | 0.011 | 61.08 | 30.68 | 0.26 | 0.14 | - | - | - | " |
| | 23 | 0.022 | 0.40 | 0.37 | 0.010 | 0.009 | 60.61 | 30.99 | 0.26 | 0.15 | - | 0.22 | - | " |
| | 24 | 0.029 | 0.44 | 0.40 | 0.013 | 0.010 | 60.88 | 31.11 | 0.29 | 0.15 | - | - | 0.26 | " |
| | 25 | 0.028 | 0.39 | 0.37 | 0.011 | 0.012 | 60.09 | 31.16 | 0.31 | 0.13 | 0.11 | 0.05 | - | " |
| | 26 | 0.026 | 0.46 | 0.40 | 0.010 | 0.010 | 60.69 | 30.08 | 0.28 | 0.13 | - | 0.05 | 0.11 | " |

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Table 7

| | Alloy No. | Estimation of Pitting Corrosion Resistance |
|---|---|---|
| Alloys of the Present Invention | 1 | Δ |
| | 2 | O |
| | 3 | O |
| | 4 | O |
| | 5 | Δ |
| | 6 | O |
| | 7 | O |
| | 8 | O |
| | 9 | Δ |
| | 10 | O |
| | 11 | O |
| | 12 | O |
| | 13 | Δ |
| | 14 | O |
| | 15 | O |
| | 16 | Δ |
| | 17 | O |
| | 18 | O |
| Alloys for Comparison | 19 | x |
| | 20 | x |
| | 21 | x |
| | 22 | x |
| | 23 | x |
| | 24 | x |
| | 25 | x |
| | 26 | x |

What is claimed is:

1. A nickel-chromium alloy characterized in that it is obtained by carrying out an annealing treatment under required conditions, said alloy having the following composition:

in terms of % by weight,

25 - 35% of Cr; 40 - 70% of Ni;
1.0% or less of Mn; 0.015% or less of C;
0.030% or less of P; 1.0% or less of Si;
0.020% or less of S and
the residue comprising Fe and usual impurities.

2. A nickel-chromium alloy according to claim 1 wherein said nickel based alloy for a material which will be subjected to a high-temperature and high-pressure water or vapor comprises, in terms of % by weight, 58% or more of Ni, 25 to 35% of Cr, 0.003% or less of B, 0.012 to 0.035% of C, 1% or less of Mn, 0.5% or less of Si, 0.015% or less of P, 0.015% or less of S, and the residue of Fe and usual impurities; in a first thermal treatment process, said nickel based alloy is heated and retained at a temperature of T°C (at which a carbide is thoroughly solubilized) to (T + 100)°C and is cooled at a cooling rate of a furnace cooling rate or more, and in a second thermal treatment process, said nickel based alloy is then retained at a temperature of 600 to 750°C and at a

temperature within a sensitization recovery range for a period of 0.1 to 100 hours and is cooled at a cooling rate of said furnace cooling rate or more.

3. A nickel-chromium alloy according to claim 1 wherein said nickel-chromium alloy is obtained by carrying out an annealing treatment under required conditions, said alloy having the following composition:

in terms of % by weight,

0.04% or less of C; 1.0% or less of Si;

1.0% or less of Mn; 0.030% or less of P;

0.02% or less of S; 40 to 70% of Ni;

25 to 35% of Cr; 0.1 to 0.5% of Al;

0.05 to 1.0% of Ti;

0.5 to 5.0% in all of one or more of Mo, W and V; and the residue comprising substantially Fe.

4. A nickel-chromium alloy according to claim 3 wherein said required conditions are in a range (Y) surrounded by points, A, B,C, D and E in Figure 4.

5. A nickel-chromium alloy according to claim 3 wherein said required conditions are that an annealing temperature for said annealing treatment is within the range of 900 to 975°C and said composition further includes 0.2 to 5.0% of Nb subject to Nb/C = 10 to 125 and Ti = 0.2 to 1.0%.

6. A nickel-chromium alloy for heat transfer pipes

according to claim 1 wherein said nickel-chromium alloy is obtained by heating and retaining said alloy at a temperature within the range of a temperature (T°C), at which a carbide in said alloy is thoroughly solubilized, to T + 100°C for 1 minute or more; cooling it once to a level of 200°C or less; and carrying out a thermal treatment under conditions within a hatched range(Z)in Figure 15, said alloy comprising:

in terms of % by weight,

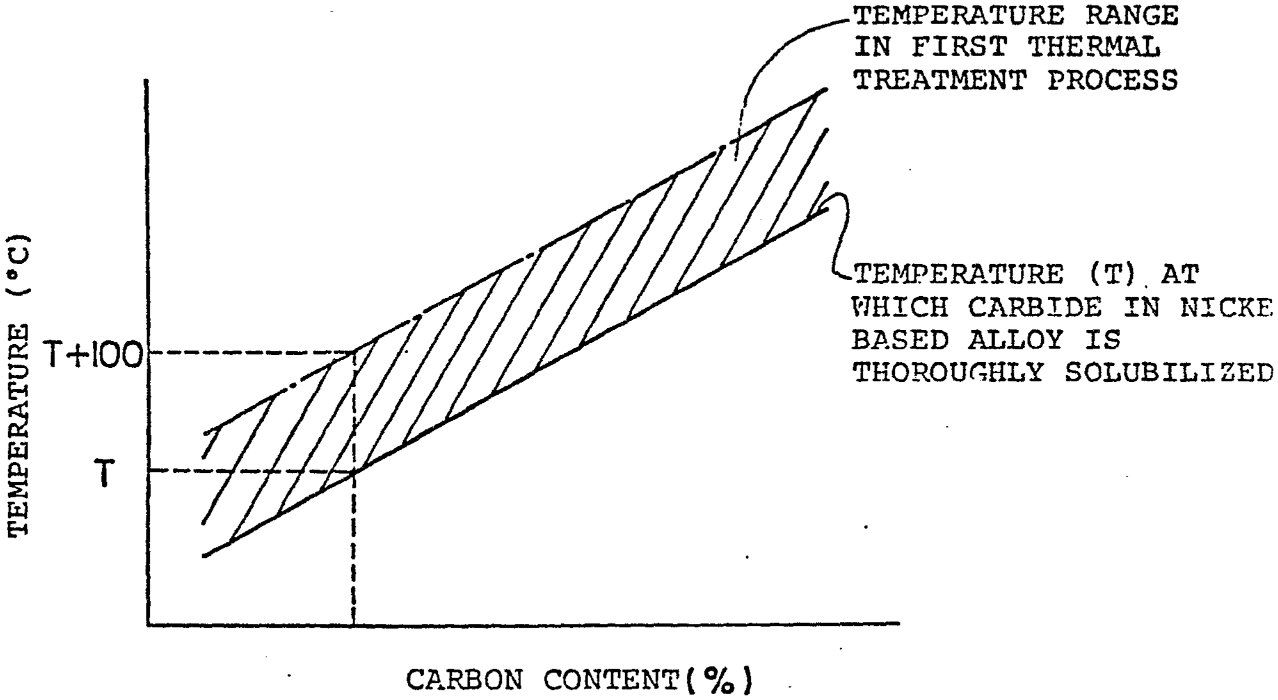
| | |
|---|---|
| 0.15% or less of C; | 1.0% or less of Si; |
| 1.0% or less of Mn; | 25 to 35% of Cr; |
| 40 to 70% of Ni; | 0.5% or less of Al; |
| 0.01 to 1.0% of Ti; | |

0.5 to 5.0%, in all, of one or more of Mo, W and V;

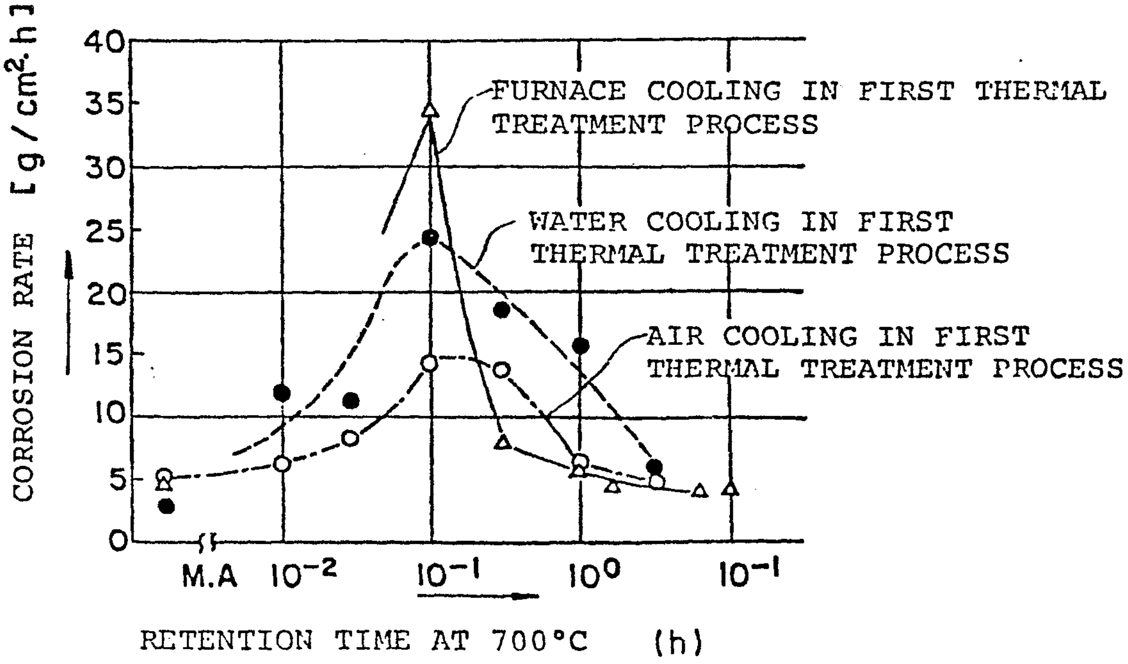
| | |
|---|---|
| 0.030% or less of P; | 0.020% or less of S; |

and the residue of Fe and impurities.

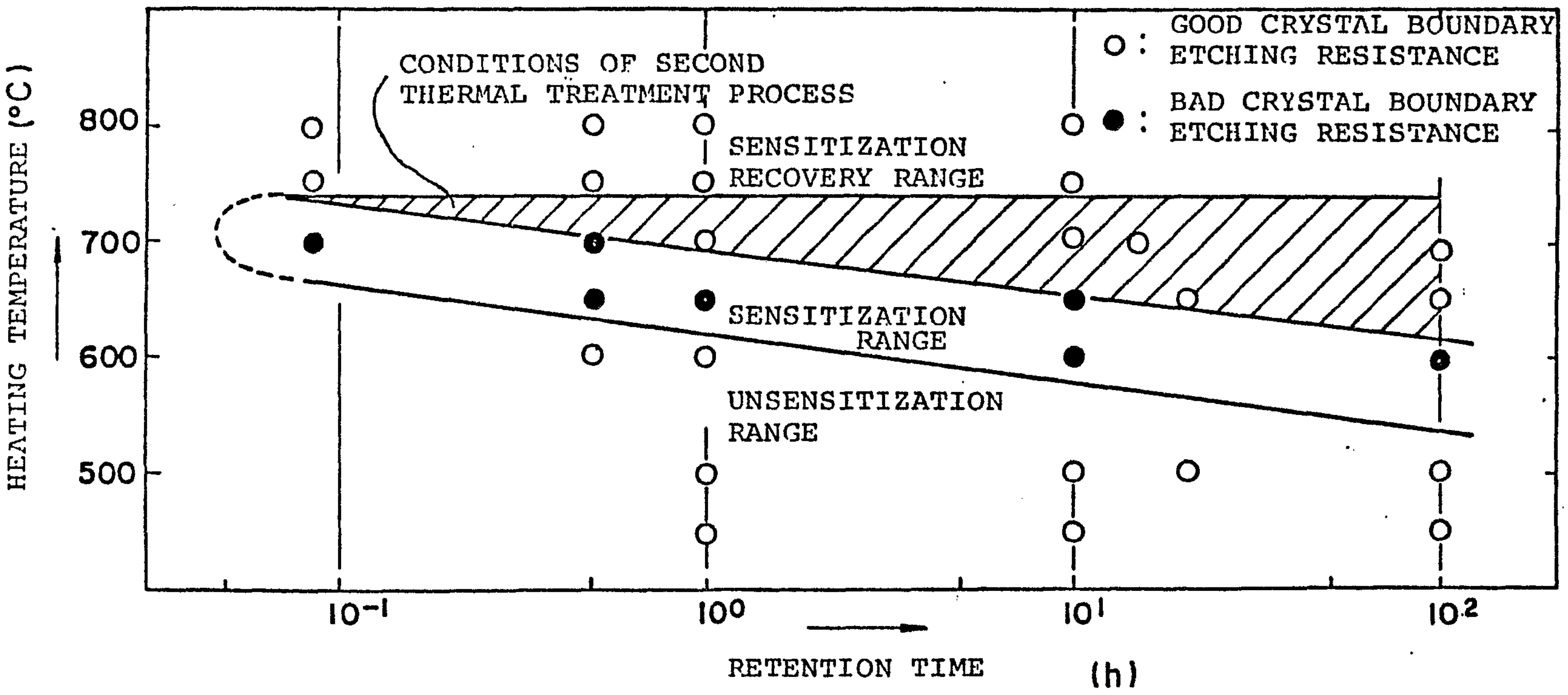
# F I G. 1


TEMPERATURE RANGE IN FIRST THERMAL TREATMENT PROCESS
TEMPERATURE (T) AT WHICH CARBIDE IN NICKE BASED ALLOY IS THOROUGHLY SOLUBILIZED
TEMPERATURE (°C)
T+100
T
CARBON CONTENT(%)

# F I G. 3


CORROSION RATE [g/cm$^2$.h]
40
35
30
25
20
15
10
5
0
FURNACE COOLING IN FIRST THERMAL TREATMENT PROCESS
WATER COOLING IN FIRST THERMAL TREATMENT PROCESS
AIR COOLING IN FIRST THERMAL TREATMENT PROCESS
M.A
$10^{-2}$
$10^{-1}$
$10^{0}$
$10^{-1}$
RETENTION TIME AT 700°C (h)

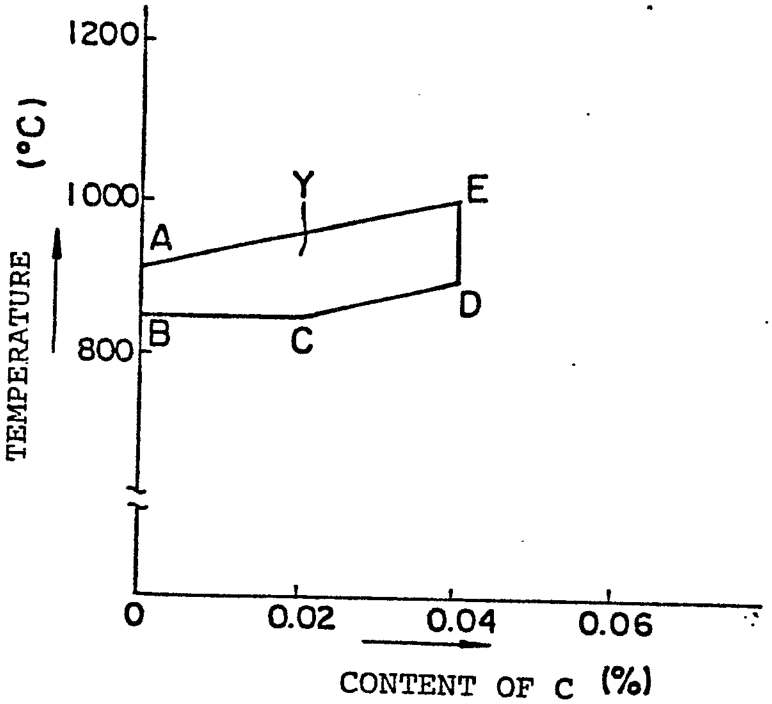
# F I G. 2


○ : GOOD CRYSTAL BOUNDARY ETCHING RESISTANCE
● : BAD CRYSTAL BOUNDARY ETCHING RESISTANCE
CONDITIONS OF SECOND THERMAL TREATMENT PROCESS
SENSITIZATION RECOVERY RANGE
SENSITIZATION RANGE
UNSENSITIZATION RANGE
HEATING TEMPERATURE (°C)
800
700
600
500
$10^{-1}$
$10^{0}$
$10^{1}$
$10^{2}$
RETENTION TIME (h)

3/11

0109350

# FIG. 4



# FIG. 5

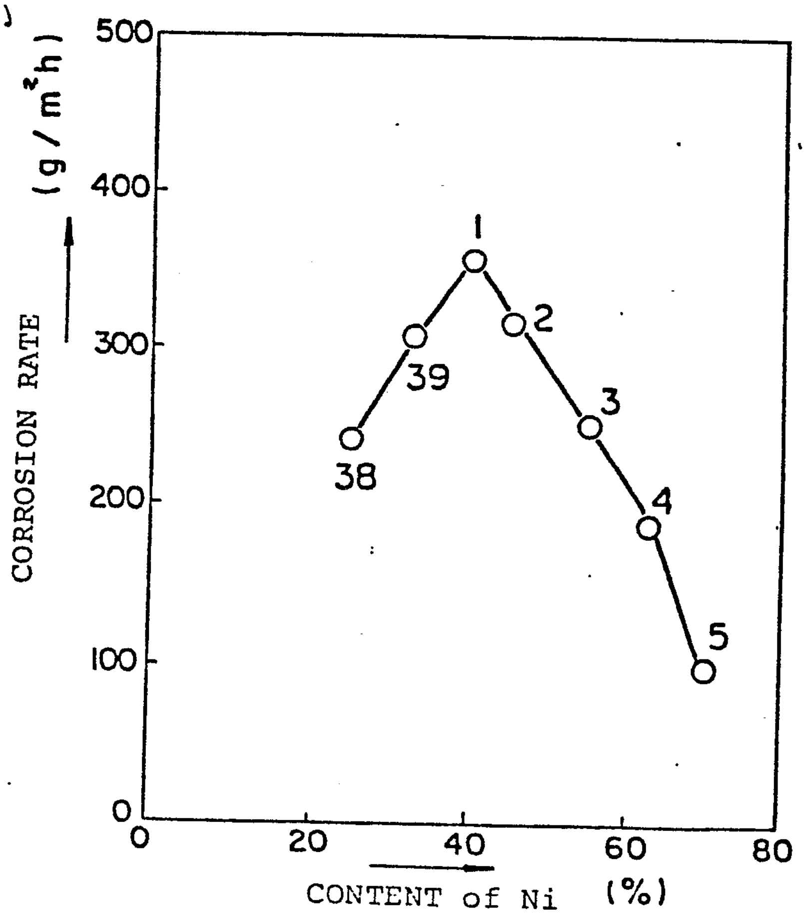
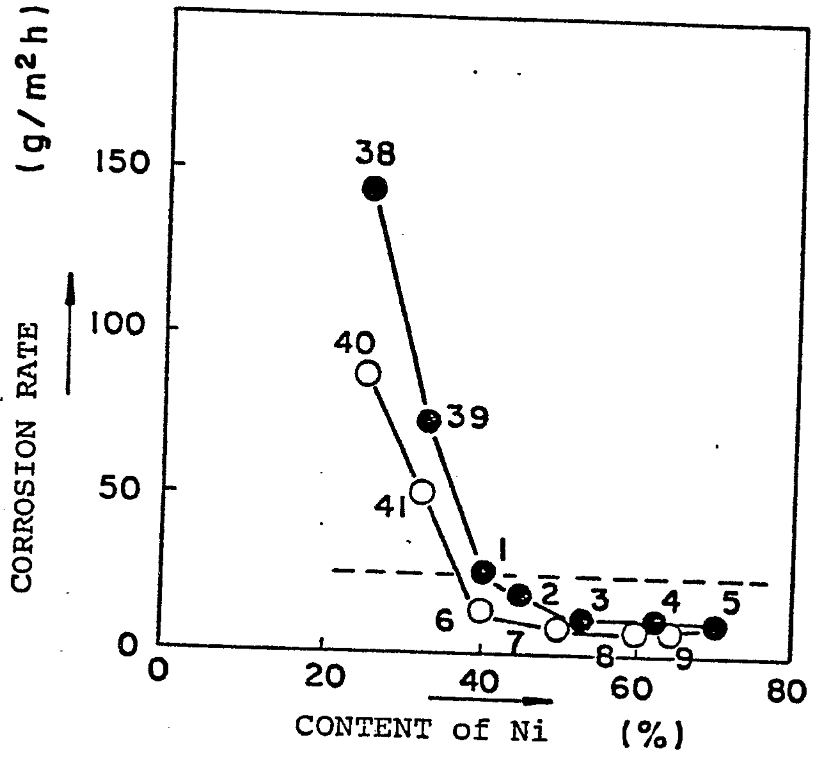
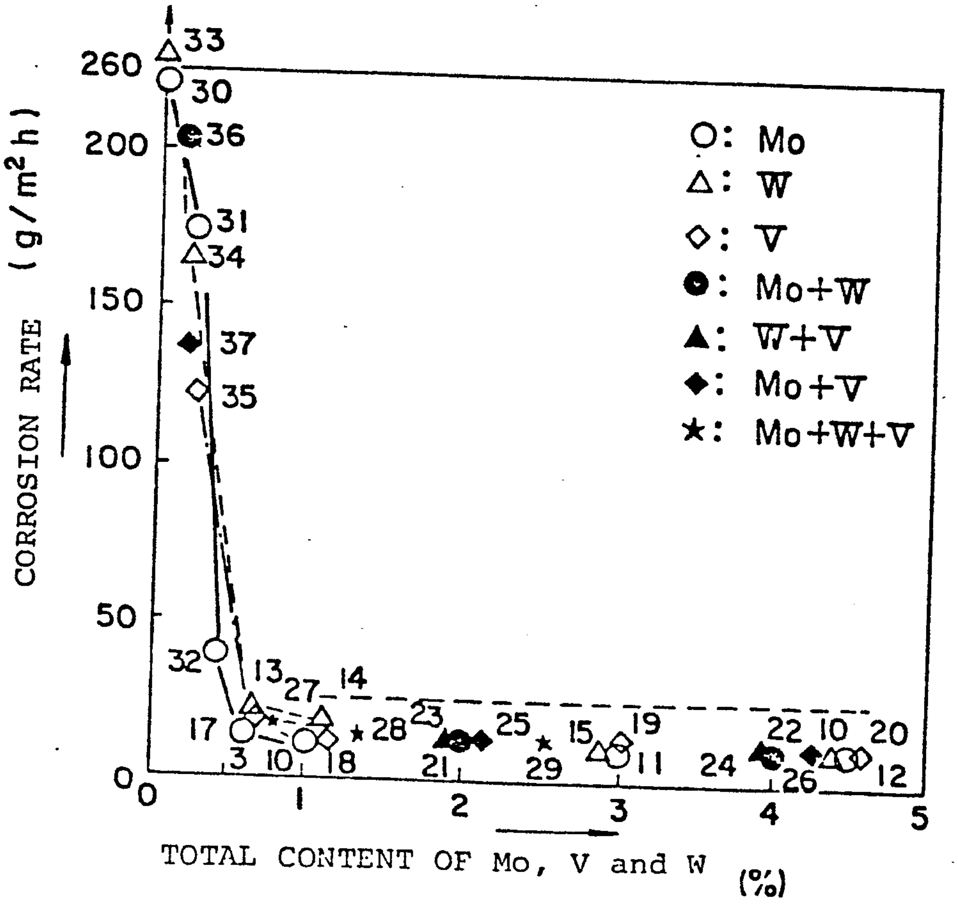


FIG. 6



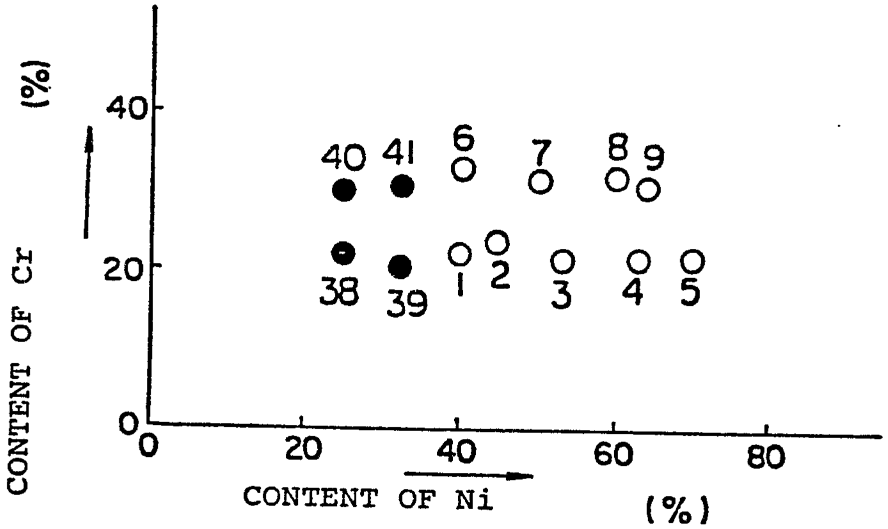
(g/m²h)
CORROSION RATE
150
100
50
0
0
20
40
60
80
CONTENT of Ni (%)
38
40
39
41
1
2
3
4
5
6
7
8
9

FIG. 7



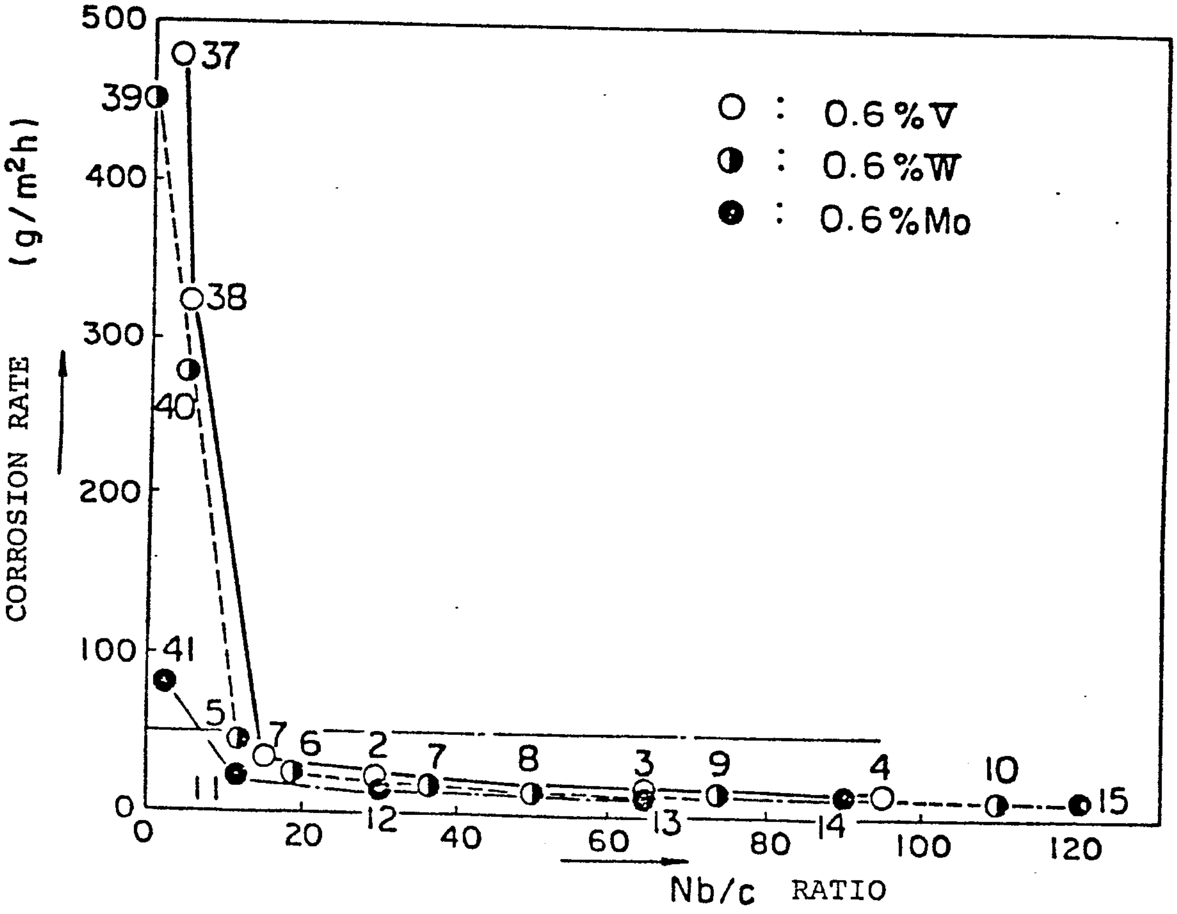
(g/m²h)
CORROSION RATE
260
200
150
100
50
0
0
1
2
3
4
5
TOTAL CONTENT OF Mo, V and W (%)
○: Mo
△: W
◇: V
●: Mo+W
▲: W+V
◆: Mo+V
★: Mo+W+V
33
30
36
31
34
37
35
32
13
27
14
17
3
10
18
28
23
21
25
29
15
19
11
24
22
26
10
20
12

## FIG. 8



CONTENT OF Cr (%)
40
20
0
0
20
40
60
80
CONTENT OF Ni (%)
40
41
6
7
8
9
38
39
1
2
3
4
5

## FIG. 9



CORROSION RATE (g/m²h)
500
400
300
200
100
0
0
20
40
60
80
100
120
Nb/c RATIO
○ : 0.6%V
◐ : 0.6%W
● : 0.6%Mo
37
39
38
40
41
5
11
7
6
2
12
7
8
3
13
9
14
4
10
15

FIG. 10

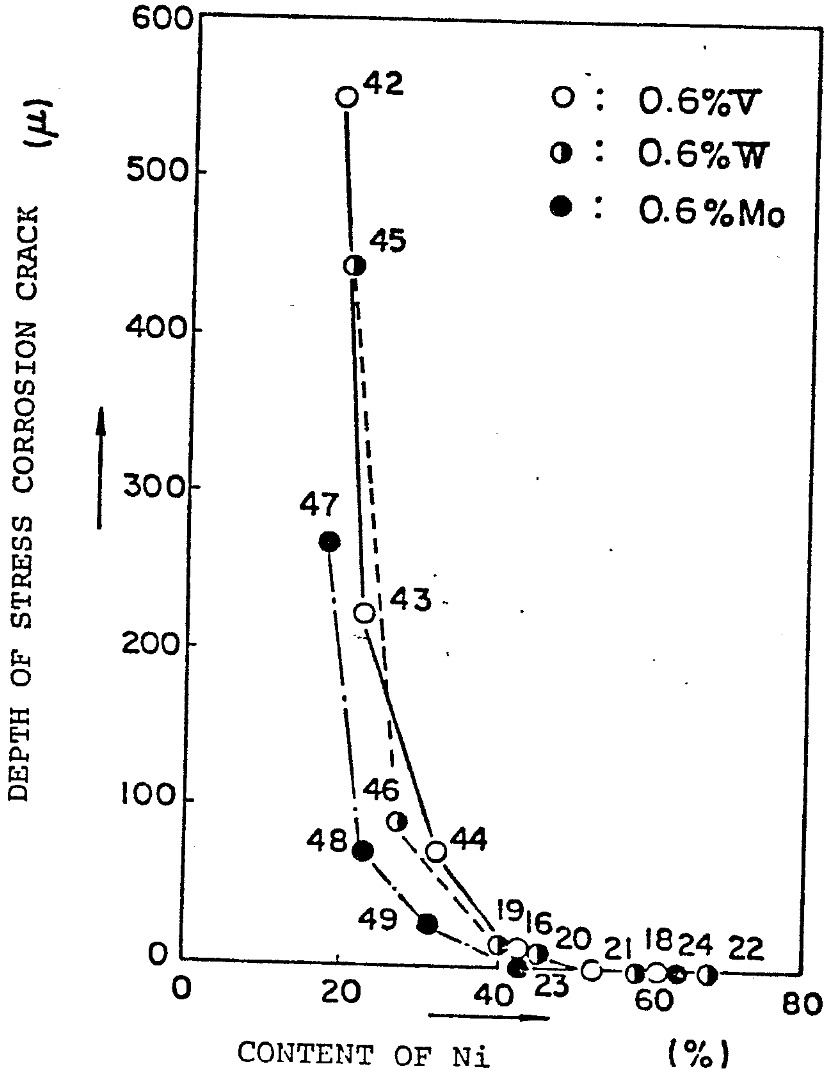
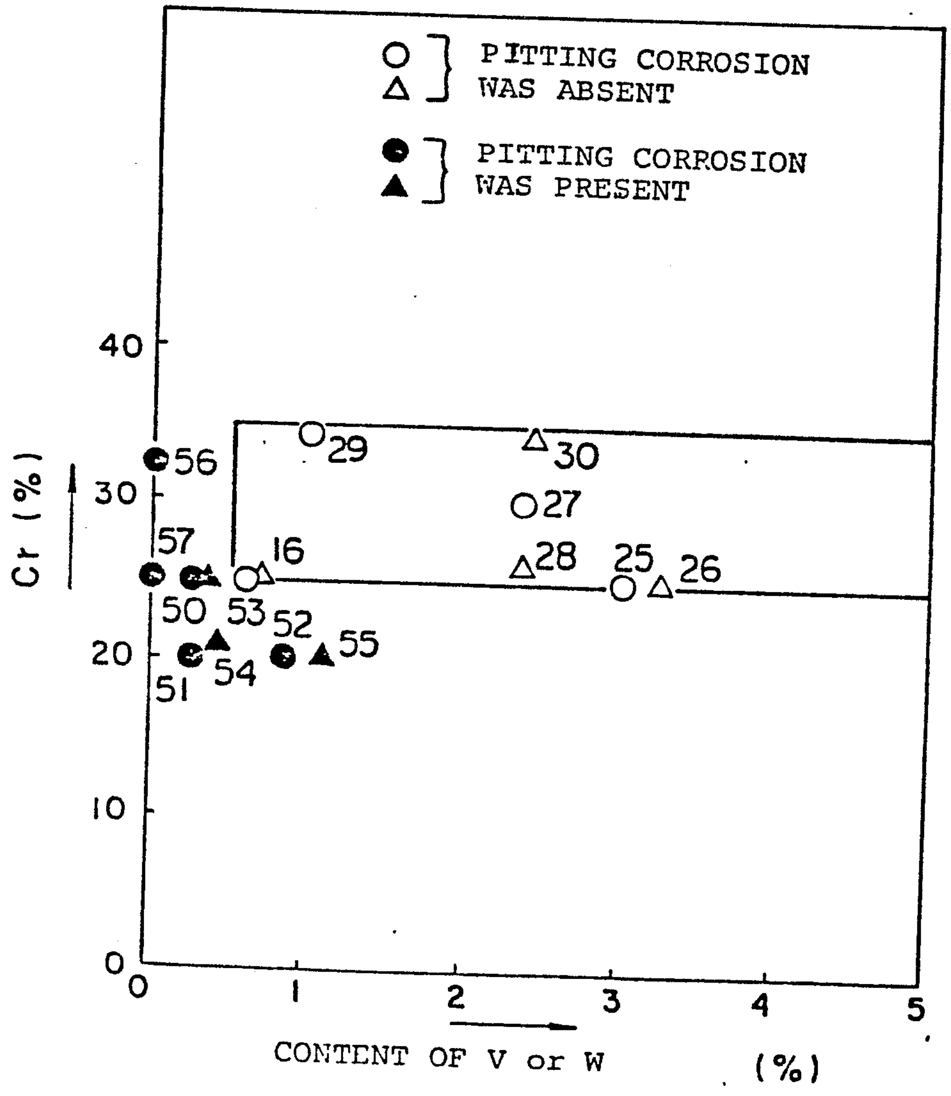
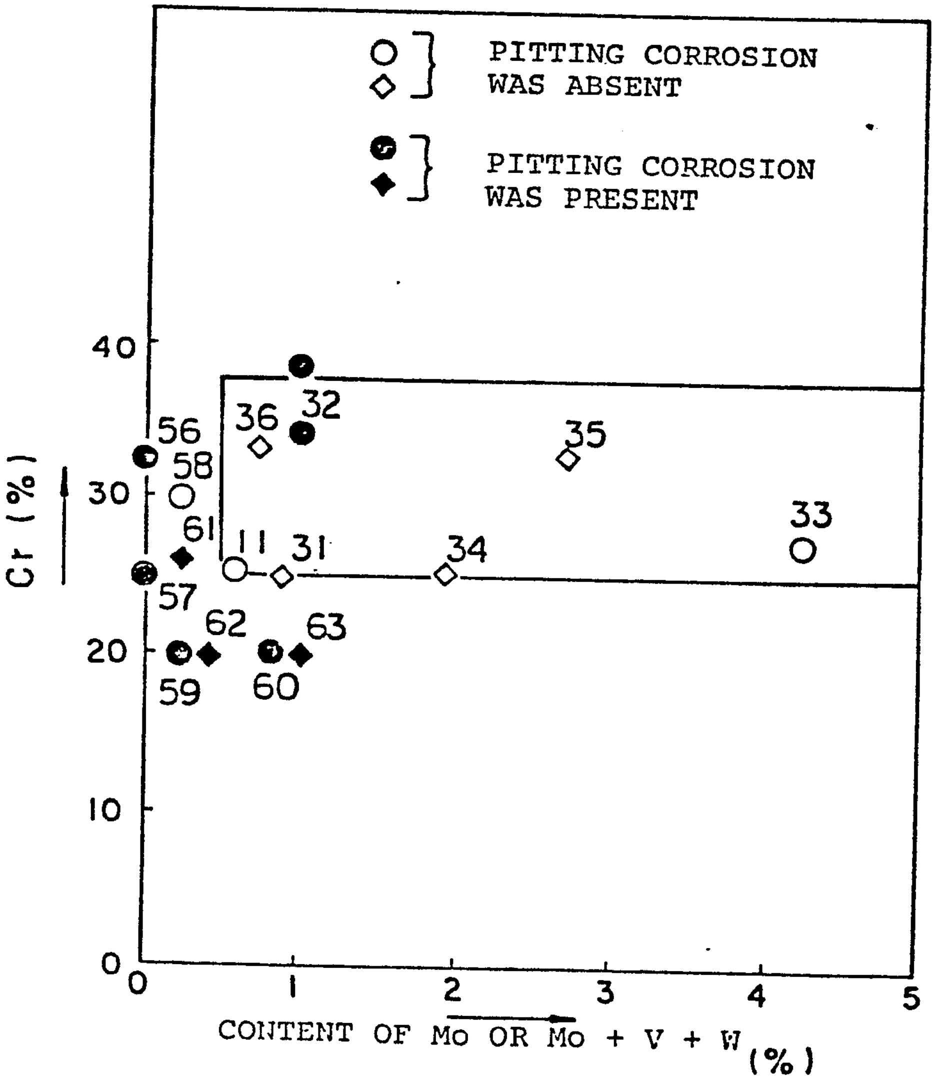

○ : 0.6%V
◑ : 0.6%W
● : 0.6%Mo
DEPTH OF STRESS CORROSION CRACK (μ)
600
500
400
300
200
100
0
0
20
40
60
80
CONTENT OF Ni (%)
42
45
47
43
46
48
44
49
19
16
20
21
18
24
22
23

FIG. 11


○ △ PITTING CORROSION WAS ABSENT
● ▲ PITTING CORROSION WAS PRESENT
Cr (%)
40
30
20
10
0
0
1
2
3
4
5
CONTENT OF V or W (%)
29
30
27
28
25
26
16
56
57
50
53
52
55
51
54

8/11

FIG. 12


○ ◇ PITTING CORROSION WAS ABSENT
● ◆ PITTING CORROSION WAS PRESENT
Cr (%)
0
10
20
30
40
0
1
2
3
4
5
CONTENT OF Mo OR Mo + V + W (%)
56
58
61
57
59
62
60
63
11
31
36
32
34
35
33

# FIG. 13

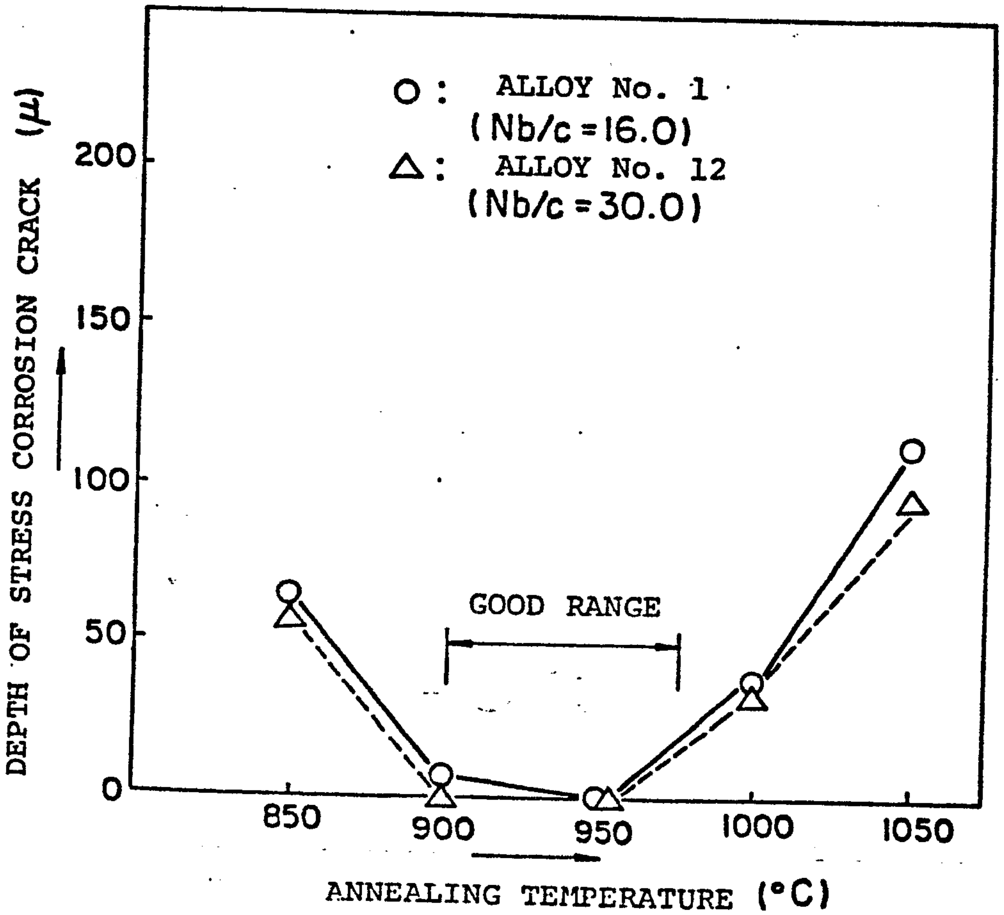

○ : ALLOY No. 1
(Nb/c = 16.0)
△ : ALLOY No. 12
(Nb/c = 30.0)
DEPTH OF STRESS CORROSION CRACK (μ)
200
150
100
50
0
GOOD RANGE
850
900
950
1000
1050
ANNEALING TEMPERATURE (°C)

FIG. 14

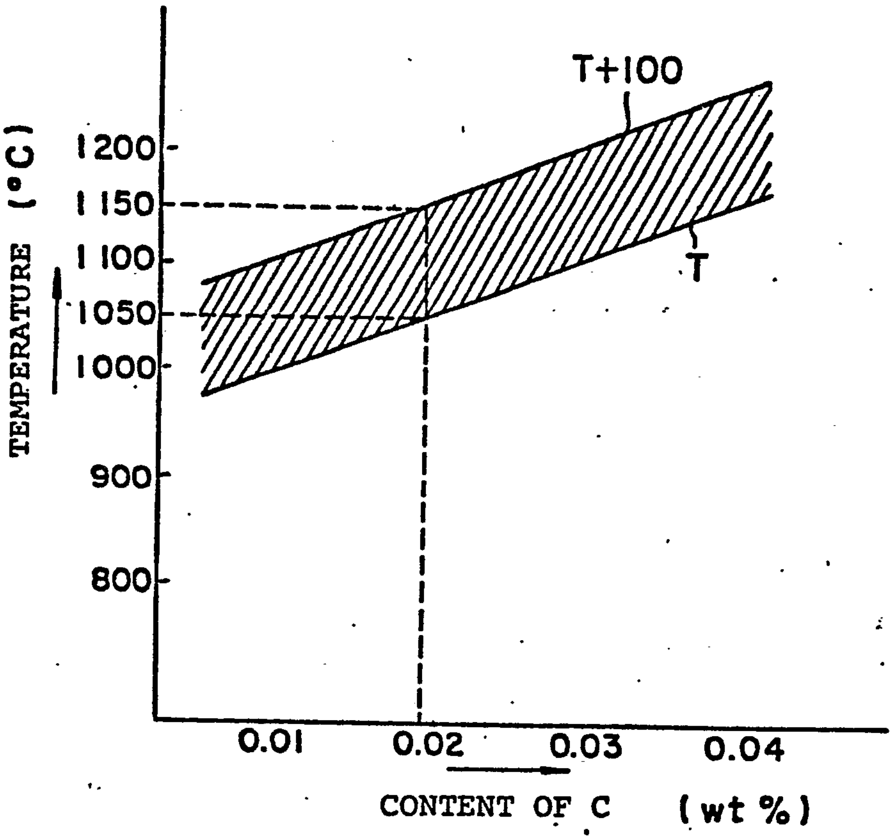

T+100
T
TEMPERATURE (°C)
1200
1150
1100
1050
1000
900
800
0.01
0.02
0.03
0.04
CONTENT OF C (wt %)

FIG. 15

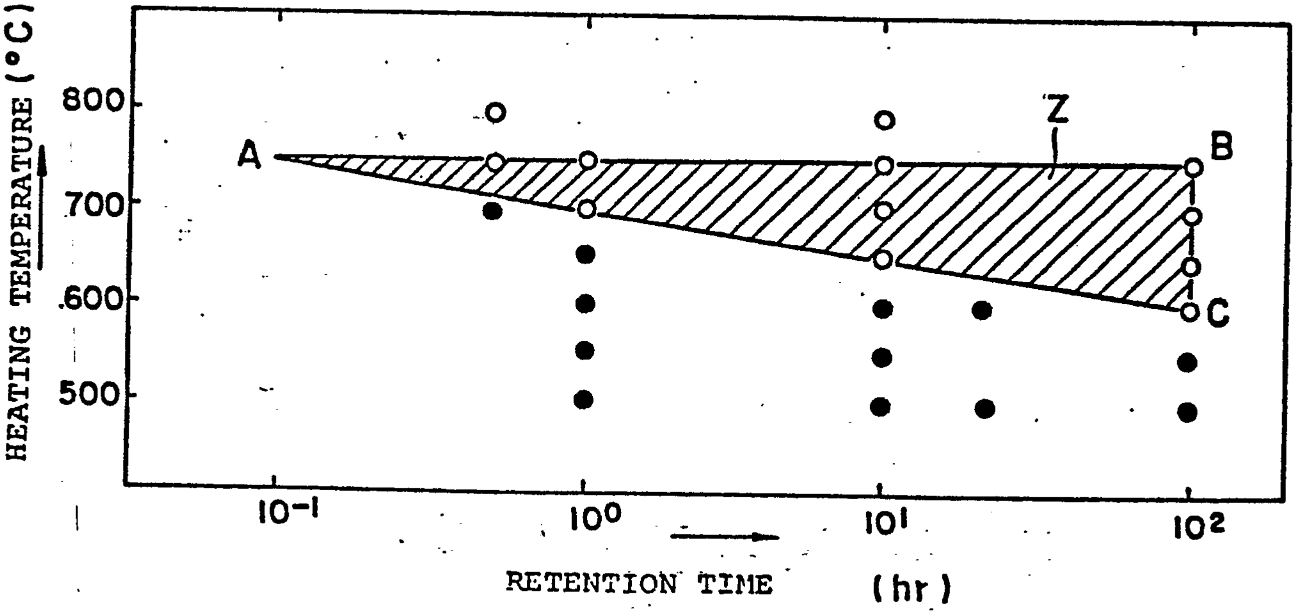
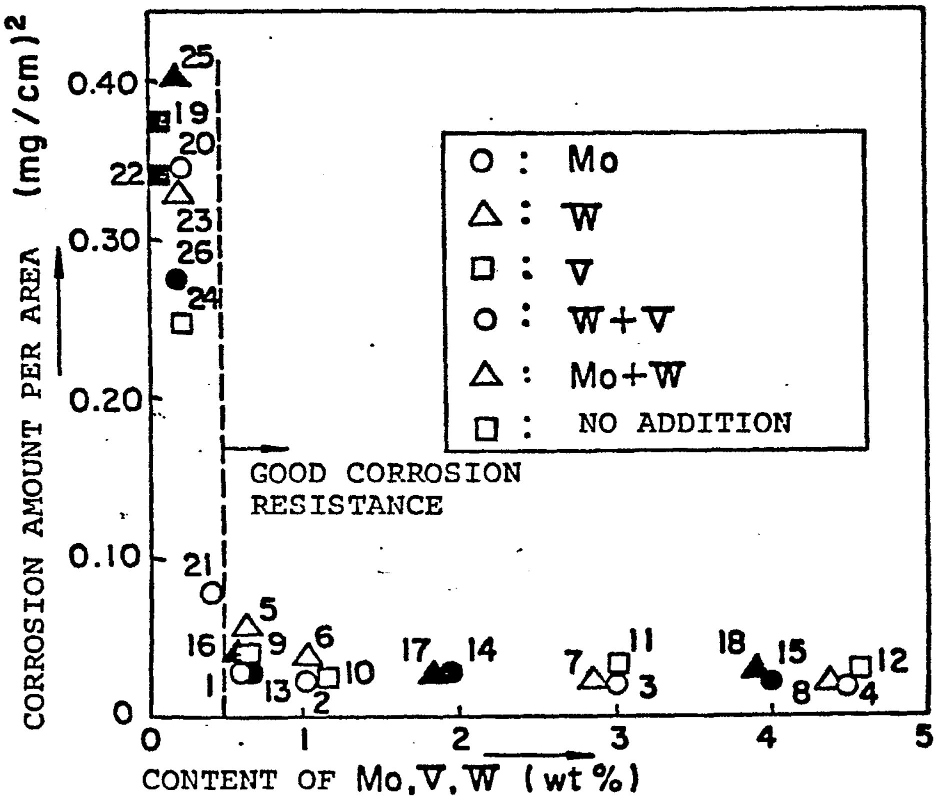

HEATING TEMPERATURE (°C)
800
700
600
500
A
B
C
Z
10⁻¹
10⁰
10¹
10²
RETENTION TIME (hr)

FIG. 16


CORROSION AMOUNT PER AREA (mg/cm)²
0.40
0.30
0.20
0.10
0
CONTENT OF Mo, V, W (wt %)
0
1
2
3
4
5
○ : Mo
△ : W
□ : V
● : W+V
▲ : Mo+W
▣ : NO ADDITION
GOOD CORROSION RESISTANCE
25
19
20
22
23
26
24
21
5
9
6
16
1
13
2
10
17
14
7
11
3
18
15
8
12
4