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(54) **Zirconium based alloys having excellent creep resistance**

(57) The present invention relates to a zirconium based alloy composite having an excellent creep resistance and, more particularly, to a zirconium based alloy composite finally heat-treated to have the degree of recrystallization in the range of 40-70% in order to improve the creep resistance. The zirconium based alloy comprises 0.8~1.8 wt.% niobium(Nb); 0.38~0.50 wt.% tin (Sn); one or more elements selected from 0.1~0.2 wt.% iron(Fe), 0.05~0.15 wt.% copper(Cu), and 0.12 wt.% chromium(Cr); 0.10~0.15 wt.% oxygen(O); 0.006~0.010

wt.% carbon(C); 0.006~0.010 wt.% silicon(Si); 0.0005~0.0020 wt.% sulfur (S); and the balance zirconium(Zr). The zirconium alloy manufactured with the composition in accordance with the present invention has an excellent creep resistance compared to a conventional Zircaloy -4, and may effectively be used as a nuclear cladding tube, supporting lattice and inner structures of reactor core in the nuclear power plant utilizing light or heavy water reactor.

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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to a zirconium based alloy composite having an excellent creep resistance and, more particularly, to a zirconium based alloy composite finally heat-treated to have a degree of recrystallization in the range of 40~70% in order to improve the creep resistance. The zirconium based alloy composite comprises 0.8~1.8 wt. % niobium(Nb); 0.38~0.50 wt.% tin(Sn); one or more elements selected from 0.1~0.2 wt.% iron(Fe), 0.05~0.15 wt.% copper(Cu), and 0.12 wt.% chromium(Cr); 0.10~0.15 wt.% oxygen(O); 0.006~0.010 wt.% carbon(C); 0.006~0.010 wt.% silicon(Si); 0.0005~0.0020 wt.% sulfur(S); and the balance zirconium(Zr).

Description of the Prior Art

[0002] A nuclear fuel cladding tube for nuclear power plant is one of the important parts for nuclear reactor core. The cladding tube confines nuclear fuel and prevents nuclear fission products from flowing into cooling water. The outer wall of cladding tube is exposed to the cooling water at 320°C under the pressure of 15 MPa. Composition of alloy is very important, because a cladding tube accompanies deterioration of mechanical properties by embrittlement and growth phenomena due to irradiation of neutrons and corrosive environment of high temperature and pressure. Zirconium alloys such as Zircaloy -4, which have excellent mechanical strength at high temperature, creep resistance, corrosion resistance, thermal conductivity, and low absorption of neutrons, were developed in the early 1960's, and have generally been used up to now.

[0003] However, the conventional Zircaloy-4 cladding tube is faced with difficulties in use, because the nuclear power plant is being operated in the condition of high inflammation, long-term period, high temperature coolant and high pH, for the improvement of economical efficiency.

[0004] Accordingly, a new nuclear fuel cladding tube having highly improved reliability in the prevention of breakages and thermal allowance is required to enhance the stability and economical efficiency of nuclear reactor. For this purpose, development of new alloy cladding tube is being carried out to improve the corrosion resistance and creep resistance. The development of new alloy for cladding tube has a trend toward reducing or eliminating the content of tin(Sn) and adding niobium(Nb).

[0005] US Patent No. 5,832,050 disclosed a zirconium alloy composite and a manufacturing method thereof, which improved corrosion resistance and creep resistance by containing more than 96 wt.% zirconium and adding 8-100 ppm sulfur (hereinafter, % indicates weight percent). The above patent has an independent claim describing the composition of zirconium alloy containing 8-100 ppm sulfur (preferably 8-30 ppm) and more than 96% zirconium, and 8 dependant claims for 8 alloys as follows.

Alloy 1: zirconium alloy containing 1.2~1.7% Sn, 0.18~0.25% Fe, 0.05~0.15% Ni, and 0.05~0.15% Cr

Alloy 2: zirconium alloy containing 1.2~1.7% Sn, 0.07~0.2% Fe, 0.05~0.15% Ni, and 0.05~0.15% Cr

Alloy 3: zirconium alloy containing 0.7~1.3% Nb, and 900-1600 ppm O

Alloy 4: zirconium alloy containing 0.3~1.4% Sn, 0.4~1% Fe, 0.2~0.7% V, and 500-1800 ppm O

Alloy 5: zirconium alloy containing 0.7~1.3% Nb, 0.8~1.5% Sn, 0.1~0.6% Fe, 0.01~0.2% Cr, and 500-1800 ppm O

Alloy 6: zirconium alloy containing 0.1~0.3% Nb, 0.7~1.25% Sn, 0.1~0.3% Fe, 0.05~0.2% Cr, 0.01~0.02% Ni, and 500-1800 ppm O

Alloy 7: zirconium alloy containing 2.2~2.8% Nb

Alloy 8: zirconium alloy containing 0.3~0.7% Sn, 0.3~0.7% Fe, 0.1~0.4% Cr, 0.01~0.04% Ni, 70-120 ppm Si, and 500-1800 ppm O

[0006] US Patent Application Publication No. 2004/0018491 disclosed the following alloy composite with improved corrosion resistance by heat treatment for recrystallization and limiting the composition and size of precipitate, and a manufacturing method thereof.

[0007] Zirconium alloy containing (0.03~0.25% Fe) + (one or more elements selected from 0.8~1.3% Cr, V, Nb, less than 2000 ppm Sn, 500-2000 ppm O, less than 100 ppm C, 3-35 ppm S, and less than 50 ppm Si)

[0008] Additionally, the page 78 of *J. Nucl. Mater.*, vol. 255 (1998) describes Zr-1.0%Nb and Zr-0.5%Sn-0.6%Fe-0.4%V alloys with improved thermal creep resistance by adding sulfur, and the page 246 of the same magazine vol. 304 (2002) describes the correlation between precipitate and corrosion characteristic of unalloyed zirconium containing sulfur up to 850 ppm.

[0009] Besides the above prior art, US Patent No. 5,254,308 disclosed an alloy containing niobium and iron to maintain the mechanical characteristic of alloy according to the reduction of tin content. The alloy comprises 0.45–0.75% Sn (preferably 0.6%), 0.4–0.53% Fe (preferably 0.45%), 0.2–0.3% Cr (preferably 0.25%), 0.3–0.5% Nb (preferably 0.45%), 0.012–0.03% Ni (preferably 0.02%), 50–200 ppm Si (preferably 100 ppm), and 1000–2000 ppm O (preferably 1600 ppm), where Fe/Cr ratio is controlled to 1.5, and addition of niobium is decided according to the iron content, which gives an influence to hydrogen absorption. Additionally, the alloy has been produced to have excellent corrosion resistance and strength by controlling the contents of Ni, Si, C, and O. US Patent No. 5,334,345 disclosed an alloy composite containing 1.0–2.0% Sn, 0.07–0.70% Fe, 0.05–0.15% Cr, 0.16–0.40% Ni, 0.015–0.30% Nb (preferably 0.015–0.20%), 0.002–0.05% Si (preferably 0.015–0.05%), and 900–1600 ppm O to improve the corrosion resistance and hydrogen absorption resistance. US Patent No. 5,366,690 disclosed an alloy composite containing 0–1.5% Sn (preferably 0.6%), 0–0.24% Fe (preferably 0.12%), 0–0.15% Cr (preferably 0.10%), 0–2300 ppm N, 0–100 ppm Si (preferably 100 ppm), 0–1600 ppm oxygen (preferably 1200 ppm), and 0–0.5% Nb (preferably 0.45%) by mainly controlling the contents of Sn, N, and Nb. US Patent No. 5,211,774 disclosed a zirconium alloy composite developed for the purpose of improving ductility, creep strength and corrosion resistance in the environment of neutron irradiation. The alloy is formed in the composition of 0.8–1.2% Sn, 0.2–0.5% Fe (preferably 0.35%), 0.1–0.4% Cr (preferably 0.25%), 0–0.6% Nb, 50–200 ppm Si (preferably 50ppm), and 900–1800 ppm O (preferably 1600ppm), and the decrease of corrosion resistance due to hydrogen absorption and difference of process is prevented by controlling the silicon content.

[0010] European Patent No. 195,155 disclosed a duplex cladding tube using a zirconium alloy, which contains 0.1–0.3% Sn, 0.05–0.2% Fe, 0.05–0.4% Nb, 0.03–0.1% Cr and/or Ni, where in Fe+Cr+Ni content should not exceed 0.25% and oxygen content is 300–1200 ppm. European Patent No. 46 8,093 or US Patent No. 5,080,861 disclosed a zirconium alloy containing 0–0.6% Nb, 0–0.2% Sb, 0–0.2% Te, 0.5–1.0% Sn, 0.18–0.24% Fe, 0.07–0.13% Cr, 900–2000 ppm O, 0–70 ppm Ni, and 0–200 ppm C to improve the corrosion resistance of alloy in high inflammation. It is reported that the size of precipitate is limited in 1200–1800 Å and up to 2% bismuth may be added instead of tellurium or antimony. European Patent No. 345,531 disclosed a similar composition of zirconium alloy to the above patent. The alloy is formed in the composition of 0–0.6% Nb, 0–0.1% Mo, 1.2–1.70% Sn, 0.07–0.24% Fe, 0.05–0.13% Cr, 0–0.08% Ni, and 900–1800 ppm O. European Patent No. 532,830 disclosed a zirconium alloy containing 0–0.6% Nb, 0.8–1.2% Sn, 0.2–0.5% Fe (preferably 0.35%), 0.1–0.4% Cr (preferably 0.25%), 50–200 ppm Si (preferably 100ppm), and 900–1800 ppm O (preferably 1600ppm) for the improvement of corrosion resistance, irradiation stability, mechanical strength and creep resistance of alloy. French Patent No. 2,624,136 disclosed a zirconium alloy by adding both Nb and V, which contains 0.1–0.35% Fe, 0.1–0.4% V, 0.05–0.3% O, 0–0.25% Sn, 0–0.25% Nb, and more than 0.5% V/Fe, and an optimum manufacturing method of alloy.

[0011] Japanese Patent No. 62,180,027 disclosed a zirconium alloy containing 1.7–2.5% Nb, 0.5–2.2% Sn, 0.04–1.0% Fe to improve the mechanical strength and nodular corrosion resistance of alloy, where Fe+Mo content is limited in 0.2–1.0%. Japanese Patent No. 2,213,437 disclosed niobium added alloys based on Zr-Sn-Fe-V alloy also to improve the nodular corrosion resistance, This patent suggested an alloy composite containing 0.25–1.5% Zr, 0.15–1.0% Nb, and Fe, and another alloy composite containing 0.25–1.5% Zr, 0.5–1.0% Nb, 0.05–0.15% Sn, and Ni. Japanese Patent No. 62,207,835 disclosed a ternary alloy containing 0.2–2.0% Zr, 0.5–3.0% Nb, 900–2500 ppm Sn, and O. Japanese Patent No. 62,297,449 disclosed an alloy containing 1–2.5% Nb, 0.5–2.0% Sn, 0.1–1.0% Mo, 1.5–2.5% Mo+Nb to improve corrosion resistance, ductility and strength, and a manufacturing method by solution heat-treatment in $\alpha+\beta$ or β -phase. Japanese Patent No. 62,180,027 disclosed an alloy having a similar composition of 1.7–2.5% Nb, 0.5–2.2% Sn, 0.04–1.0% Fe, 0.2–1.0% Mo, 0.2–1.0% Fe+Mo, where Fe is further added.

[0012] US Patent No. 4,863,685, No. 4,986,975, No. 5,024,809, and No. 5,026,516 disclosed zirconium alloys containing 0.5–2.0% Sn and about 0.5–1.0% other solute atoms. These alloys further contain 0.09–0.16% oxygen. The alloy in accordance with US Patent No. 4,863,685 contains tin and other solute atoms such as Mo, Te, mixture thereof, Nb-Te, or Nb-Mo. The alloy composite in accordance with US Patent No. 4,986,975 contains solute atoms such as Cu, Ni, and Fe, wherein the content of solute atoms is limited in the range of 0.24–0.40% and at least 0.05% Cu should be added. US Patent No. 5,024,809 and No. 5,026,516 added solute atoms such as Mo, Nb, and Te, wherein the content of solute atoms is limited in the range of 0.5–1.0% like US Patent No. 4,863,685 and 0.5–2.5% Bi or Bi+Sn is added.

[0013] US Patent No. 4,938,920 intended to develop an alloy with improved corrosion resistance by modifying conventional Zircaloy-4. This patent reduces Sn content to 0–0.8% and adds 0–0.3% V and 0–1% Nb, wherein Fe content is 0.2–0.8%, Cr content is 0–0.4%, and Fe+Cr+V content is limited in 0.25–1.0%. Additionally, oxygen content is 1000–1600 ppm. In a corrosion test of alloy having the composition of 0.8%Sn-0.22%Fe-0.11%Cr-0.14%O, 0.4%Nb-0.67%Fe-0.33%Cr-0.15%O, 0.75%Fe-0.25%V-0.1%O, or 0.25%Sn-0.2%Fe-0.15%V-0.1%O under the condition of 400°C for 200 days in steam atmosphere, the alloy showed an excellent corrosion resistance. The corrosion of alloy was about 60% to that of Zircaloy-4, and tensile strength of the alloy was similar to that of Zircaloy-4.

[0014] US Patent No. 4,963,323 or Japanese Patent No. 1,188,646 modified alloy composition of the conventional Zircaloy-4 in order to develop a nuclear cladding material having improved corrosion resistance. In these patents, Sn content is reduced, and Nb is added to compensate the strength loss due to the reduction of Sn, maintaining nitrogen

content below 60 ppm. The alloy has the composition of 0.2~1.15% Sn, 0.19~0.6% Fe (preferably 0.19~0.24%), 0.07~0.4% Cr (preferably 0.07~0.13%), 0.05~0.5% Nb, and less than 60 ppm N. Additionally, US Patent No. 5,017,336 controlled the alloy composition of Zircaloy-4 by adding Nb, Ta, V, and Mo, and suggested a zirconium alloy containing 0.2~0.9% Sn, 0.18~0.6% Fe, 0.07~0.4% Cr, 0.05~0.5% Nb, 0.01~0.2% Ta, 0.05~1% V, and 0.05~1% Mo. US Patent No. 5,196,163 or Japanese Patent No. 63,035,751 also modified alloy composition of the conventional Zircaloy-4 by adding Ta as well as Sn, Fe, and Cr, and by selectively adding Nb. The patent disclosed zirconium alloy containing 0.2~1.15% Sn, 0.19~0.6% Fe (preferably 0.19~0.24%), 0.07~0.4% Cr (preferably 0.07~0.13%), 0.01~0.2% Ta, 0.05~0.5% Nb, and less than 60 ppm N. French Patent No. 2,769,637 disclosed a similar composition of zirconium alloy to the above patents, containing 0.2~1.7% Sn, 0.18~0.6% Fe, 0.07~0.4% Cr, 0.05~1.0% Nb, and selectively 0.01~0.1% Ta or less than 60 ppm N. Additionally, this patent presented heat-treatment factors with regard to the composition.

[0015] US Patent No. 5,560,790 disclosed an alloy composite containing 0.5~1.5% Nb, 0.9~1.5% Sn, 0.3~0.6% Fe, 0.005~0.2% Cr, 0.005~0.04% C, 0.05~0.15% O, and 0.005~0.015% Si, wherein the distance between precipitates of $(Zr(Nb,Fe)_2)$, $Zr(Fe,Cr,Nb)$, $(Zr,Nb)_3Fe$ containing Sn or Fe is 0.20~0.40 μm , and the precipitate containing Fe is limited to 60% by volume of total precipitate.

[0016] Japanese Patent No. 5,214,500 suggested an alloy composite and size of precipitate in order to improve the corrosion resistance. The alloy composite contains 0.5~2.0% Sn, 0.05~0.3% Fe, 0.05~0.3% Cr, 0.05~0.15% Ni, 0.05~0.2% O, 0~1.2% Nb, and the balance Zr, wherein the average size of precipitate is limited to below 0.5 μm . Japanese Patent No. 8,086,954 suggested heat-treatment factors induced in the hot/cold-working of α -phase and disclosed a zirconium alloy composite containing 0.4~1.7% Sn, 0.25~0.75% Fe, 0.05~0.30% Cr, 0~0.10% Ni, and 0~1.0% Nb. Japanese Patent No. 8,114,688 suggested a duplex zirconium alloy having an inner layer of Sn-Fe-Cr-Ni containing 0.05~0.75% Nb and 0~0.02% Si, in order to reduce stress corrosion cracking at high temperature and the secondary damage due to hydrogen absorption. Japanese Patent No. 9,111,379 suggested a zirconium alloy containing 0.5~1.7% Sn, 0.1~0.3% Fe, 0.05~0.02% Cr, 0.05~0.2% Cu, 0.01~1.0% Nb, and 0.01~0.20% Ni to avoid nodular corrosion. Japanese Patent No. 10,273,746 suggested a zirconium alloy containing 0.3~0.7% Sn, 0.2~0.25% Fe, 0.1~0.15% Cr, and 0.05~0.20% Nb to improve the processability and corrosion resistance of alloy.

[0017] European Patent No. 198,570 limited the niobium content in 1~2.5% in a binary alloy formed of Zr-Nb, and suggested a heat-treatment temperature in a manufacturing process of alloy, wherein the second phase containing Nb should be uniformly distributed and the size of the second phase should be maintained below 800 Å. US Patent No. 5,125,985 suggested an alloy containing 0.07~0.28% of one or more elements selected from 0.5~2.0% Nb, 0.7~1.5% Sn, Fe, Ni, and Cr, and stated that the creep characteristic of material may be controlled by utilizing various manufacturing processes, where in one of the characteristics in manufacturing process is to utilize β -quenching heat-treatment as an intermediate process.

[0018] As described above, various researches on zirconium alloys such as Zircaloy-4 have been carried out. However, nuclear power plants are presently operated in a severe condition to increase the economical efficiency, and thereby a nuclear cladding tube manufactured with conventional alloy such as Zircaloy-4 reached the limit of use. Therefore, it is necessary to develop a new zirconium alloy having more excellent creep resistance.

[0019] During the research to develop a new zirconium alloy having more excellent creep resistance, the inventors found out that creep resistance can be improved by properly controlling the degree of recrystallization of alloy, and the present invention has been completed with the development of zirconium alloy having a new composition.

SUMMARY OF THE INVENTION

[0020] An object of the present invention is to provide a zirconium alloy having an excellent creep resistance, which has higher stability and economical efficiency than a conventional material, by minimizing creep deformation of cladding tube or reactor core structures during the operation of light or heavy water reactor in the nuclear power plant.

[0021] In order to achieve the above object, the present invention provides a zirconium alloy containing 0.8~1.8 wt.% niobium(Nb); 0.38~0.50 wt.% tin(Sn); one or more elements selected from 0.1~0.2 wt.% iron(Fe), 0.05~0.15 wt.% copper(Cu), and 0.12 wt.% chromium(Cr); 0.10~0.15 wt.% oxygen(O); 0.006~0.010 wt.% carbon(C); 0.006~0.010 wt.% silicon(Si); 0.0005~0.0020 wt.% sulfur(S); and the balance zirconium(Zr).

BRIEF DESCRIPTION OF THE DRAWINGS

[0022]

Fig. 1 is a graph showing the degree of recrystallization of zirconium alloy in accordance with an example embodiment of the present invention.

Fig. 2 is a graph showing creep deformation rate with regard to the degree of recrystallization of zirconium alloy in accordance with example embodiments of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0023] Hereinafter, the present invention will be described in more detail.

[0024] A zirconium alloy composite in accordance with the present invention preferably contains 0.8~1.8 wt.% niobium; 0.05~0.15 wt.% copper; 0.10~0.15 wt.% oxygen; 0.006~0.010 wt.% carbon; 0.006~0.010 wt.% silicon; 0.0005~0.0020 wt.% sulfur; and the balance zirconium.

[0025] Another zirconium alloy composite in accordance with the present invention contains 0.8~1.8 wt.% niobium; 0.38~0.50 wt.% tin; 0.10~0.15 wt.% oxygen; 0.006~0.010 wt.% carbon; 0.006~0.010 wt.% silicon; 0.0005~0.0020 wt.% sulfur; and the balance zirconium.

[0026] In the zirconium alloy composites in accordance with the present invention, the composites may further contain one or more elements selected from 0.1~0.2 wt.% iron, 0.05~0.15 wt.% copper, and 0.12 wt.% chromium, in addition to the composition of 0.8~1.8 wt.% niobium; 0.38~0.50 wt.% tin; 0.10~0.15 wt.% oxygen; 0.006~0.010 wt.% carbon; 0.006~0.010 wt.% silicon; 0.0005~0.0020 wt.% sulfur; and the balance zirconium. More preferably, one or more elements selected from 0.1~0.2 wt.% iron, 0.05~0.15 wt.% copper and 0.12 wt.% chromium may be contained.

[0027] A zirconium alloy having a very excellent creep resistance may be manufactured by use of the zirconium alloy composite with the degree of recrystallization maintained in the range of 40~70% by controlling final heat-treatment in vacuum, in accordance with the present invention

[0028] Hereinafter, the role of each element used in the alloy composite and the reason of limiting the content of element, in accordance with the present invention, will be described in detail.

[0029] Niobium(Nb) improves the corrosion resistance of zirconium alloy. However, in the case that solid solubility (about 0.3-0.6%) of niobium is used, the improvement of corrosion resistance may be obtained only when the composition and size of precipitate are properly controlled. It is known that mechanical characteristic of alloy is improved by high precipitation when niobium is added above the solid solubility. However, alloy performance becomes more sensitive to the condition of heat-treatment, in the case that a large amount of precipitate is formed. Therefore, it is preferable to limit the niobium content up to 1.8 wt.% and control in the range of 0.8~1.8 wt.%.

[0030] Tin(Sn) is known as a α -phase stabilizing element in the zirconium alloy, and improves mechanical strength by solution strengthening. However, it shows that corrosion of alloy is very rapidly accelerated in the environment of LiOH, if tin is not added at all. Accordingly, the present invention preferably controls the tin content in the range of 0.38~0.50 wt.% according to the content of niobium, where the content of tin does not give a great influence to the reduction of corrosion resistance.

[0031] Iron(Fe) is a major element added to the alloy to improve the corrosion resistance. The present invention preferably adds iron in the range of 0.05~0.2 wt.% and, more preferably, in 0.1~0.2 wt.%.

[0032] Chromium(Cr) is also a major element added to the alloy to improve the corrosion resistance like Fe. The present invention preferably adds chromium in the range of 0.05~0.2 wt.% and, more preferably, at 0.12 wt.%.

[0033] Copper(Cu) is also a major element added to the alloy to improve the corrosion resistance like iron and chromium, and has an excellent effect when added in a small amount. Accordingly, the present invention limits the content of copper in the range of 0.05~0.2 wt.% and, more preferably in the range of 0.05~0.15 wt.%.

[0034] Oxygen(O) contributes to the improvement of mechanical strength and creep resistance by solution strengthening. However, the present invention preferably controls the content of oxygen in the range of 1000-1500 ppm (0.1-0.15 wt.%), because a problem may occur when an excessive amount is added.

[0035] Carbon(C) and silicon(Si) reduce hydrogen absorption and delay transition time of corrosion speed. Additionally, these two elements are impurity elements having a relationship with the corrosion resistance, and are preferably added in the range of 60-100 ppm (0.006-0.010 wt.%).

[0036] Sulfur(S) is an impurity element contributing to the improvement of creep resistance without affecting corrosion characteristic when used below 30 ppm. When the sulfur is added more than 0.0020 wt.%, creep deformation is no more decreased. Accordingly, the present invention preferably controls the content of sulfur in the range of 6-20 ppm (0.0006-0.0020 wt.%) to improve the creep resistance.

[0037] The zirconium alloy having an excellent creep resistance in accordance with the present invention may be manufactured by controlling the degree of recrystallization of alloy in the range of 40-70%.

[0038] The zirconium alloy having an excellent creep resistance in accordance with the present invention may be manufactured by a conventional method in the field of invention, however, more preferably, the zirconium alloy is manufactured by final heat-treatment controlling the degree of recrystallization in the range of 40-70%, after β -heat-treatment and cold-working.

[0039] The manufacturing method of zirconium alloy composite in accordance with the present invention comprises the steps of: destroying structure of individual zirconium alloy ingots having the above composition by forging in β -phase; β -quenching which performs rapid cooling after solution heat-treatment in β -phase to homogenize the alloy composite, wherein the β -quenching process is performed to disperse precipitate uniformly in a metal matrix and to control the size of precipitate; hot-rolling the β -quenched material; heat-treating in vacuum between four times of cold-working; and final

heat-treating in vacuum by controlling the degree of recrystallization in the range of 40~70%. In order to improve the creep resistance, the final heat-treatment process is preferably performed at 470-570°C for 3-8 hours under monitoring of the degree of recrystallization of metal within the range of 40~70%.

[0040] The creep resistance of zirconium alloy in accordance with the present invention may be improved by controlling the degree of recrystallization of alloy in the range of 40-70%, and thereby the zirconium alloy composite has an excellent creep resistance. As described above, the safety and economical efficiency of zirconium alloy composite in accordance with the present invention may be much improved by minimizing the creep deformation, compared to a conventional material. Accordingly, the zirconium alloy composite in accordance with the present invention may be effectively used as a nuclear cladding tube, supporting lattice, and material for the structures of reactor core in the nuclear power plant utilizing light or heavy water reactor. Additionally, the safety of nuclear fuel rod may be secured in the reactor core operating in high inflammation and long-term period by using the zirconium alloy composite in accordance with the present invention as the above structural material.

[0041] Exemplary, non-limiting embodiments of the present invention will now be described more fully hereinafter. This invention may, however, be embodied in many different forms and should not be construed as limited to the exemplary embodiments set forth herein.

EXAMPLE 1~13: Manufacturing method of zirconium alloy

[0042] Four examples of alloy with niobium content from 0.8% to 1.8%:

- (1)Zr-0.8%Nb-0.07%Cu-0.14%O-0.008%C-0.008%Si-0.002%S;
- (2)Zr-1.1%Nb-0.07%Cu-0.14%O-0.008%C-0.008%Si-0.002%S;
- (3)Zr-1.5%Nb-0.07%Cu-0.14%O-0.008%C-0.008%Si-0.002%S; and
- (4)Zr-1.8%Nb-0.07%Cu-0.14%O-0.008%C-0.008%Si-0.002%S

[0043] Alloy of Zr-1.5%Nb-0.4%Sn:

- (5)Zr-1.5%Nb-0.4%Sn-0.14%O-0.008%C-0.008%Si-0.002%S

[0044] Four examples of alloy manufactured by adding one or more elements from Cu, Fe, and Cr to the above alloy containing Zr-1.5%Nb-0.4%Sn:

- (6)Zr-1.5%Nb-0.4%Sn-0.1%Cu-0.14%O-0.008%C-0.008%Si-0.002%S;
- (7)Zr-1.5%Nb-0.4%Sn-0.1%Fe-0.14%O-0.008%C-0.008%Si-0.002%S;
- (8)Zr-1.5%Nb-0.4%Sn-0.1%Cu-0.1%Fe-0.14%O-0.008%C-0.008%Si-0.002%S; and
- (9)Zr-1.5%Nb-0.4%Sn-0.2%Fe-0.1%Cr-0.14%O-0.008%C-0.008%Si-0.002%S

[0045] Four examples of alloy with S content from 0.0005% to 0.005%:

- (10)Zr-1.1%Nb-0.07%Cu-0.14%O-0.008%C-0.008%Si-0.0005%S;
- (11)Zr-1.1%Nb-0.07%Cu-0.14%O-0.008%C-0.008%Si-0.0010%S;
- (12)Zr-1.1%Nb-0.07%Cu-0.14%O-0.008%C-0.008%Si-0.0020%S; and
- (13)Zr-1.1%Nb-0.07%Cu-0.14%O-0.008%C-0.008%Si-0.0050%S

[0046] Compositions of the above 13 embodiments are arranged as the following table 1, where % indicates weight percent.

Table 1. Zirconium based alloy composites

Examples of alloy	Composition (wt.%)	Remarks
Example 1	Zr-0.8Nb-0.07Cu-0.14O-0.008C-0.008Si-0.002S	PRX
Example 2	Zr-1.1Nb-0.07Cu-0.14O-0.008C-0.008Si-0.002S	PRX
Example 3	Zr-1.5Nb-0.07Cu-0.14O-0.008C-0.008Si-0.002S	PRX
Example 4	Zr-1.8Nb-0.07Cu-0.14O-0.008C-0.008Si-0.002S	PRX
Example 5	Zr-1.5Nb-0.4Sn-0.14O-0.008C-0.008Si-0.002S	PRX
Example 6	Zr-1.5Nb-0.4Sn-0.1Cu-0.14O-0.008C-0.008Si-0.002S	PRX

(continued)

Examples of alloy	Composition (wt.%)	Remarks
Example 7	Zr-1.5Nb-0.4Sn-0.1Fe-0.140-0.008C-0.008Si-0.002S	PRX
Example 8	Zr-1.5Nb-0.4Sn-0.1Cu-0.1Fe-0.140-0.008C-0.008Si-0.002S	PRX
Example 9	Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr-0.140-0.008C-0.008Si-0.002S	PRX
Example 10	Zr-1.1Nb-0.07Cu-0.14O-0.008C-0.008Si-0.0005S	PRX
Example 11	Zr-1.1Nb-0.07Cu-0.14O-0.008C-0.008Si-0.0010S	PRX
Example 12	Zr-1.1Nb-0.07Cu-0.14O-0.008C-0.008Si-0.0020S	PRX
Example 13 Zircaloy-4	Zr-1.1Nb-0.07Cu-0.14O-0.008C-0.008Si-0.0050S Zr-1.38Sn-0.2Fe-0.1Cr-0.120	PRX

[0047] Ingots are manufactured by melting the zirconium having the above compositions, and then forged at 1000-1200°C in β -phase to destroy the ingot structure. Subsequently, solution heat treatment is performed at 1015-1075°C to distribute atoms of the alloy more uniformly, and rapid cooling is performed to obtain β -quenched structure (martensite). The β -quenched material is hot-rolled at 590 °C with the reduction rate of 70% followed by a first cold working with the reduction rate of 50%, and heat treatment in vacuum is performed at 570~580°C for 3 hours. The test pieces heat-treated in vacuum are processed through 3 times of cold working, wherein intermediate heat treatment between the cold working is performed at 570 °C for 2 hours. Subsequently, the test pieces of zirconium alloy in a substrate form are manufactured by final heat treatment at 510 °C for 3-8 hours. Additionally, the test pieces of examples 2, 3, 7, 8, and 9 in a substrate form are manufactured to evaluate the creep characteristic with regard to the degree of recrystallization controlled by the final heat treatment condition at intervals of 20°C from 470°C to 570°C.

[0048] The present invention controls the degree of recrystallization in the range of 40-70% by properly selecting the temperature and time of heat treatment. The degree of recrystallization is calculated by analyzing a number of microstructural photos (minimum 5 cuts) of metal matrix taken by transmission electron microscope with image analyzer, and by taking an average value.

[0049] The result is shown in Fig. 1, which shows the change of the degree of recrystallization according to the heat treatment temperature, when the temperature of final heat treatment is changed in the manufacturing process of zirconium alloy. It showed a trend that the degree of recrystallization increases along S-curve as the heat treatment temperature increases under the condition of heat treatment for a designated time.

EXPREIMENT 1: Analysis of chemical composition

[0050] Chemical composition is analyzed by collecting samples from 13 alloys in accordance with the embodiments of the present invention and a conventional Zircaloy-4. The result is shown in the following Table 2.

Table 2. Analysis of alloy composites in accordance with example embodiments of the present invention

	Chemical Composition, wt.%									
	Nb	Sn	Fe	Cu	Cr	O	C	Si	C	Zr
Example 1	0.82	-	-	0.068	-	0.139	0.0085	0.0082	0.0017	balance
Example 2	0.11			0.081		0.122	0.0077	0.0075	0.0022	
Example 3	1.49			0.072		0.133	0.0081	0.0083	0.0019	
Example 4	1.77			0.077		0.144	0.0090	0.0089	0.0021	
Example 5	1.47	0.45	-	-	-	0.133	0.0069	0.0079	0.0016	
Example 6	1.53	0.48		0.112		0.144	0.0090	0.0086	0.0018	
Example 7	1.50	0.44	0.12	-		0.129	0.0086	0.0092	0.0020	
Example 8	1.53	0.39	0.11	0.133		0.135	0.0081	0.0063	0.0019	
Example 9	1.49	0.42	0.19	-	0.12	0.147	0.0075	0.0081	0.0021	
Example 10	1.12			0.066	-	0.127	0.0077	0.0088	0.0006	

(continued)

	Chemical Composition, wt. %									
	Nb	Sn	Fe	Cu	Cr	O	C	Si	C	Zr
Example 11	1.13	-	-	0.073		0.139	0.0072	0.0091	0.0012	
Example 12	1.09			0.079		0.150	0.0079	0.0069	0.0019	
Example 13	1.08			0.062		0.143	0.0082	0.0078	0.0055	
Zircaloy-4	-	1.38	0.21	-	0.10	0.135	-	-	-	

[0051] As shown in Table 2, the analyzed values coincide with the nominal values shown in Table 1, which indicates that compositions of all the alloys are well controlled to meet the test purpose.

EXPREIMENT 2: Creep test with regard to the degree of recrystallization of zirconium alloy

[0052] In order to evaluate creep deformation of alloy manufactured by examples 2-3 and 7-9, creep tests have been carried out at 350 °C for 192 hours by loading the weight of 120MPa to the samples. The result is shown in Fig. 2.

[0053] The creep deformation has a tendency to decrease as the degree of recrystallization increases, and all the alloys having the degree of recrystallization of 40~70% showed minimum creep deformation. However, the creep deformation has an adverse tendency to increase, when the degree of recrystallization is out of the above range. This indicates that the creep characteristic of zirconium alloy has a close relationship with the potential distribution in a matrix structure. The resistance to creep deformation is most excellent when the degree of recrystallization is controlled in medium level of about 40~70%.

EXPREIMENT 3: Creep test with regard to the content of element in alloy

[0054] In order to evaluate the degree of recrystallization and creep deformation of 13 alloys manufactured by examples 1-13, creep tests have been carried out at 350°C both for 192 and 7200 hours by loading the weight of 120MPa to the samples. The result is shown in Fig. 3.

Table 3. Degree of recrystallization and creep deformation rate of alloy in accordance with example embodiments

	Degree of recrystallization %	Creep deformation rate, %	
		350□ /120MPa ×192 h	350□ /120MPa × 7200 h
Example 1	68	0.31	0.62
Example 2	60	0.26	0.53
Example 3	53	0.24	0.51
Example 4	42	0.22	0.48
Example 5	48	0.19	0.45
Example 6	50	0.17	0.43
Example 7	49	0.21	0.46
Example 8	46	0.18	0.45
Example 9	44	0.23	0.47
Example 10	62	0.55	0.82
Example 11	59	0.35	0.67
Example 12	59	0.27	0.54
Example 13	57	0.25	0.52
Zircaloy-4	8	0.72	1.12

[0055] As shown in Fig. 3, the creep deformation of alloys having the compositions in examples 1-4, where the niobium

content is changed in the range of 0.8~1.8 wt.%, showed low values of 0.22~0.31% and 0.48~0.62% respectively under the condition of 192 hours and 7200 hours, which are lower than that of commercial Zircaloy-4.

[0056] Additionally, Zr-1.5%Nb-0.4%Sn alloys having the compositions in accordance with example embodiments 5-9 showed excellent creep resistances due to addition of tin.

[0057] In order to find out an influence of added sulfur to the creep characteristic, the creep deformation of alloys having the compositions in accordance with example embodiments 10-13 has been evaluated. As shown in Table 3, the creep deformation has an apparent tendency to decrease as the addition of sulfur increases, and the creep deformation doesn't decrease any more when 0.002 wt.% sulfur is added. This indicates that the creep resistance is most effectively improved when sulfur is added in the range of 0.0006~0.0020 wt.%.

[0058] It is shown in Fig. 3 that all the alloys of example embodiments 1-13 have the degree of recrystallization in the range of 40~70%. It is also found out that the creep resistance is improved at least more than 160% compared to the conventional Zircaloy -4 when the degree of recrystallization is in the above range.

[0059] As described above, the zirconium alloy in accordance with the present invention has an excellent creep resistance by controlling the temperature and time of final heat -treatment to maintain the degree of recrystallization in 40-70%, and has a better creep resistance than Zircaloy-4 as a conventional and commercial nuclear cladding material. Additionally, the degree of recrystallization disclosed in the present invention may be applied to a manufacturing method of zirconium alloy having an excellent creep resistance, and will make a great contribution to the improvement of creep resistance. Accordingly, the zirconium alloy in accordance with the present invention will significantly improve the safety and economical efficiency by minimizing the creep deformation in high inflammation and long -term operation condition, and may effectively be used as a nuclear cladding tube, supporting lattice, and material for the structures of reactor core in the nuclear power plant utilizing light or heavy water reactor. The zirconium alloy in accordance with the present invention may replace Zircaloy-4 being used as a conventional nuclear cladding material.

Claims

1. A Zirconium based alloy composite comprising: 0.8~1.8 wt.% niobium ; 0.05~0.15 wt.% copper; 0.10~0.15 wt.% oxygen; 0.006~0.010 wt.% carbon; 0.006~0.010 wt.% silicon; 0.0005~0.0020 wt.% sulfur; and the balance zirconium.
2. A zirconium based alloy composite comprising: 0.8~1.8 wt.% niobium; 0.38~0.50 wt.% tin; 0.10~0.15 wt.% oxygen; 0.006~0.010 wt.% carbon; 0.006~0.010 wt.% silicon; 0.0005~0.0020 wt.% sulfur; and the balance zirconium.
3. The zirconium based alloy composite of claim 2, wherein the composite further includes one or more elements selected from 0.05~0.2 wt.% iron, 0.05~0.2 wt.% copper and 0.05~0.2 wt.% chromium.
4. The zirconium based alloy composite of claim 2, wherein the composite further includes one or more elements selected from 0.1~0.2 wt.% iron, 0.05~0.15 wt.% copper and 0.12 wt.% chromium.
5. The zirconium based alloy composite in any of claims 1 to 4 , wherein the degree of recrystallization of the zirconium alloy composite is controlled in the range of 40-70%.

FIGURE 1

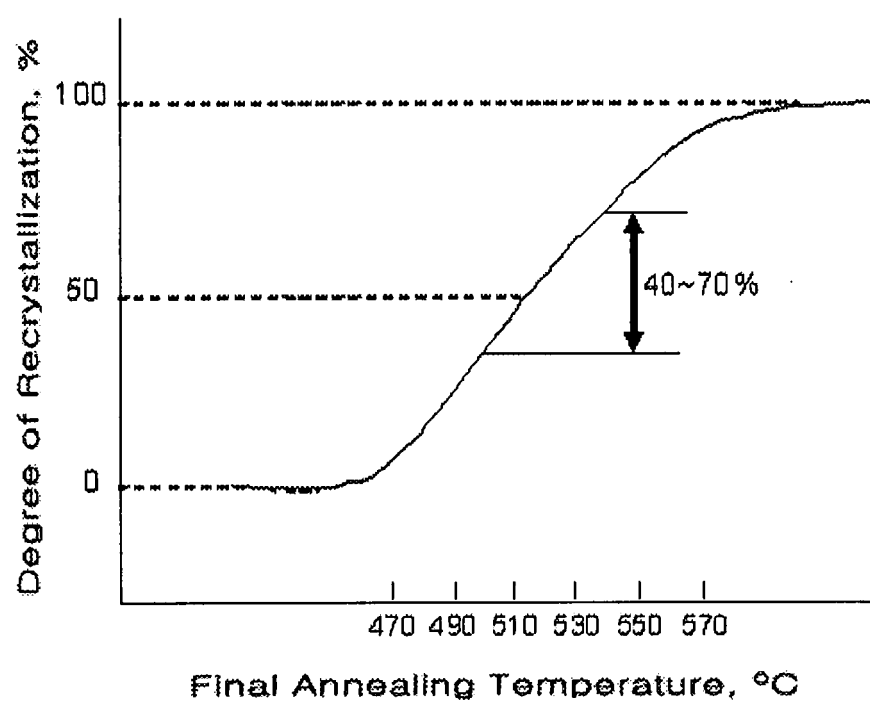
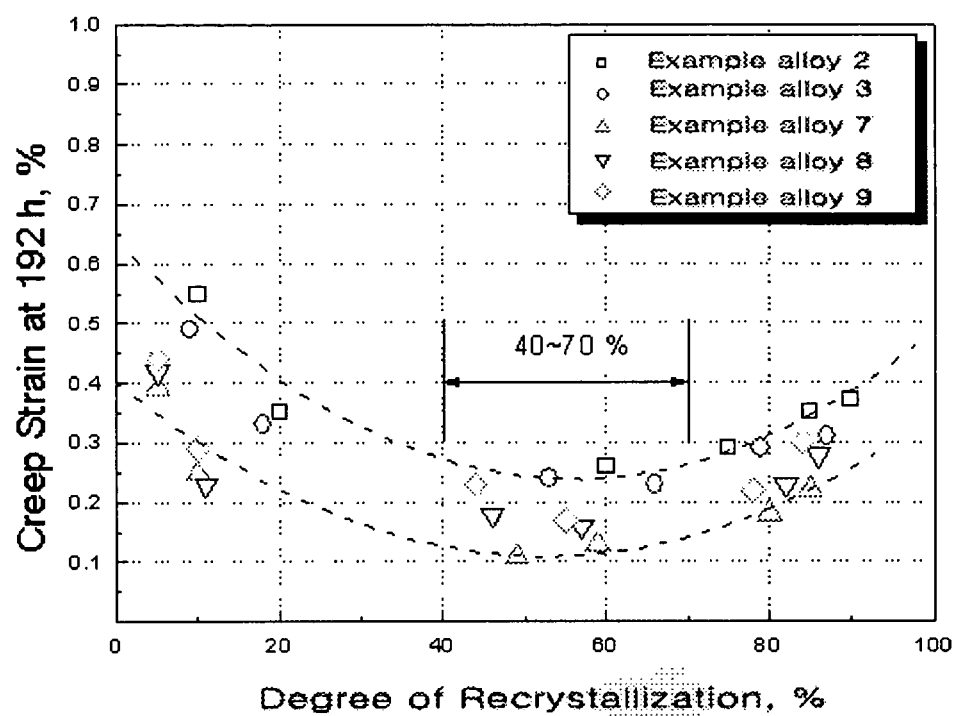


FIGURE 2





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