(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 483 646 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **91117990.1**

(51) Int. Cl.$^5$: **C22C 19/05**

(22) Date of filing: **22.10.91**

(30) Priority: **29.10.90 JP 288574/90**

(43) Date of publication of application:
**06.05.92 Bulletin 92/19**

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

(71) Applicant: **YOSHIDA KOGYO K.K.**
**No. 1 Kanda Izumi-cho Chiyoda-ku**
**Tokyo(JP)**

(72) Inventor: **Aikawa, Kazuo**
**526-2, Kamikoizumi**
**Namerikawa-shi, Toyama(JP)**
Inventor: **Yamagata, Keiko**
**1008, Dogenji, Tateyama-machi**
**Nakaniikawa-gun, Toyama(JP)**
Inventor: **Nagahora, Junichi**
**14-6, Sumiyoshidai, Modori-ku**
**Yokohama-shi, Kanagawa(JP)**
Inventor: **Ohtera, Katsumasa**
**4-11-20, Chuorinkan**
**Yamato-shi, Kanagawa(JP)**
Inventor: **Takeda, Hideki**
**2-25-14, Sugekitaura, Tama-ku**
**Kawasaki-shi, Kanagawa(JP)**
Inventor: **Osawa, Fumiko**
**690, Mizuhashi, Taisho-machi**
**Toyama-shi, Toyama(JP)**

(74) Representative: **Patentanwälte Leinweber & Zimmermann**
**Rosental 7/II Aufg.**
**W-8000 München 2(DE)**

# (54) Corrosion-resistant nickel-based alloy.

(57) The present invention provides a corrosion resistant nickel-based alloy consisting of an amorphous phase or a composite consisting of an amorphous phase and a fine crystalline phase, the nickel-based alloy consisting of a composition represented by the general formula $Ni_aCr_bMo_cX_d$ wherein X is at least one element selected from the group consisting of Zr and Hf, and a, b, c and d are, in atomic percent, $50 \leqq a \leqq 88$, $5 \leqq b \leqq 35$, $3 \leqq c \leqq 20$ and $4 \leqq d \leqq 20$, preferably, $50 \leqq a \leqq 88$, $5 \leqq b \leqq 35$, $3 \leqq c \leqq 15$ and $4 \leqq d \leqq 15$, and more preferably, $55 \leqq a \leqq 75$, $10 \leqq b \leqq 25$, $5 \leqq c \leqq 12$ and $5 \leqq d \leqq 12$. The alloys have a greatly improved corrosion resistance together with an advantageous combination of properties of high hardness, high strength, high heat-resistance and high wear-resistance which are all characteristic of amorphous alloys and, therefore, very useful for various industrial applications.

Rank Xerox (UK) Business Services
(-/2.18/2.1)

## BACKGROUND OF THE INVENTION

### 1. Field of the invention

The present invention relates to amorphous nickel-based alloys having an excellent corrosion-resistance, which are useful in various industrial applications.

### 2. Description of the Prior Art

Conventionally, as materials having a superior corrosion resistance, for example, Hastelly C-276 (made by Haynes Co.) and Carpenter Cb2 and Cb3 (both made by Carpenter Technology Co.) have been extensively used in corrosive environments. Japanese Patent Laid-Open No. 57-54242 discloses amorphous alloys which include Fe, Co or Ni or a mixture thereof as a basic component and which have superior saturation magnetic flux density, corrosion resistance and thermal stability due to addition of specified amounts of certain ferromagnetic metals or corrosion-resistance improving metals in combination with elemental metals, such as Zr, Ti, Hf, etc., to the foregoing basic component.

However, since the above-mentioned alloys are susceptible to pitting and corrosion in highly corrosive environments containing halogen ions, they have been used only in relatively mild corrosive environments. The latter alloys disclosed in the Japanese Patent Application Laid-Open No. 57-54242 were developed to obtain a corrosion resistance adequate to use as magnetic materials. However, the latter alloys can also be used only in relatively mild environments, like the above-mentioned alloys. In addition, although the Japanese Application describes that the corrosion resistance can be improved by addition of phosphorus in combination with chromium, the addition of phosphorus significantly deteriorates the mechanical properties, processability, etc., and, thereby, gives rise to a further problem of brittleness.

## SUMMARY OF THE INVENTION

It is accordingly an object of this invention to provide a novel corrosion resistant nickel-based alloy which is endurable over long periods of time in severely corrosive environments and, thereby, suitable for a wide variety of applications, such as outer materials for buildings, sashes, roofs, etc.; structural component materials for marine equipment and nuclear reactors, etc.

The present invention provides a corrosion resistant nickel-based alloy consisting of an amorphous phase or a composite consisting of an amorphous phase and a fine crystalline phase, the nickel-based alloy consisting of a composition represented by the general formula:
$Ni_aCr_bMo_cX_d$
wherein:
X is at least one element selected from the group consisting of Zr and Hf, and
a, b, c and d are, in atomic percent,
$50 \leqq a \leqq 88$, $5 \leqq b \leqq 35$, $3 \leqq c \leqq 20$ and $4 \leqq d \leqq 20$, preferably,
$50 \leqq a \leqq 88$, $5 \leqq b \leqq 35$, $3 \leqq c \leqq 15$ and $4 \leqq d \leqq 15$, and more preferably,
$55 \leqq a \leqq 75$, $10 \leqq b \leqq 25$, $5 \leqq c \leqq 12$ and $5 \leqq d \leqq 12$.

## BRIEF DESCRIPTION OF THE DRAWING

The single figure shows a schematic view illustrating an embodiment of the production of alloy thin ribbons according to the present invention.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Generally, an alloy has a crystalline structure in the solid state. However, in the preparation of an alloy with a certain composition, an amorphous structure, which is similar to liquid, is formed by preventing the formation of long-range order structure during solidification through, for example, rapid solidification from the liquid state, without forming a crystalline structure. The thus obtained alloy is called an amorphous alloy. Amorphous alloys are generally composed of a homogeneous single phase of supersaturated solid solution and have a significantly higher strength as compared with ordinary practical metallic materials. Further, some amorphous alloys exhibit a very high corrosion resistance and other various superior properties, depending on their compositions.

The nickel-based alloys of the present invention can be produced by rapidly quenching and solidifying a melt of an alloy having the composition as specified above, employing liquid quenching method. Liquid quenching methods are known as methods for the rapid quenching of alloy melts and, for example, single roller melt-spinning, twin-roller melt-spinning and in-rotating-water melt-spinning are especially effective. In these methods, a cooling rate of about $10^4$ to $10^7$ K/sec can be obtained. In order to produce thin ribbon materials by single-roller melt-spinning, twin-roller melt spinning or the like, the molten alloy is ejected from the opening of nozzle onto a roll of, for example, copper or steel, with a diameter of 30 to 300 mm, which is rotating at a constant rate of about 300 to 10000 rpm. Thus, various thin ribbon materials with a width of about 1 to 300 mm and a thickness of about 5 to 500 $\mu$m can be easily obtained. Alternatively, in order to produce fine wire materials by in-rotating- water melt-spinning, a jet of the molten alloy is directed, under application of a back pressure of argon gas, through a nozzle into a liquid refrigerant layer with a depth of about 1 to 10 cm which is held by centrifugal force in a drum rotating at a rate of about 50 to 500 rpm. Thus, fine wire materials can be readily obtained. In this process, the angle between the molten alloy ejecting from the nozzle and the liquid refrigerant surface is preferably in the range of about 60 to 90° and the ratio of the relative velocity of the ejecting molten alloy to the liquid refrigerant surface is preferably in the range of about 0.7 to 0.9.

Further, the nickel-based alloys of the present invention may be also obtained by depositing a source material having the composition represented by the above general formula onto a substrate employing thin film formation techniques, such as sputtering, vacuum deposition, ion plating, etc. and, thereby, forming a thin film having the above composition.

As the sputtering deposition process, there may be mentioned diode sputtering process, triode sputtering process, tetrode sputtering process, magnetron sputtering process, opposing target sputtering process, ion beam sputtering process, dual ion beam sputtering process, etc. and, in the former five processes, there are a direct current application type and a high-frequency application type.

The sputtering deposition process will be more specifically described hereinafter. In the sputtering deposition process, a target having the same composition as that of the thin film to be formed is bombarded by ion sources produced in the ion gun or the plasma, etc., so that neutral particles or ion particles in the state of atoms, molecules or cluster are produced from the target by its bombardment and deposited onto the substrate. It is known that various thin films have been obtained in such a manner.

Particularly, ion beam sputtering, plasma sputtering, etc., are effective and these sputtering processes provide a cooling rate of the order of $10^5$ to $10^7$ K/sec. Due to such a cooling rate, it is possible to produce an alloy thin film having an amorphous phase. The thickness of the thin film can be adjusted by the processing time and, usually, the thin film formation rate is on the order to 2 to 7 $\mu$m per hour.

Besides the above processes, the alloy of the present invention can be also obtained as rapidly solidified powder by various atomizing processes, for example, high pressure gas atomizing; or a spray process.

Whether the rapidly solidified nickel-based alloys thus obtained are amorphous or not can be determined by checking the presence of the characteristic halo pattern of an amorphous structure using an ordinary X-ray diffraction method.

In the nickel-based alloy of the present invention having the general formula as defined above, the reason why a, b, c and d are limited as above by the atomic percentages is that when they fall outside the respective ranges, amorphization becomes difficult and the resulting alloys become very brittle. Consequently, it becomes impossible to obtain the intended alloys having an amorphous phase by industrial processes, such as sputtering deposition.

Cr has an important effect of forming a passive film in cooperation with Ni and Mo when contained in coexistence with these elements in the alloy, thereby improving the corrosion resistance of the alloy. Another reason why the atomic percentage (b) of Cr is limited to the aforesaid range is that an amount of Cr of less than 5 atomic % is insufficient to provide an improved corrosion resistance contemplated by the present invention. On the other hand, when the Cr atomic percentage exceeds 35 atomic %, the resultant alloy becomes too brittle and impractical for industrial applications.

Mo has an effect of improving the ability to form an amorphous phase and, in addition, improves the hardness, strength and heat resistance.

When the Mo addition is less than 3 atomic % or more than 20 atomic %, the desired effects can not be obtained. Particularly, addition of Mo not exceeding 15 atomic % is more advantageous to improve the hardness, strength, toughness and processability.

Element X, which is at least one element selected from the group consisting of the group of Zr and Hf, is effective to improve the amorphizing ability of the above-mentioned alloy and, at the same time, has an effect of forming a passive film, thereby improving the corrosion resistance of the alloy. In the type of alloys as previously described, Cr unfavorably affects the amorphizing ability of the alloys, although it has a considerable effect in improving the corrosion resistance. However, the X element of the present invention permits the addition of large amounts of Cr and makes it possible to form alloys comprising an amorphous phase, even if Cr is added in large amounts. When the X element is less than 4 atomic % or more than 20 atomic %, the effects contemplated by the present invention will not be achieved. Particularly, addition not exceeding 15 atomic % is more preferable in the hardness, strength, toughness and processability.

Particularly, atomic percentages of $55 \leqq a \leqq 75$, $10 \leqq b \leqq 25$, $5 \leqq c \leqq 12$ and $5 \leqq d \leqq 12$ are more advantageous.

Further, when the nickel-based alloy of the present invention is prepared as a thin film, it has a high degree of toughness depending upon its composition. Therefore, some alloys can be bond-bent to 180° without cracking or peeling from a substrate.

Now, the present invention will described with reference to the following examples.

Example 1

Molten alloy 3 having a predetermined composition was prepared using a high-frequency melting furnace and charged into a quartz tube 1 having a small opening 5 (diameter: 0.5 mm) at the tip thereof, as shown in the drawing. After being heated to melt the alloy 3, the quartz tube 1 was disposed right above a copper roll 2. Then, the molten alloy 3 contained in the quartz tube 1 was ejected from the small opening 5 of the quartz tube 1, under the application of an argon gas pressure of 0.7 kg/cm$^2$, and brought into contact with the surface of the roll 2 rapidly rotating at the rate of 5,000 rpm. The molten alloy 3 was rapidly solidified and an alloy thin ribbon 4 was obtained.

Alloy thin ribbons prepared under the processing conditions as described above were each subjected to X-ray diffraction analysis. It was confirmed from the results that the obtained alloys had an amorphous phase and consisted of an amorphous single phase or of an amorphous phase and a fine crystalline phase. As to the alloys consisting of an amorphous phase and a fine crystalline phase, it can be confirmed which phase was contained in lager percentages by volume. If necessary, further detailed observation can be made by means of TEM (transmission electron microscopy). The composition of each thin ribbon was determined by a quantitative analysis using an X-ray microanalyzer.

Test specimens having a predetermined length were cut from the nickel-based alloy thin ribbons and immersed in 1N-HCl aqueous solution at 30° C, 1N-NaOH aqueous solution at 30° C and diluted aqua regia ($HCl : HNO_3 : H_2O = 3 : 1 : 4$) at 30° C, respectively, to test their corrosion resistance against the HCl, NaOH and diluted aqua regia. The test results are set forth in Table 1. In the table, corrosion resistance was evaluated in terms of corrosion rate. "Structure" in the same table shows the results of the X-ray diffraction analysis. "Amo" represents an amorphous single phase; "Amo < Cry" represents a composite of an amorphous phase and a crystalline phase in which the later phase was contained in larger percentages by volume than the former phase; and "Amo > Cry" represents a composite of an amorphous phase and a crystalline phase in which the former phase was contained in larger percentage by volume than the latter phase. "Toughness" in the table shows the results of a 180° bond-bending test. "Bri" represents "brittleness" causing cracking or peeling from a substrate. "Duc" represents "ductility" sufficient to permit bond-bending of 180° without cracking or peeling from a substrate.

Table 1

| No. | Sample | Structure | Toughness | Corrosion Rate (μm/year) | | |
|---|---|---|---|---|---|---|
| | | | | 1N-HCl at 30°C | 1N-NaOH at 30°C | Diluted Aqua Regia* at 30°C |
| 1 | $Ni_{62}Mo_9Zr_9Cr_{20}$ | Amo > Cry | Duc | 0.3 | 0.1 | 6.0 |
| 2 | $Ni_{60}Mo_9Zr_{11}Cr_{20}$ | Amo > Cry | Bri | 0 | 1.0 | 4.6 |
| 3 | $Ni_{64}Mo_9Zr_7Cr_{20}$ | Amo > Cry | Bri | 0.2 | 0.1 | 10.0 |
| 4 | $Ni_{58}Mo_9Zr_{14}Cr_{19}$ | Amo < Cry | Bri | 0.5 | 0 | 366.7 |
| 5 | $Ni_{68}Mo_9Zr_9Cr_{14}$ | Amo > Cry | Duc | 0.5 | 0 | 355.5 |
| 6 | $Ni_{66}Mo_9Zr_{11}Cr_{14}$ | Amo > Cry | Duc | 0 | 0.6 | 306.1 |
| 7 | $Ni_{70}Mo_9Zr_7Cr_{14}$ | Amo > Cry | Duc | 0.8 | 0.3 | 436.2 |
| 8 | $Ni_{64}Mo_9Zr_{14}Cr_{13}$ | Amo > Cry | Bri | 1.1 | 0 | 212.7 |
| 9 | $Ni_{63}Mo_6Zr_{11}Cr_{20}$ | Amo | Duc | 0.5 | 0.4 | 27.1 |
| 10 | $Ni_{57}Mo_{14}Zr_{10}Cr_{19}$ | Amo > Cry | Bri | 0.7 | 0.2 | 187.1 |
| 11 | $Ni_{57}Mo_8Zr_8Cr_{27}$ | Amo > Cry | Bri | 0.4 | 0.1 | 1.9 |
| Comparative Sample | | | | | | |
| 1 | Carpenter Cb2 | - | - | 5.8 | 1.1 | - |

* $HCl : HNO_3 : H_2O = 3 : 1 : 4$

It is clear from Table 1 that the nickel-based alloys of the present invention have a superior corrosion resistance to the hydrochloric acid aqueous solution, sodium hydroxide aqueous solution and diluted aqua regia.

Example 2

Seven kinds of alloy thin ribbons having the respective compositions (by atomic %), as shown in Table 2, were obtained in the same way as set forth in Example 1 except that the rotating rate of the roll 2 was changed to 6000 rpm in the preparation of Sample No. 3.

Test specimens having a predetermined length were cut from the thin ribbons obtained above and immersed in aqua regia (HCl : $HNO_3$ = 1 : 1) at 20 °C to examine the corrosion resistance to aqua regia. Further, hardness and tensile measurements were also conducted on each thin ribbon. The hardness values are indicated by values measured using a Vickers micro hardness tester under a load of 25 g. The results are shown in Table 2. The structure and toughness of each thin ribbon are also shown in Table 2.

Table 2

| No. | Sample | Structure | Toughness | Aqua Regia at 20°C (HCl:$HNO_3$ = 1:1) Corrosion Rate (µm/year) | Hardness Hv (DPN) | Tensile Strength σf(MPa) |
|---|---|---|---|---|---|---|
| 1 | $Ni_{62}Mo_9Zr_9Cr_{20}$ | Amo > Cry | Duc | 320 | 550 | 1540 |
| 2 | $Ni_{62}Mo_7Zr_8Cr_{23}$ | Amo < Cry | Duc | 246 | 595 | 1060 |
| 3 | $Ni_{62}Mo_7Zr_8Cr_{23}$ | Amo > Cry | Duc | 328 | 490 | 1650 |
| 4 | $Ni_{65}Mo_7Zr_7Cr_{21}$ | Amo < Cry | Duc | 420 | 575 | 780 |
| 5 | $Ni_{60}Mo_{10}Hf_{10}Cr_{20}$ | Amo | Duc | 96.1 | 570 | 1380 |
| 6 | $Ni_{61}Mo_8Zr_{11}Cr_{20}$ | Amo | Duc | 274 | 610 | 1050 |
| 7 | $Ni_{66}Mo_6Zr_7Cr_{21}$ | Amo > Cry | Duc | 235 | 555 | 900 |
| Comparative Sample | | | | | | |
| 1 | Hastelly C-276 | - | - | 746 | 235 | 810 |
| 2 | Carpenter Cb3 | - | - | 6,360,000 | 305 | 630 |

It is clear from Table 2 that the nickel-based alloys of the present invention have not only a superior corrosion resistance to the aqua regia but also a high level of hardness, tensile strength and toughness. Especially, Sample Nos. 3 and 5 had a very high toughness and, thus, could be bond-bent to 180 ° and, then, bent back to 360° without breaking or peeling from a substrate.

Further, Sample Nos. 1 and 7 and Comparative Sample Nos. 1 and 2 were further tested for their corrosion resistance in a mixed solution of hydrofluoric acid, nitric acid and water in a mixing ratio of 1 : 1 : 2, at 30 ° C and the results are shown in Table 3.

Table 3

| No. | Sample | Mixed Solution (hydrofluoric acid:nitric acid:water=1:1:2) Corrosion Rate (µm/year) |
|---|---|---|
| 1 | $Ni_{62}Mo_9Zr_9Cr_{20}$ | 60.5 |
| 7 | $Ni_{66}Mo_6Zr_7Cr_{21}$ | 72 |
| Comparative Sample | | |
| 1 | Hastelly C-276 | 249 |
| 2 | Carpenter Cb3 | 475 |

Table 3 shows that the nickel-based alloys of the present invention also have a superior corrosion resistance against the above-mentioned mixed solution.

Utility:

The amorphous alloys of the present invention prepared by the production procedure set forth in Example 1 were ground or crushed into a powder form. When the resulting powders were used as pigments for metallic paints, they exhibited a high resistance to corrosion attack in the metallic paints over a long period of time and provided highly durable metallic paints.

As described above, since the nickel-based alloys of the present invention have an amorphous phase, they have an advantageous combination of properties of high hardness, high strength, high heat-resistance and high wear-resistance which are all characteristic of amorphous alloys. Further, the alloys form a stable protective film by self-passivation. The resulting passive film is durable for a long period of time in severe corrosive environments containing chlorine ions, etc., and has a very high corrosion-resistance. Therefore, the alloys of the present invention are very useful in various industrial applications.

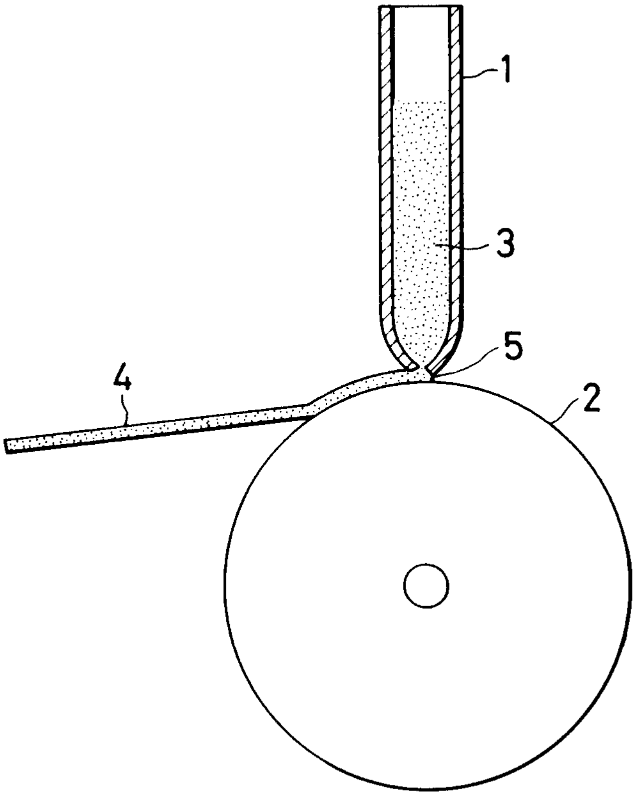
Additionally, the compositional range as defined above can provide materials having superior properties of high hardness and strength coupled with high toughness, strength and processability.

## Claims

**1.** A corrosion resistant nickel-based alloy consisting of an amorphous phase or a composite consisting of an amorphous phase and a fine crystalline phase, the nickel-based alloy consisting of a composition represented by the general formula:
$Ni_aCr_bMo_cX_d$
wherein:
X is at least one element selected from the group consisting of Zr and Hf, and
a, b, c and d are, in atomic percent,
$50 \leqq a \leqq 88$, $5 \leqq b \leqq 35$, $3 \leqq c \leqq 20$ and $4 \leqq d \leqq 20$.

2. A corrosion resistant nickel-based alloy as claimed in Claim 1 in which a, b, c and d of the general formula are, in atomic percent, $50 \leqq a \leqq 88$, $5 \leqq b \leqq 35$, $3 \leqq c \leqq 15$ and $4 \leqq d \leqq 15$.

3. A corrosion resistant nickel-based alloy as claimed in Claim 1 in which a, b, c and d of the general formula are, in atomic percent,
$55 \leqq a \leqq 75$, $10 \leqq b \leqq 25$, $5 \leqq c \leqq 12$ and $5 \leqq d \leqq 12$.


1
3
5
4
2

European Patent
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 91 11 7990

## 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 | US-A-4 668 310 (M. KUDO ET AL)<br>* claim 2 *<br>--- | 1 | C22C19/05 |
| A | US-A-4 854 980 (R.V. RAMAN ET AL)<br>* claims 1,7 *<br>--- | 1 | |
| A | EP-A-0 036 892 (SHIN-GIJUTSU KAIHATSU JIGYODAN)<br>* claims 1,3; table 2A *<br>----- | 1 | |
| | | | TECHNICAL FIELDS SEARCHED (Int. Cl.5 ) |
| | | | C22C |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 09 JANUARY 1992 | GREGG N.R. |

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