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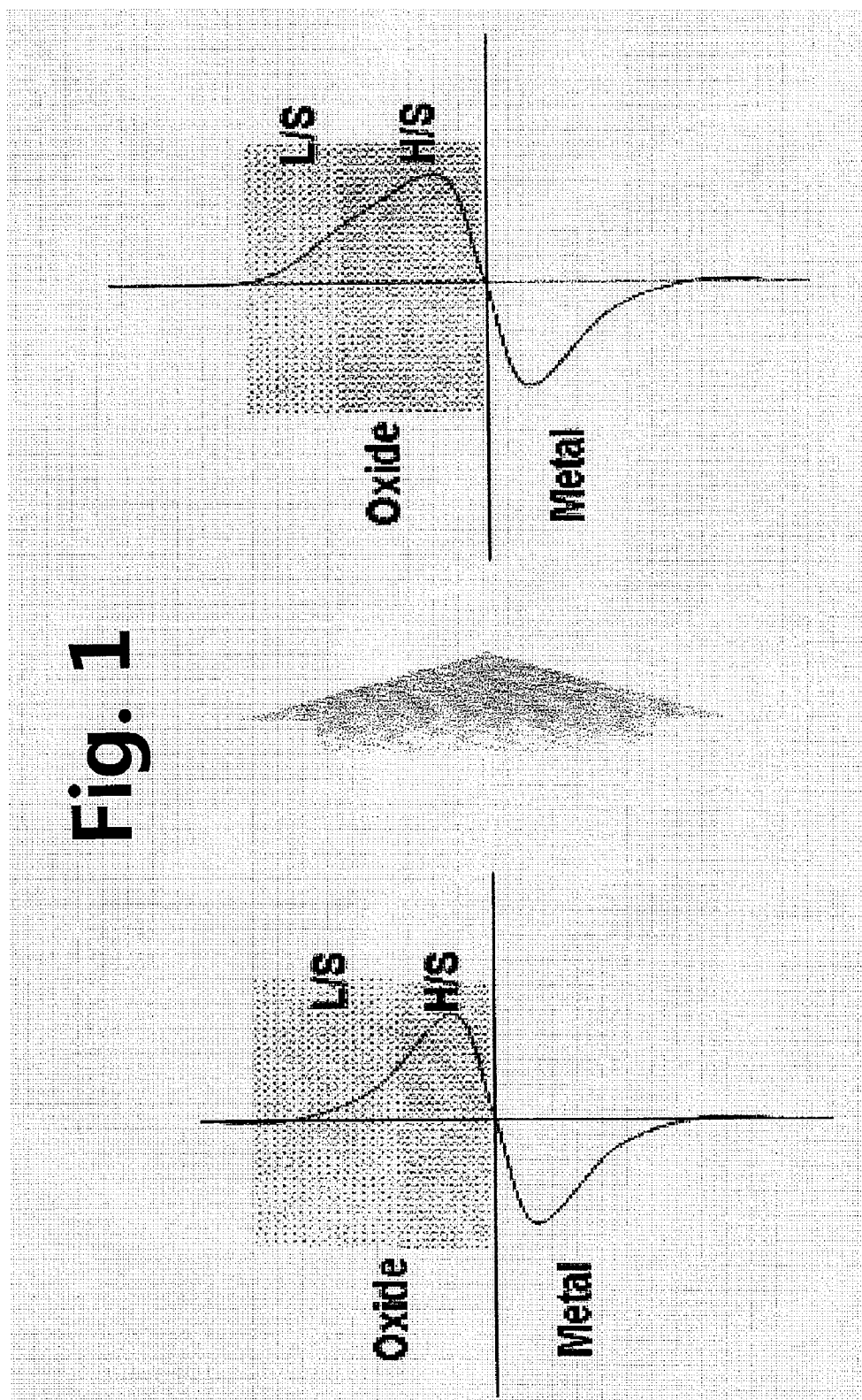
(19) **United States**(12) **Patent Application Publication**
Kim et al.(10) **Pub. No.: US 2012/0145287 A1**(43) **Pub. Date: Jun. 14, 2012**(54) **ZIRCONIUM ALLOY COMPOSITIONS
HAVING EXCELLENT CORROSION
RESISTANCE BY THE CONTROL OF
VARIOUS METAL-OXIDE AND PRECIPITATE
AND PREPARATION METHOD THEREOF****Publication Classification**(51) **Int. Cl.**
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(52) **U.S. Cl.** **148/557; 148/407**(75) Inventors: **Hyun Gil Kim**, Daejeon (KR);
Yong Hwan Jeong, Daejeon (KR);
Byoung Kwon Choi, Daejeon
(KR); **Sang Yoon Park**, Daejeon
(KR); **Myung Ho Lee**, Daejeon
(KR); **Jeong Yong Park**, Daejeon
(KR); **Jun Hwan Kim**, Daejeon
(KR)(57) **ABSTRACT**

Disclosed herein are a zirconium alloy composition, which exhibits excellent corrosion resistance by varying the kinds of metal oxides and controlling the size of precipitates of the composition, including: 1.05~1.45 wt % of Nb; one or more selected from the group consisting of 0.1~0.7 wt % of Fe and 0.05~0.6 wt % of Cr; and residual Zr, and a method of preparing the same. The zirconium alloy composition exhibits excellent corrosion resistance by controlling the kinds and amounts of the elements included in the zirconium alloy composition and the heat-treatment temperature and thus varying the kinds of metal oxides formed during an oxidation process and controlling the size of precipitates of the zirconium alloy, so that it can be usefully used as a raw material for nuclear fuel cladding tubes, spacer grids, nuclear reactor internals and the like of a light-water reactor or a heavy-water reactor in a nuclear power plant.

(73) Assignee: **Korea Atomic Energy Research
Institute**, Daejeon (KR)(21) Appl. No.: **12/392,697**(22) Filed: **Feb. 25, 2009**(30) **Foreign Application Priority Data**

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Fig. 1



**ZIRCONIUM ALLOY COMPOSITIONS
HAVING EXCELLENT CORROSION
RESISTANCE BY THE CONTROL OF
VARIOUS METAL-OXIDE AND PRECIPITATE
AND PREPARATION METHOD THEREOF**

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to a zirconium alloy composition having excellent corrosion resistance by the control of various metal oxides and precipitates of the composition, and a method of preparing the same.

[0003] 2. Description of the Related Art

[0004] Nuclear fuel cladding tubes, spacer grids and nuclear reactor internals, which are used in a nuclear fuel assembly of a nuclear power plant, are easily embrittled and corroded due to the nuclear irradiation and the corrosive environment of high temperature and high pressure, and thus their mechanical properties are deteriorated. For this reason, it is important to control their alloy compositions. Therefore, zirconium alloys having small neutron absorption cross sections, high mechanical strength and excellent corrosion resistance have been widely used in a pressurized water reactor (PWR) and a boiling water reactor (BWR). Among conventional zirconium alloys including tin (Sn), iron (Fe), chromium (Cr) and nickel (Ni), Zircaloy-2 (1.20~1.70 wt % of Sn, 0.07~0.20 wt % of Fe, 0.05~1.15 wt % of Cr, 0.03~0.08 wt % of Ni, 900~1500 ppm of O, and residual Zr) and Zircaloy-4 (1.20~1.70 wt % of Sn, 0.18~0.24 wt % of Fe, 0.07~1.13 wt % of Cr, 900~1500 ppm of O, less than 0.007 wt % of Ni and residual Zr) have been most widely used.

[0005] However, recently, in order to improve the economical efficiency of a nuclear reactor, a high burn-up and long period of operation, in which the replacement period of nuclear fuel increases in order to reduce the nuclear fuel cycle cost per period, has been employed. However, with the increase of the replacement period of nuclear fuel, the time for reacting nuclear fuel with high-temperature and high pressure cooling water and water vapor has increased. Therefore, when the conventional Zircaloy-2 or Zircaloy-4 is used as a raw material for a nuclear fuel cladding tube, there is a problem in that the corrosion phenomenon of the nuclear fuel becomes serious.

[0006] Therefore, it is urgently required to develop a material which has excellent corrosion resistance to high-temperature and high pressure cooling water and water vapor and which therefore can be used to make a nuclear fuel assembly for a high burn-up and long period of operation. Thus, research into developing zirconium alloys having improved corrosion resistance is being conducted. In this case, since the corrosion resistance of zirconium alloy is greatly influenced by the kinds and amounts of its constituents, working conditions, heat treatment conditions and the like, it is most important to establish optimal conditions for providing excellent corrosion resistance to the zirconium alloy.

[0007] Zirconium (Zr) is used as a raw material for a nuclear reactor because it is similar to stainless steel in external appearance. Generally, zirconium is stable at room temperature and has reactivity at high temperature. Zircaloy, which is an alloy prepared by adding a small amount of tin, iron, chromium and the like to zirconium, has strong corrosion resistance, and other alloys including zirconium also have corrosion resistance. Zirconium (IV) oxide having a chemically stable oxidation number of 4 is a material having

a very high melting point of 2715° C., high corrosion resistance and a low thermal expansion coefficient.

[0008] Niobium (Nb) is characterized in that it is a metal having a silver white gloss, but is blue to the naked eye, and in that it has similar specific gravity, hardness and the like to copper (Cu), but it is resistant to corrosion and it is easily changed. Further, niobium has a very high melting point of 2468° C., has good heat resistance, thermal conductivity and corrosion resistance, and is used to form a stable anodic oxide film. Furthermore, niobium is an insoluble metal, and is used in the form of a niobium-iron (Fe—Nb) alloy in the steel industry. Niobium oxides are used to manufacture the final products of niobium. Examples of niobium alloys used to prepare high-performance alloys may include a nickel-niobium alloy, a niobium-zirconium alloy, a niobium-titanium alloy, pure niobium, lithium-niobic acid salt alloys, and the like.

[0009] Iron (Fe) including carbon or other elements is referred to as steel. Among the elements included in iron, carbon greatly influences the properties of iron. That is, since carbon atoms interposed between iron atoms serve to prevent the movement of iron atoms, as the amount of carbon included in iron is increased, the hardness of iron increases, whereas as the hardness of iron increases, iron is easily broken. Iron having such properties may be alloyed with various elements. Among such elements, chromium (Cr) serves to improve the corrosion resistance of iron by forming a chromium film on the surface of iron, nickel (Ni) serves to improve the corrosion resistance of iron by forming a nickel film on the surface of iron, vanadium (V) serves to impart hardness, tensile strength and grindability to iron, molybdenum (Mo) serves to impart grindability to iron by reducing friction, tungsten (W) serves to increase the wear resistance of iron, manganese (Mn) serves to increase the corrosion resistance and wear resistance of iron, and titanium (Ti) serves to increase the corrosion resistance of iron.

[0010] Chromium (Cr) is very stable at room temperature, and is not corroded by air or water. Chromium dissolves in hydrochloric acid or diluted sulfuric acid while generating hydrogen to be formed into a solution of a chromium (II) salt. The chromium (II) included in the solution is oxidized to chromium (III). When chromium is immersed in an oxidizing acid, such as nitric acid, chromic acid, phosphoric acid, chloric acid, perchloric acid, nitrohydrochloric acid (aqua regia/royal water) or the like, a hard oxide thin film is formed on the surface of the chromium, so that the chromium is passivated, with the result that the chromium does not dissolve. Owing to the above characteristics of chromium, chromium or chromium alloys have corrosion resistance.

[0011] Tin (Sn) does not easily change in air, so that it is used in the surface treatment of iron, steel, copper or the like. Tin is widely used in the plating of tableware, industrial artworks, electronic parts and the like, and is also used in soldering and to make bronze, antifriction alloys, fusible alloys and the like.

[0012] U.S. Pat. No. 5,940,464 discloses a zirconium-base alloy comprising 0.02~0.4 wt % of iron, 0.8~1.8 wt % of niobium, 0.2~0.6 wt % of tin, 30~180 ppm of carbon, 10~120 ppm of silicon, 600~1800 ppm of oxygen and residual zirconium, and a method of making the same. Here, the weight of iron included in the zirconium-based alloy was about 20 times of that of iron included in the zirconium-based alloy disclosed in U.S. Pat. No. 5,648,995, and its corrosion resistance and creep resistance were improved.

[0013] U.S. Pat. No. 5,211,774 discloses a zirconium-based alloy comprising 0.2~0.5 wt % of iron, 0.8~1.2 wt % of tin, 0.1~0.4 wt % of chromium, 0.0~0.6 wt % of niobium, 50~200 ppm of silicon, 900~1800 ppm of oxygen and residual zirconium, and a method of making the same. Here, the corrosivity of the zirconium-based alloy attributable to hydrogen absorption and process change was decreased by adjusting the amount of silicon added to the zirconium-based alloy.

[0014] U.S. Pat. No. 5,254,308 discloses a zirconium-based alloy comprising 0.4~0.53 wt % of iron, 0.45~0.75 wt % of tin, 0.2~0.3 wt % of chromium, 0.3~0.5 wt % of niobium, 0.012~0.030 wt % of nickel, 50~200 ppm of silicon, 1000~2000 ppm of oxygen and residual zirconium. Here, the weight ratio of iron to chromium was 1.5, the amount of niobium was determined by the amount of iron influencing hydrogen absorptivity, and the amounts of niobium, silicon, carbon and oxygen were determined to impart excellent corrosion resistance and mechanical strength to the zirconium-base alloy.

[0015] European Patent Registration No. 198,570 discloses a zirconium-niobium alloy in which the amount of niobium is limited to 1.0~2.5 wt %. In this patent document, it was proposed that the corrosion resistance of the zirconium-niobium alloy can be improved by controlling the heat-treatment temperature during a process of preparing the zirconium-niobium alloy.

[0016] As described above, efforts to improve the corrosion resistance and mechanical properties of a zirconium alloy used as a raw material for a nuclear fuel assembly in a nuclear power plant are being made. However, considering that a high burn-up and long period of operation, in which the nuclear fuel loading cycle and target burn-up of a nuclear reactor are increased in order to improve the economical efficiency of a nuclear power plant, are becoming increasingly desired, it is required to prepare a zirconium alloy having excellent corrosion resistance which can improve the economical efficiency of nuclear fuel during the high burn-up and long period of operation.

[0017] Therefore, the present inventors have conducted research into improving the corrosion acceleration phenomenon of nuclear fuel cladding tubes, spacer grids and nuclear reactor internals occurring under a high burn-up and long period of operation, and thus they found that a zirconium alloy composition comprising: 1.05~1.45 wt % of niobium; at least one of 0.1~0.7 wt % of iron and 0.05~0.6 wt % of chromium; and residual zirconium, exhibited excellent corrosion resistance by controlling the kinds and amounts of the elements included in the zirconium alloy composition and the heat-treatment temperature and thus varying the kinds of metal oxides formed during an oxidation process and controlling the size of precipitates of the zirconium alloy. Based on these findings, the present invention was completed.

SUMMARY OF THE INVENTION

[0018] Accordingly, the present invention has been made keeping in mind the above problems occurring in the prior art, and an object of the present invention is to provide a zirconium alloy composition, which can be used as a raw material for nuclear fuel cladding tubes, spacer grids, nuclear reactor internals and the like used during a high burn-up and long period of operation, and which can exhibit excellent corrosion resistance by the control of various metal oxides and precipitates of the composition.

[0019] Another object of the present invention is to provide a method of preparing the zirconium alloy composition.

[0020] In order to accomplish the above object, the present invention provides a zirconium alloy composition, which exhibits excellent corrosion resistance by the control of various metal oxides and precipitates of the composition, comprising 1.05~1.45 wt % of Nb; at least one of 0.1~0.7 wt % of Fe and 0.05~0.6 wt % of Cr; 0.12 wt % of Sn; and residual Zr, and a method of preparing the same.

[0021] Since the zirconium alloy composition according to the present invention exhibits excellent corrosion resistance by controlling the kinds and amounts of the elements included in the zirconium alloy composition and the heat-treatment temperature and thus varying the kinds of metal oxides formed during an oxidation process and controlling the size of precipitates of the zirconium alloy, it can be usefully used as a raw material of nuclear fuel cladding tubes, spacer grids, nuclear reactor internals and the like of a light-water reactor or a heavy-water reactor in a nuclear power plant.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] The above and other objects, features and advantages of the present invention will be more clearly understood from the following detailed description taken in conjunction with the accompanying drawing, in which:

[0023] FIG. 1 is a schematic view showing the stress state in an oxide film at the interface between a metal and the oxide film according to the present invention, in which a low stress region is represented by L/S, and a high stress region is represented by H/S.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0024] The present invention provides a zirconium alloy composition, which can be used as a raw material of nuclear fuel cladding tubes, spacer grids, nuclear reactor internals and the like used during a high burn-up and long period of operation, and which can exhibit excellent corrosion resistance by the control of various metal oxides and precipitates of the composition.

[0025] Hereinafter, preferred embodiments of the present invention will be described in detail with reference to the attached drawing.

[0026] The present invention provides a zirconium alloy composition, including: 1.05~1.45 wt % of Nb; one or more selected from the group consisting of 0.1~0.7 wt % of Fe and 0.05~0.6 wt % of Cr; and residual Zr.

[0027] The zirconium alloy composition may further include 0.12 wt % of Sn.

[0028] Further, the present invention provides a zirconium alloy composition, including: 1.15~1.25 wt % of Nb, 0.12~0.45 wt % of Fe, and residual Zr.

[0029] The zirconium alloy composition may further include 0.12 wt % of Sn.

[0030] Moreover, the present invention provides a zirconium alloy composition, including: 1.15~1.25 wt % of Nb, 0.05~0.45 wt % of Cr, and residual Zr.

[0031] The zirconium alloy composition may further include 0.12 wt % of Sn.

[0032] Furthermore, the present invention provides a zirconium alloy composition, including: 1.05~1.45 wt % of Nb, 0.10~0.45 wt % of Fe, 0.05~0.45 wt % of Cr, and residual Zr.

[0033] The zirconium alloy composition may further include 0.12 wt % of Sn.

[0034] In order to obtain a zirconium alloy having excellent corrosion resistance, based on the fact that an oxide film having a columnar structure acts as a major factor determining the corrosion rate, the corrosion resistance of the zirconium alloy composition of the present invention can be improved by enabling a large columnar crystal layer to be maintained in the oxide film for a long period of time (see FIG. 1). Further, since the columnar oxide film is formed and stabilized by the compression stress applied to an oxide film, metal oxides which can apply the compression stress to the oxide film must be formed in the oxide film. As the elements meeting the above requirements, Nb, Fe and Cr serve as major alloy elements, and Sn serves as an auxiliary alloy element.

[0035] The zirconium alloy composition according to the present invention includes various metal oxides produced in an oxidation process. The metal oxides include niobium oxides, iron oxides, chromium oxides, tin oxides. Among these metal oxides, the niobium oxides may include NbO, Nb₂O₃, Nb₃O₅ and the like, the iron oxides may include FeO, Fe₂O₃, Fe₂O₄ and the like, the chromium oxides may include CrO, Cr₂O₃ and the like, and the tin oxides may include SnO.

[0036] Hereinafter, respective components (elements) of the zirconium alloy composition according to the present invention will be described in detail.

[0037] Niobium (Nb) serves to greatly improve the corrosion resistance of a zirconium alloy. However, when it is added in a high concentration of 0.3% or more, the improvement of the corrosion resistance of the zirconium alloy can be expected only when the size and composition of precipitates is controlled by employing a predetermined heat treatment temperature and time [Y. H. Jeong et al. J. Nucl. Mater. vol 317 p. 1]. Considering the niobium content required to solid-dissolve in a matrix and form a suitable amount of precipitates, it is preferred that the amount of niobium included in the zirconium alloy composition of the present invention be 1.05~1.45 wt %.

[0038] Iron (Fe) is an element added to improve the corrosion resistance of a zirconium alloy. It is known that, when the amount of iron included in the zirconium alloy is 0.3 wt % or more, the corrosion resistance of the zirconium alloy is improved [A. Seibold et al.; Proceedings, International KTGENS Topical Meeting on Nuclear Fuel, TOPFUEL 95, Wurzburg, Germany, 12-15 Mar. 1995, vol 2, p. 117]. For this reason, in the present invention, iron is added to the zirconium alloy composition in an amount of 0.1 wt % or more. However, when the amount of iron is more than 0.7 wt %, there is a problem in that the workability of the zirconium alloy composition is deteriorated. Therefore, it is preferred that the amount of iron included in the zirconium alloy composition of the present invention be 0.1~0.7 wt %.

[0039] Like iron, chromium (Cr) is a main element added to improve the corrosion resistance of a zirconium alloy. It is known that, when the amount of chromium included in the zirconium alloy is 0.2 wt % or more, the corrosion resistance of the zirconium alloy is improved [F. Garzarolli et al. ASTM-STP 1245 (1994) p. 709]. However, in the present invention, when both niobium and chromium are added to the zirconium alloy composition, it is preferred that chromium be added to the zirconium alloy composition at a minimum amount of 0.05 wt %, because highly-concentrated niobium is used.

[0040] Tin (Sn) is known as an element which stabilizes the α -phase in a zirconium alloy, and serves to improve the

mechanical strength of the zirconium alloy through solid-solution hardening. However, when the amount of tin added to the zirconium alloy composition is excessively increased, the corrosion resistance of the zirconium alloy is decreased. Therefore, it is preferred that tin be added to the zirconium alloy composition in an amount of 0.12 wt % such that it does not greatly influence the decrease in the corrosion resistance of the zirconium alloy.

[0041] Further, the present invention provides a method of preparing a zirconium alloy composition, which exhibits excellent corrosion resistance by varying the kinds of metal oxides and controlling the size of precipitates of the composition, comprising the steps of: mixing the elements constituting the zirconium alloy composition of claim 1 or 2 to form a mixture and then melting the mixture to obtain an ingot (step 1); forging the obtained ingot in a β -phase region (step 2); solution-heat-treating the forged ingot in the β -phase region and then quenching the solution-heat-treated ingot (step 3); hot-working the quenched ingot and then extruding the hot-worked ingot to obtain an intermediate product (step 4); primarily heat-treating the obtained intermediate product (step 5); cold-working and then secondarily heat-treating the primarily heat-treated intermediate product several times (step 6); and cold-working the secondarily heat-treated intermediate product and then finally heat-treating the cold-worked intermediate product (step 7).

[0042] Hereinafter, the steps of the method of preparing a zirconium alloy composition according to the present invention will be described in more detail.

[0043] First, in step 1, the elements constituting the zirconium alloy composition are mixed with each other to form a mixture, and then the mixture is melted to obtain an ingot.

[0044] The ingot may be formed through a vacuum arc remelting (VAR) process. Specifically, the ingot is formed by melting the mixture by applying an electric current of 500~1000 Å thereto and then cooling the melted mixture in a state in which the vacuum in a chamber was maintained at a pressure of 1×10^{-5} torr and then high-purity argon gas was charged in the chamber to a pressure of 0.1~0.3 torr.

[0045] In this case, in order to prevent the segregation of impurities and the nonuniform distribution of a zirconium alloy composition in the ingot, the vacuum arc remelting process may be repeatedly conducted 3~5 times. Further, in order to prevent the surface of a sample from being oxidized during the cooling procedure, inert gas, such as argon, may be introduced.

[0046] Next, in step 2, the ingot formed in step 1 is forged in a β -phase region.

[0047] In this step, the ingot is forged in a β -phase region of 1000° C. or more to break the cast structure in the ingot. In this case, it is preferred that the forging of the ingot be conducted at a temperature of 1000~1200° C. When the forging temperature is less than 1000° C., there is a problem in that the cast structure in the ingot is not easily broken. In contrast, when the forging temperature is more than 1200° C., there is a problem in that heat treatment costs are increased.

[0048] Next, in step 3, the ingot forged in step 2 is solution-heat-treated in the β -phase region, and is then quenched.

[0049] In this step, the ingot is solution-heat-treated in the β -phase region and then quenched in order to homogenize the alloy composition in the ingot and obtain fine precipitates. In this case, in order to prevent the oxidation phenomenon of an ingot sample, the ingot sample may be encapsulated with stainless steel and then heat-treated at 1000~1200° C. for

50~70 minutes. After the heat treatment, the ingot sample may be quenched to a temperature of 400° C. or less in a β -phase region using water.

[0050] Next, in step 4, the ingot quenched in step 3 is hot-worked and then extruded.

[0051] In this step, the ingot quenched in step 3 is hot-worked to obtain an intermediate product (for example, an extruded shell) suitable for cold working. It is preferred that the hot working in step 4 be conducted at a temperature of 560~650° C. for 15~40 minutes. When the hot working temperature deviates from the temperature range, it is difficult to obtain an intermediate product suitable for subsequent processes.

[0052] Next, in step 5, the intermediate product obtained in step 4 is primarily heat-treated.

[0053] It is preferred that the primary heat treatment is conducted at a temperature of 550~650° C. for 1~5 hours. When the primary heat treatment temperature is less than 550° C., there is a problem of the workability being decreased. In contrast, when the primary heat treatment temperature is more than 650° C., there is a problem of the corrosion resistance being decreased due to the formation of coarse precipitates.

[0054] Next, in step 6, the intermediate product primarily heat-treated in step 5 is repeatedly cold-worked and secondarily heat-treated several times to prepare a zirconium alloy composition.

[0055] The cold working and secondary heat treatment in step 6 may be conducted by cold-working the intermediate product primarily heat-treated in step 5 2~5 times and conducting secondary heat treatment 1~4 times between the cold working processes. It is preferred that the secondary heat treatment be conducted at a temperature of 550~650° C. for 3~5 hours. When the secondary heat treatment temperature is less than 550° C., there is a problem of the workability being decreased. In contrast, when the secondary heat treatment temperature is more than 650° C., there is a problem of the corrosion resistance being decreased due to the formation of coarse precipitates. Further, it is preferred that the cold working ratio be 50~85% during the cold working process. Specifically, it is more preferred that the primary cold working ratio be 60~80%, the secondary cold working ratio be 60~85%, and the tertiary cold working be 65~85. When the cold working ratio is less than 50%, there is a problem in that a product having the desired thickness cannot be obtained. In contrast, when the cold working ratio is more than 85%, there is a problem of the workability being decreased.

[0056] Next, in step 7, the intermediate product secondarily heat-treated in step 6 is cold-worked and then finally heat-treated.

[0057] The cold working in step 7 is conducted in order to increase creep resistance. It is preferred that the final heat treatment be conducted in a vacuum at a temperature of 450~580° C. for 2~10 hours. When the final heat treatment temperature is less than 450° C., there is a problem of the creep resistance being decreased, and, when the final heat treatment temperature is more than 580° C., there is a problem of the mechanical strength being decreased. Further, when the final heat treatment time is less than 2 hours, there is a problem in that hot-worked and cold-worked structures remain, and, when the final heat treatment time is more than 10 hours, there is a problem of the corrosion resistance being decreased due to the formation of coarse precipitates.

[0058] Hereinafter, the present invention will be described in more detail with reference to the following Examples and Experimental Examples. Here, the following Examples and Experimental Examples are set forth to illustrate the present invention, and the scope of the present invention is not limited thereto.

Example 1

Preparation of a Zirconium Alloy Composition

[0059] (1) Ingot Formation

[0060] 1.2 wt % of niobium, 0.2 wt % of iron and residual zirconium were formed into an ingot through a vacuum arc remelting (VAR) process. Reactor-grade sponge zirconium defined clearly in the ASTM B349 was used as the zirconium, and other alloy elements had a purity of 99.99%. In order to prevent the segregation of impurities and the nonuniform distribution of a zirconium alloy composition, the vacuum arc remelting process was repeatedly conducted four times. Subsequently, the zirconium alloy composition was formed into the ingot in a water-cooled copper crucible having a cooling water pressure of 1 kgf/cm² and a diameter of 60 mm by applying an electric current of 500 Å thereto in a state in which the vacuum in a chamber was maintained at a pressure of 1×10^{-5} torr and then high-purity argon gas (99.99%) was charged in the chamber in order to prevent the oxidization of the zirconium alloy composition.

[0061] (2) β -Forging

[0062] The ingot was forged in a β -phase region of 1100° C. in order to break the cast structure in the ingot.

[0063] (3) β -Quenching

[0064] The ingot was solution-heat-treated in a β -phase region of 1050° C. for 15 minutes in order to break the cast structure in the ingot. Thereafter, the ingot was quenched by dropping it into a water tank filled with water of room temperature to form a martensite or widmanstatten structure in the ingot.

[0065] (4) Hot Working

[0066] The ingot quenched in the β -phase region was formed into a hollow billet, and then the hollow billet was hot-extruded at 630° C. for 15 minutes to obtain an intermediate product suitable for cold working.

[0067] (5) Primary Heat Treatment

[0068] The hot-extruded intermediate product was primarily heat-treated at 580° C. for 3 hours.

[0069] (6) Cold Working and Secondary Heat Treatment

[0070] The primarily heat-treated intermediate product was cold-worked, and was then secondarily heat-treated at 580° C. for hours.

[0071] (7) Final Heat Treatment

[0072] The secondarily heat-treated intermediate product was cold-worked, and was then finally heat-treated at 510° C. in a vacuum for 3 hours.

Examples 2 to 18

[0073] The zirconium alloy compositions having excellent corrosion resistance of Examples 2 to 18 were prepared using the same method as in Example 1, except that chemical compositions constituting the zirconium alloy compositions and stepwise heat treatment conditions were changed. The chemi-

cal compositions constituting the zirconium alloy compositions and stepwise heat treatment conditions are shown in Table 1.

Comparative Examples 1 to 6

[0074] The zirconium alloy compositions having excellent corrosion resistance of Comparative Examples 1 to 6 were prepared using the same method as in Example 1, except that chemical compositions constituting the zirconium alloy compositions and stepwise heat treatment conditions were changed. The chemical compositions constituting the zirconium alloy compositions and stepwise heat treatment conditions are also shown in Table 1.

Experimental Example 1

Manufacturability of a Zirconium Alloy Composition

[0075] The manufacturability of the zirconium alloy composition according to the present invention was evaluated by the zirconium alloy composition preparation processes of Examples 1 to 18 and Comparative Examples 1 to 6.

[0076] In Examples 1 to 18 and Comparative Examples 3 to 6, the zirconium alloy compositions were smoothly prepared without damage, but, in Comparative Examples 1 and 2, the zirconium alloy compositions were seriously damaged during their preparation processes. From this phenomenon, it can

TABLE 1

Class.	Chemical composition					Stepwise heat treatment condition		
	Ni (wt %)	Fe (wt %)	Cr (wt %)	Sn (wt %)	Zr (wt %)	Primary heat	Secondary heat	Final heat
						treatment (h: hour)	treatment (h: hour)	treatment (h: hour)
Exp. 1	1.2	0.2	—	—	residual	580° C. x 3 h	580° C. x 3 h	510° C. x 3 h
Exp. 2	1.2	0.2	—	—	residual	600° C. x 2 h	600° C. x 2 h	510° C. x 3 h
Exp. 3	1.2	0.35	—	—	residual	580° C. x 3 h	580° C. x 3 h	510° C. x 3 h
Exp. 4	1.2	0.35	—	—	residual	600° C. x 2 h	600° C. x 2 h	510° C. x 3 h
Exp. 5	1.2	0.6	—	—	residual	580° C. x 3 h	580° C. x 3 h	510° C. x 3 h
Exp. 6	1.2	0.6	—	—	residual	600° C. x 2 h	600° C. x 2 h	510° C. x 3 h
Exp. 7	1.2	0.6	—	0.12	residual	580° C. x 3 h	580° C. x 3 h	510° C. x 3 h
Exp. 8	1.2	0.6	—	0.12	residual	600° C. x 2 h	600° C. x 2 h	510° C. x 3 h
Exp. 9	1.2	—	0.1	—	residual	580° C. x 3 h	580° C. x 3 h	510° C. x 3 h
Exp. 10	1.2	—	0.1	—	residual	600° C. x 2 h	600° C. x 2 h	510° C. x 3 h
Exp. 11	1.2	—	0.3	—	residual	580° C. x 3 h	580° C. x 3 h	510° C. x 3 h
Exp. 12	1.2	—	0.3	—	residual	600° C. x 2 h	600° C. x 2 h	510° C. x 3 h
Exp. 13	1.2	—	0.3	0.12	residual	580° C. x 3 h	580° C. x 3 h	510° C. x 3 h
Exp. 14	1.2	—	0.3	0.12	residual	600° C. x 2 h	600° C. x 2 h	510° C. x 3 h
Exp. 15	1.2	—	0.5	—	residual	580° C. x 3 h	580° C. x 3 h	510° C. x 3 h
Exp. 16	1.2	—	0.5	—	residual	600° C. x 2 h	600° C. x 2 h	510° C. x 3 h
Exp. 17	1.2	0.35	0.3	—	residual	580° C. x 3 h	580° C. x 3 h	510° C. x 3 h
Exp. 18	1.2	0.35	0.3	0.12	residual	600° C. x 2 h	600° C. x 2 h	510° C. x 3 h
Comp. Exp. 1	1.2	0.85	—	—	residual	580° C. x 3 h	580° C. x 3 h	510° C. x 3 h
Comp. Exp. 2	1.2	—	0.75	—	residual	600° C. x 2 h	600° C. x 2 h	510° C. x 3 h
Comp. Exp. 3	0.8	—	—	—	residual	580° C. x 3 h	580° C. x 3 h	510° C. x 3 h
Comp. Exp. 4	0.8	—	—	—	residual	600° C. x 2 h	600° C. x 2 h	510° C. x 3 h
Comp. Exp. 5	0.5	—	—	1.0	residual	580° C. x 3 h	580° C. x 3 h	510° C. x 3 h
Comp. Exp. 6	0.5	—	—	1.0	residual	600° C. x 2 h	600° C. x 2 h	510° C. x 3 h

be seen that, when 0.85 wt % or more of Fe or 0.75 wt % or more of Cr is added to a zirconium alloy composition including 1.2 wt % of Nb, it is difficult to impart excellent manufacturability to the zirconium alloy composition, and thus it is not preferred that the amount of iron or chromium be excessively increased.

Experimental Example 2

Corrosion Test

[0077] In order to evaluate the corrosion resistance of the zirconium alloy composition including niobium according to the present invention, the following corrosion test was conducted.

[0078] The zirconium alloy compositions prepared in Examples 1 to 18 and Comparative Examples 3 to 6 were formed into test samples having a size of 25×15×1 mm, and then the test samples were immersed in a mixed solution having a volume ratio of water:nitric acid:fluorine acid (HF) of 50:40:10 to remove impurities and defects from the surfaces of the test samples. The surface areas and initial weights of the surface-treated test samples were measured immediately before they were put into an autoclave. Thereafter, the test samples were corroded under the conditions of 360° C. cooling water and 360° C. 70 ppm LiOH for 90 days, and then the increases in weight of the test samples were measured, and thus the degree of corrosion of the test samples was quantitatively evaluated by calculating the ratio of weight increase to surface thereof. The results of the corrosion test are shown in Table 2.

TABLE 2

Class.	Increase in weight (mg/dm ²)	
	360° C. cooling water	360° C. 70 ppm LiOH
Example 1	29.59	30.49
Example 2	32.28	33.33
Example 3	29.51	29.94
Example 4	31.94	31.18
Example 5	29.44	30.74
Example 6	31.04	31.47
Example 7	30.18	31.17
Example 8	32.42	32.62
Example 9	27.94	36.95
Example 10	31.43	41.54
Example 11	28.32	38.94
Example 12	31.51	42.33
Example 13	28.43	36.60
Example 14	31.54	42.26
Example 15	29.21	36.37
Example 16	30.72	39.57
Example 17	29.33	35.52
Example 18	30.24	38.72
Comp. Example 3	33.24	47.51
Comp. Example 4	34.12	50.22
Comp. Example 5	35.15	44.47
Comp. Example 6	35.22	44.53

[0079] From Table 2, it can be seen that the increase in weight of the test samples of Examples 1 to 16 under the condition of cooling water is in the range of 27~32 mg/dm², which is less than that of the test samples of Comparative Examples 3 to 6 (33~35 mg/dm²), so that the corrosion resistance of the test samples of Examples 1 to 16 is better than those of the test samples of Comparative Examples 3. Further, it can also be seen that the increase in weight of the test samples of Examples 1 to 16 under the condition of 70 ppm

LiOH is in the range of 29~42 mg/dm², which is less than that of the test samples of Comparative Examples 3 to 6 (44~50 mg/dm²), so that the corrosion resistance of the test samples of Examples 1 to 16 is better than those of the test samples of Comparative Examples 3.

[0080] Comparing the corrosion performance of the test samples of Examples 1, 3, 5, 7, 9, 11, 13, 15 and 17 with that of the test samples of Examples 2, 4, 6, 8, 10, 12, 14, 16 and 18 in order to determine the influence of corrosion resistance according to the heat treatment temperature adjusted to control the size of precipitates, it can be seen that the increase in weight of the test samples of Examples 1, 3, 5, 7, 9, 11, 13, 15 and 17 in which primary heat treatment and secondary heat treatment are conducted at 580° C. is decreased by 2~3 mg/dm² compared to that of the test samples of Examples 2, 4, 6, 8, 10, 12, 14, 16 and 18 in which primary heat treatment and secondary heat treatment are conducted at 600° C., because the average size of the precipitates of the test samples of Examples 1, 3, 5, 7, 9, 11, 13, 15 and 17 in which primary heat treatment and secondary heat treatment are conducted at 580° C. is decreased compared to that of the test samples of Examples 2, 4, 6, 8, 10, 12, 14, 16 and 18 in which primary heat treatment and secondary heat treatment are conducted at 600° C. Therefore, in the method of preparing the zirconium alloy composition of the present invention, it can be seen that it is very important to control the secondary heat treatment temperature. When the primary heat treatment temperature and secondary heat treatment temperature are excessively low, the corrosion resistance of the zirconium alloy composition is increased due to the control of the size of precipitates, but it is difficult to treat the zirconium alloy composition. In contrast, when the primary heat treatment temperature and secondary heat treatment temperature are excessively high, the corrosion resistance of the zirconium alloy composition can be decreased because the average size of precipitates becomes coarse. Consequently, it is preferred that the primary heat treatment temperature and secondary heat treatment temperature be 550~650° C.

[0081] Although the preferred embodiments of the present invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.

1. A zirconium alloy composition, which exhibits excellent corrosion resistance by varying the kinds of metal oxides and controlling the size of precipitates of the composition, comprising:

1.05~1.45 wt % of Nb;
one or more selected from the group consisting of 0.1~0.7 wt % of Fe and 0.05~0.6 wt % of Cr; and
residual Zr.

2. The zirconium alloy composition according to claim 1, further comprising: 0.12 wt % of Sn.

3. The zirconium alloy composition according to claim 1, wherein the zirconium alloy composition comprises: 1.15~1.25 wt % of Nb, 0.12~0.45 wt % of Fe, and residual Zr.

4. The zirconium alloy composition according to claim 3, further comprising: 0.12 wt % of Sn.

5. The zirconium alloy composition according to claim 1, wherein the zirconium alloy composition comprises: 1.15~1.25 wt % of Nb, 0.05~0.45 wt % of Cr, and residual Zr.

6. The zirconium alloy composition according to claim 5, further comprising: 0.12 wt % of Sn.

7. The zirconium alloy composition according to claim 1, wherein the zirconium alloy composition comprises: 1.05~1.45 wt % of Nb, 0.10~0.45 wt % of Fe, 0.05~0.45 wt % of Cr, and residual Zr.

8. The zirconium alloy composition according to claim 7, further comprising: 0.12 wt % of Sn.

9. The zirconium alloy composition according to claim 1, wherein the metal oxides are selected from the group consisting of niobium oxides, iron oxides, and chromium oxides.

10.-14. (canceled)

15. A method of preparing a zirconium alloy composition, which exhibits excellent corrosion resistance by varying the kinds of metal oxides and controlling the size of precipitates of the composition, comprising the steps of:

mixing elements constituting a zirconium alloy composition comprising 1.05~1.45 wt % of Nb, one or more selected from the group consisting of 0.1~0.7 wt % of Fe and 0.05~0.6 wt % of Cr, and residual Zr to form a mixture and then melting the mixture to obtain an ingot (step 1);

forging the obtained ingot in a β -phase region (step 2);

solution-heat-treating the forged ingot in the β -phase region and then quenching the solution-heat-treated ingot (step 3);

hot-working the quenched ingot and then extruding the hot-worked ingot to obtain an intermediate product (step 4);

primarily heat-treating the obtained intermediate product (step 5);

cold-working and secondarily heat-treating the primarily heat-treated intermediate product several times (step 6); and

cold-working the secondarily heat-treated intermediate product and then finally heat-treating the cold-worked intermediate product (step 7).

16. The method of preparing a zirconium alloy composition according to claim 15, wherein the hot working in step 4 is conducted at 560~650° C. for 15~40 minutes.

17. The method of preparing a zirconium alloy composition according to claim 15, wherein the primary heat treatment in step 5 is conducted at 550~650° C. for 1~5 hours.

18. The method of preparing a zirconium alloy composition according to claim 15, wherein the final heat treatment in step 7 is conducted at 450~580° C. for 2~10 hours.

19. The method of preparing a zirconium alloy composition according to claim 15, wherein the elements constituting the zirconium alloy composition further comprise 0.12 wt % of Sn.

20. The method of preparing a zirconium alloy composition according to claim 15, wherein the elements constituting the zirconium alloy composition comprise 1.15~1.25 wt % of Nb, 0.12~0.45 wt % of Fe, and residual Zr.

21. The method of preparing a zirconium alloy composition according to claim 20, wherein the elements constituting the zirconium alloy composition further comprise 0.12 wt % of Sn.

22. The method of preparing a zirconium alloy composition according to claim 15, wherein the elements constituting the zirconium alloy composition comprise 1.15~1.25 wt % of Nb, 0.05~0.45 wt % of Cr, and residual Zr.

23. The method of preparing a zirconium alloy composition according to claim 22, wherein the elements constituting the zirconium alloy composition further comprise 0.12 wt % of Sn.

24. The method of preparing a zirconium alloy composition according to claim 15, wherein the elements constituting the zirconium alloy composition comprise 1.05~1.45 wt % of Nb, 0.10~0.45 wt % of Fe, 0.05~0.45 wt % of Cr, and residual Zr.

25. The method of preparing a zirconium alloy composition according to claim 24, wherein the elements constituting the zirconium alloy composition further comprise 0.12 wt % of Sn.

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