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(54) **ZIRCONIUM ALLOY HAVING EXCELLENT CORROSION RESISTANCE AND CREEP RESISTANCE, AND METHOD FOR MANUFACTURING SAME**

ZIRCONIUMLEGIERUNG MIT HERVORRAGENDER KORROSIONSBESTÄNDIGKEIT UND KRIECHFESTIGKEIT UND VERFAHREN ZUR HERSTELLUNG DAVON

ALLIAGE DE ZIRCONIUM AYANT D'EXCELLENTE RÉSISTANCE À LA CORROSION ET RÉSISTANCE AU FLUAGE ET PROCÉDÉ DE FABRICATION DE CE DERNIER

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(56) References cited:
CN-A- 103 409 661 CN-A- 103 589 910
JP-A- H04 224 648 JP-A- H08 253 828
KR-A- 20070 039 906 KR-A- 20120 126 205
KR-A- 20120 126 205 US-A1- 2012 145 287

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Description**Technical Field**

[0001] The present invention relates to a zirconium alloy having excellent corrosion resistance and creep resistance and a method of manufacturing the same and, more particularly, to a zirconium alloy composition and annealing conditions, suitable for use in nuclear fuel cladding tubes and spacer grids for light and heavy water reactor nuclear power plants.

Background Art

[0002] Zirconium alloys, having a low neutron absorption cross-section, superior corrosion resistance and mechanical properties, have been widely used for decades as materials for nuclear fuel cladding tubes, nuclear fuel assembly spacer grids, and internal structures in nuclear reactors.

[0003] Among the alloys, Zircaloy-2 (Sn: 1.20 to 1.70 wt%, Fe: 0.07 to 0.20 wt%, Cr: 0.05 to 1.15 wt%, Ni: 0.03 to 0.08 wt%, O: 900 to 1500 ppm, Zr: balance) and Zircaloy-4 (Sn: 1.20 to 1.70 wt%, Fe: 0.18 to 0.24 wt%, Cr: 0.07 to 1.13 wt%, O: 900 to 1500 ppm, Ni: <0.007 wt%, Zr: balance) are widely used in nuclear industry.

[0004] With the goal of reducing nuclear fuel cycle cost in order to improve the economic efficiency of reactors, high-burnup nuclear fuel is receiving increased consideration these days. Mechanical properties of conventional zircaloy, such as corrosion and creep properties in severe operating conditions may deteriorate.

[0005] Accordingly, the need for a material having high corrosion resistance and creep resistance, which are difficult to ensure under conditions of high burn-up and extended fuel cycles, has come to the fore, and thus research into appropriate zirconium alloys, such as Zr-Nb alloys, etc., is ongoing.

[0006] With regard to conventional techniques, U.S. Patent No. 4,649,023 discloses a zirconium alloy composed essentially of 0.5 to 2.0 wt% of Nb and 0.9 to 1.5 wt% of Sn, and including 0.09 to 0.11 wt% of any one selected from among Fe, Cr, Mo, V, Cu, Ni and W, and 0.1 to 0.16 wt% of O, and the balance of Zr. Also, there is disclosed a method of manufacturing a product in which precipitates having a small size of 80 nm or less are uniformly distributed in a matrix using the above alloy.

[0007] U.S. Patent No. 5,648,995 discloses a cladding tube using a zirconium alloy comprising 0.8 to 1.3 wt% of Nb, 50 to 250 ppm of Fe, 1600 ppm or less of O, and 120 ppm or less of Si.

[0008] This alloy is annealed at 600 to 800°C, extruded, and subjected to cold rolling four to five times. As such, intermediate annealing between the cold rolling processes is performed in the temperature range of 565 to 605°C for 2 to 4 hr, and final annealing is performed at 580°C, thereby manufacturing a nuclear fuel cladding tube.

[0009] As such, in order to increase creep resistance, the alloy composition is configured such that the amounts of Fe and O are limited to 250 ppm or less and 1000 to 1600 ppm, respectively.

[0010] U.S. Patent No. 6,325,966 discloses an alloy having superior corrosion resistance and mechanical properties, composed essentially of 0.15 to 0.25 wt% of Nb, 1.10 to 1.40 wt% of Sn, 0.35 to 0.45 wt% of Fe, and 0.15 to 0.25 wt% of Cr, and including 0.08 to 0.12 wt% of any one selected from among Mo, Cu, and Mn, 1000 to 1400 ppm of O, and the balance of Zr.

[0011] As is apparent from the above conventional techniques, research into high-burnup zirconium alloy compositions having improved corrosion resistance and mechanical properties is carried out by changing the kinds and amounts of added elements or changing the annealing conditions in conventional zirconium alloys in which Nb is added with Sn.

[0012] In this case, optimal conditions for ensuring superior corrosion resistance and mechanical properties of zirconium alloys are affected by the kinds and amounts of added elements, processing conditions, and annealing conditions, and thus the establishment of a suitable alloy design and annealing conditions is required above all.

[0013] Therefore, the present inventors have ascertained that an Zr-Nb alloy, from which Sn is removed and to which P, Ta and the like are added, and which is controlled in terms of composition and annealing temperatures, may improve creep resistance while significantly increasing corrosion resistance, thus culminating in the present invention.

[Citation List]

[Patent Literature]

[0014] U.S. Patent No. 4649023 (Registration Date: March 10, 1987)

[0015] U.S. Patent No. 5648995 (Registration Date: July 15, 1997)

[0016] U.S. Patent No. 6325966 (Registration Date: December 04, 2001)

[0017] US 2012/145287 A1 discloses a Zr alloy 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.

[0018] KR 2012/0126205 A discloses a Zr alloy with excellent mechanical property and corrosion resistance for a nuclear fuel cladding tube.

Disclosure

Technical Problem

[0019] Accordingly, the present invention has been made keeping in mind the problems encountered in the related art, and an object of the present invention is to provide a zirconium alloy composition and final annealing conditions, in which Sn, which negatively affects corrosion resistance, is removed and Nb, P, Ta and the like are added to maintain creep resistance, thus ensuring optimal annealing conditions while improving corrosion resistance and creep resistance.

Technical Solution

[0020] In order to accomplish the above object, the present invention provides a zirconium alloy, comprising: 1.1 to 1.2 wt% of Nb, 0.01 to 0.2 wt% of P, 0.2 to 0.3 wt% of Fe, optionally 0.01 to 0.15 wt% of Ta, and the balance of Zr.

[0021] Preferably, P is added in an amount of 0.02 to 0.07 wt%.

[0022] Preferably, the zirconium alloy also comprises 0.01 to 0.15 wt% of Ta in order to improve corrosion resistance and creep resistance.

[0023] More preferably, Ta is added in an amount of 0.03 to 0.1 wt%.

[0024] In addition, the present invention provides a method of manufacturing a zirconium alloy, comprising the steps of: (1) melting a mixture comprising 1.1 to 1.2 wt% of Nb, 0.01 to 0.2 wt% of P, 0.2 to 0.3 wt% of Fe, optionally 0.01 to 0.15 wt% of Ta, and the balance of Zr, thus preparing an ingot; (2) subjecting the ingot prepared in step (1) to solution heat treatment at 1,000 to 1,050°C (β -phase range) for 30 to 40 min and then to β -quenching using water; (3) preheating the ingot treated in step (2) at 630 to 650°C for 20 to 30 min and subjecting the ingot to hot rolling at a reduction ratio of 60 to 65%; (4) subjecting the material hot-rolled in step (3), to primary intermediate vacuum annealing at 570 to 590°C for 3 to 4 hr and then to primarily cold-rolled at a reduction ratio of 30 to 40%; (5) subjecting the material primarily cold-rolled in step (4), to secondary intermediate vacuum annealing at 560 to 580°C for 2 to 3 hr and then to secondarily cold-rolled at a reduction ratio of 50 to 60%; (6) subjecting the material secondarily cold-rolled in step (5), to tertiary intermediate vacuum annealing at 560 to 580°C for 2 to 3 hr and then to tertiarily cold-rolled at a reduction ratio of 30 to 40%; and (7) subjecting the material tertiarily cold-rolled in step (6), to final vacuum annealing at 440 to 650°C for 7 to 9 hr.

[0025] Preferably, in step (1), P is added in an amount of 0.02 to 0.07 wt%, and in step (7), the final vacuum annealing temperature is 460 to 600°C, thereby optimizing corrosion resistance and creep resistance.

[0026] Preferably, in step (1), the mixture also comprises 0.01 to 0.15 wt% of Ta, thereby further increasing corrosion resistance.

[0027] More preferably, Ta is added in an amount of 0.03 to 0.1 wt%, and in step (7), the final vacuum annealing temperature is 460 to 530°C, thereby maximizing corrosion resistance and creep resistance.

[0028] Preferably, P is compacted in order to prevent precipitation thereof before melting the mixture in step (1).

Advantageous Effects

[0029] According to the present invention, the zirconium alloy is configured such that Sn is completely removed and the kinds and amounts of added elements and final annealing conditions are controlled, thus exhibiting corrosion resistance superior to that of Zircaloy-4 and high creep resistance. Therefore, this zirconium alloy can be effectively utilized in nuclear fuel cladding tubes and the like inside reactor cores for light and heavy water reactor nuclear power plants.

Description of Drawings

[0030] 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 drawings, in which:

FIG. 1 is a graph illustrating the weight gain over time in corrosion testing of the zirconium alloy according to the present invention; and

FIG. 2 is a graph illustrating the creep strain in creep testing of the zirconium alloy according to the present invention.

Best Mode

[0031] As disclosed in embodiments of the present invention, specific structures or functional explanations are merely

set forth to illustrate exemplary embodiments according to the concept of the present invention. It will be understood that such exemplary embodiments are able to be variously modified, are not construed as limiting the present invention, and include all variations, equivalents and substitutions incorporated in the scope of the present invention.

[0032] Hereinafter, a detailed description will be given of the present invention.

[0033] The present invention addresses a zirconium alloy, comprising: 1.1 to 1.2 wt% of Nb, 0.02 to 0.05 wt% of P, 0.2 to 0.3 wt% of Fe, optionally 0.01 to 0.15 wt% of Ta, and the balance of Zr.

[0034] Also, the present invention addresses a zirconium alloy, comprising: 1.1 to 1.2 wt% of Nb, 0.02 wt% of P, 0.2 to 0.3 wt% of Fe, and the balance of Zr.

[0035] Also, the present invention addresses a zirconium alloy, comprising: 1.1 to 1.2 wt% of Nb, 0.05 wt% of P, 0.2 to 0.3 wt% of Fe, and the balance of Zr.

[0036] Further, the present invention addresses a zirconium alloy, comprising: 1.1 to 1.2 wt% of Nb, 0.05 wt% of P, 0.03 to 0.04 wt% of Ta, 0.2 to 0.3 wt% of Fe, and the balance of Zr.

[0037] Further, the present invention addresses a zirconium alloy, comprising: 1.1 to 1.2 wt% of Nb, 0.05 wt% of P, 0.09 to 0.1 wt% of Ta, 0.2 to 0.3 wt% of Fe, and the balance of Zr.

[0038] The preparation of the zirconium alloy having the above composition according to the present invention is described below.

[0039] The present invention also addresses the method of manufacturing the zirconium alloy as outlined in claim 5.

[0040] A better understanding of the present invention may be obtained through the following examples.

<Examples 1 to 12> Preparation of Zirconium Alloys

(1) Formation of Ingot

[0041] In step (1), 1.2 wt% of Nb, 0.02 to 0.05 wt% of P, 0.03 to 0.1 wt% of Ta, 0.2 wt% of Fe, and the balance of Zr were subjected to VAR (Vacuum Arc Remelting), thus forming an ingot.

[0042] The Zr that was used is zirconium sponge (Reactor Grade ASTM B349), and the added elements Nb, P, Ta, and Fe, have a high purity of 99.99% or more.

[0043] In order to prevent the segregation of impurities and the non-uniform distribution of the alloy composition, this process was repeated about three times, and the alloy was melted under the condition that the chamber for VAR was maintained at a vacuum level of 10^{-5} torr or less, thus forming an ingot. Unlike the other alloy elements, P was melted after being compacted, in order to prevent precipitation and segregation.

[0044] To prevent the surface of the sample from being oxidized during the cooling, cooling was carried out in an inert gas environment such as argon.

(2) β -Solution Heat Treatment and β -Quenching

[0045] In step (2) for β -solution heat treatment and β -quenching, solution heat treatment was performed for 30 min at 1,000 to 1,050°C, corresponding to the β -phase range, and then, water cooling at a rate of about 300°C/sec or more was performed. This process was performed to homogenize the alloy composition in the formed ingot and to uniformly distribute the size of SPP (Secondary Phase Particles) in the matrix.

[0046] To prevent oxidation of the ingot, the ingot was clad with a 1 mm thick stainless steel plate and was then spot welded.

(3) Annealing and Hot Rolling

[0047] In step (3), the β -quenched sample was subjected to hot rolling.

[0048] The sample was preheated at 630 to 650°C for about 20 to 30 min, and was then rolled at a reduction rate of about 60 to 65%. If the processing temperature falls out of the above range, it is difficult to obtain the rolled material suitable for use in subsequent step (4). Also, if the reduction rate of hot rolling is less than 60%, the texture of the zirconium material becomes non-uniform, which leads to undesirable deterioration in hydrogen embrittlement resistance. On the other hand, if the reduction rate is higher than 80%, subsequent processability may become problematic.

[0049] The material hot-rolled was treated as follows: the clad stainless steel plate was removed, an oxide film and impurities were removed using a pickling solution comprising water, nitric acid and hydrofluoric acid at a volume ratio of 50:40:10, and the remaining oxide film was completely removed using a wire brush in order to facilitate subsequent processing.

(4) Primary Intermediate Annealing and Primary Cold Rolling

[0050] In order to remove residual stress after hot rolling and prevent damage to the sample upon primary cold processing, primary vacuum annealing was performed under the condition that a vacuum level was maintained at 10^{-5} torr or less at about 580 to 590°C for about 3 to 4 hr.

[0051] Preferably, the intermediate vacuum annealing is carried out at a temperature elevated to a fully recrystallization annealing temperature. If the temperature falls out of the above range, corrosion resistance may deteriorate.

[0052] After completion of the primary intermediate vacuum annealing, the rolled material was subjected to primary cold rolling at a reduction ratio of about 40 to 50% at an interval of about 0.3 mm for each pass.

(5) Secondary Intermediate Vacuum Annealing and Secondary Cold Rolling

[0053] After completion of the primary cold rolling, the rolled material was subjected to secondary intermediate vacuum annealing at 570 to 580°C for about 2 to 3 hr.

[0054] If the intermediate annealing temperature falls out of the above range, corrosion resistance may deteriorate.

[0055] After completion of the secondary intermediate vacuum annealing, the rolled material was subjected to secondary cold rolling at a reduction ratio of about 50 to 60% at an interval of about 0.3 mm for each pass.

(6) Tertiary Intermediate Vacuum Annealing and Tertiary Cold Rolling

[0056] After completion of the secondary cold rolling, the rolled material was subjected to tertiary intermediate vacuum annealing at 570 to 580°C for 2 to 3 hr.

[0057] If the intermediate annealing temperature falls out of the above range, corrosion resistance may deteriorate.

[0058] After completion of the tertiary intermediate vacuum annealing, the rolled material was subjected to tertiary cold rolling at a reduction ratio of about 30 to 40% at an interval of about 0.3 mm for each pass.

(7) Final Vacuum Annealing

[0059] After completion of the tertiary cold rolling, the rolled material was finally annealed in a high vacuum of 10^{-5} torr or less.

[0060] Final annealing was performed at 460 to 580°C for 8 hr.

[0061] The specific alloy compositions of the zirconium alloys according to the present invention and the final annealing temperatures are summarized in Table 1 below.

[Table 1]

	Chemical Composition (wt%)							Final Annealing Temp. (°C)
	Nb	Sn	P	Fe	Ta	Cr	Zr	
Ex. 1	1.2	-	0.02	0.2	-	-	Balance	460
Ex. 2	1.2	-	0.05	0.2	-	-	Balance	460
Ex. 3	1.2	-	0.05	0.2	0.03	-	Balance	460
Ex. 4	1.2	-	0.05	0.2	0.1	-	Balance	460
Ex. 5	1.2	-	0.02	0.2	-	-	Balance	520
Ex. 6	1.2	-	0.05	0.2	-	-	Balance	520
Ex. 7	1.2	-	0.05	0.2	0.03	-	Balance	520
Ex. 8	1.2	-	0.05	0.2	0.1	-	Balance	520
Ex. 9	1.2	-	0.02	0.2	-	-	Balance	580
Ex. 10	1.2		0.05	0.2	-			580
Ex. 11	1.2	-	0.05	0.2	0.03	-	Balance	580
Ex. 12	1.2	-	0.05	0.2	0.1	-	Balance	580
C.Ex. 1 Zircaloy-4	-	1.5	-	0.2	-	0.1	Balance	Commercially available

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(continued)

	Chemical Composition (wt%)							Final Annealing Temp. (°C)
	Nb	Sn	P	Fe	Ta	Cr	Zr	
C.Ex. 2 Zircaloy-4	-	1.5	-	0.2	-	0.1	Balance	460

<Comparative Example 1>

[0062] As a commercially available zirconium alloy for use in nuclear power plants, Zircaloy-4 was used.

<Test Example 1> Corrosion Resistance Testing

[0063] In order to evaluate the corrosion resistance of the zirconium alloy composition according to the present invention, corrosion testing was performed as follows.

[0064] Each of the zirconium alloys of Examples 1 to 12 was manufactured into a sheets through the above manufacturing process, which was then fabricated a corrosion test sample having a size of 20 mm x 20 mm x 1.0 mm, followed by stepwise mechanical polishing using #400 to #1200 SiC abrasive paper.

[0065] After completion of the surface polishing, the sample was pickled using a solution comprising water, nitric acid and hydrofluoric acid at a volume ratio of 50:40:10, sonicated with acetone, and then completely dried in an oven for 24 hr or longer.

[0066] In order to determine the extent of corrosion of the alloy, the surface area and the initial weight of the alloy were measured before the alloy was loaded into an autoclave.

[0067] The loaded sample was subjected to corrosion testing for 260 days using a static autoclave at 360°C in an 18.6 MPa pure water atmosphere.

[0068] In the corrosion testing, the samples of Examples 1 to 12 and the commercially available Zircaloy-4 of Comparative Example 1 were placed in the autoclave together.

[0069] The samples were taken out a total of eight times during the 260 days subsequent to the corrosion testing, and the weight gains were measured, after which the weight gains were calculated in order to quantitatively evaluate the extent of corrosion. The results are shown in the following tables.

[0070] The corrosion testing results were evaluated depending on 1) when P was added in amounts of 0.02 wt% and 0.05 wt% in the absence of Ta, and 2) when Ta was added in amounts of 0.03 wt% and 0.1 wt% in the presence of 0.05 wt% of P. As such, both 1) and 2) were tested at all of three final annealing temperatures of 460°C, 520°C and 580°C.

1) Results of Addition of 0.02 wt% and 0.05 wt% of P in the absence of Ta

[0071]

[Table 2]

	Weight Gain (mg/dm ²) per Unit Surface Area			
	360°C, 18.6 MPa, Pure Water			
	50 days	110 days	170 days	260 days
Ex. 1 (P 0.02 wt%)	18.1	26.6	28.4	33.5
Ex. 2 (P 0.05 wt%)	17.5	27.0	32.9	37.6
Ex. 5 (P 0.02 wt%)	19.3	26.0	28.1	33.2
Ex. 6 (P 0.05 wt%)	16.1	23.8	25.2	28.7
Ex. 9 (P 0.02 wt%)	19.5	27.7	30.4	34.6
Ex. 10 (P 0.05 wt%)	14.9	20.2	25.6	31.1
C.Ex. 1	26.3	46.1	58.2	84.1

[0072] As is apparent from Table 2, the difference in corrosion resistance was notable between Comparative Example 1 without P and Example 1 in which 0.02 wt% of P was added and the final annealing temperature was 460°C. In particular, corrosion resistance was higher in Examples 2, 6 and 10 using 0.05 wt% of P than in Examples 1, 5 and 9

using 0.02 wt% of P.

[0073] Thus, since there is a significant corrosion resistance difference so long as P is added even in a small amount, corrosion resistance is considered to be obviously increased even when the lower limit of the amount of P is 0.01 wt%, judging from Example 1 using 0.02 wt% of P.

[0074] As such, a drastic increase in corrosion resistance can be seen to be dependent on the experimental values ranging from 0.02 wt% to 0.07 wt%. Although the amount of P is 0.05 wt% in Examples 2, 6 and 10, corrosion resistance is observed to be increased more in the presence of 0.05 wt% of P than in the presence of 0.02 wt% of P. Hence, a notable increase in corrosion resistance is deemed to be assured even when the amount of P is 0.07 wt%.

[0075] 2) Results of Addition of 0.03 wt% and 0.1 wt% of Ta in the presence of 0.05 wt% of P

[Table 3]

	Weight Gain (mg/dm ²) per Unit Surface Area			
	360°C, 18.6 MPa, Pure Water			
	50 days	110 days	170 days	260 days
Ex. 2	17.5	27.0	32.9	37.6
Ex. 3(Ta 0.03 wt%)	17.1	26.7	29.0	32.5
Ex. 4(Ta 0.1 wt%)	14.8	23.7	26.9	32.3
Ex. 6	16.1	23.8	25.2	28.7
Ex. 7(Ta 0.03 wt%)	15.7	23.9	26.4	29.1
Ex. 8(Ta 0.1 wt%)	12.2	20.4	22.7	28.9
Ex. 10	14.9	20.2	25.6	31.1
Ex. 11(Ta 0.03 wt%)	18.2	27.2	27.3	30.8
Ex. 12(Ta 0.1 wt%)	15.5	25.6	27.4	33.2
C.Ex. 1	26.3	46.1	58.2	84.1

[0076] As is apparent from Table 3, only P was added, without Ta, in Examples 2, 6 and 10, 0.03 wt% of Ta was added in Examples 3, 7 and 11, and 0.1 wt% of Ta was added in Examples 4, 8 and 12.

[0077] When the amount of Ta was 0.1 wt%, corrosion resistance was significantly increased in Example 4 at a final annealing temperature of 460°C and Example 8 at a final annealing temperature of 520°C. When the amount of Ta was 0.03 wt%, corrosion resistance was insignificantly increased.

[0078] Based on the test results, corrosion resistance was increased when Ta was added in an amount of 0.01 wt% to 0.15 wt%, and was remarkably increased when Ta was added in an amount of 0.03 wt% to 0.1 wt%.

<Test Example 2> Creep testing

[0079] In order to evaluate the creep resistance of the zirconium alloy composition according to the present invention, creep testing was performed as follows.

[0080] Each of the zirconium alloys of Examples 1 to 4 was manufactured into a sheets through the above manufacturing process, which was then formed into a creep test sample.

[0081] To compare creep properties, a Zircaloy-4 sheet sample of Comparative Example 2 was manufactured through the same process by simulating the commercially available cladding tube of Comparative Example 1. The final annealing temperature of Comparative Example 2 was set to 460°C, as in Examples 1 to 4 and Comparative Example 1, and creep testing was carried out.

[0082] The creep testing was performed at 350°C under a predetermined load of 120 MPa for 120 hr, and the results thereof were compared with those of Comparative Example 2. The results are shown in Table 4 below.

[Table 4]

	Creep Strain (%)
	350°C, 120 MPa, 240 hr
Ex. 1	0.30

(continued)

	Creep Strain (%)
	350°C, 120 MPa, 240 hr
Ex. 2	0.33
Ex. 3	0.34
Ex. 4	0.22
C.Ex. 2	0.46

[0083] As is apparent from Table 4, based on the results of creep testing for 10 days at 350°C under stress of 120 MPa using the zirconium alloy compositions in Examples 1 to 4 according to the present invention, creep strain was measured to be 0.22 to 0.34. In particular, as the amount of Ta was increased, creep strain was remarkably decreased. However, creep strain of Comparative Example 2 was 0.46, which was evaluated to be much higher than in Examples 1 to 4. Therefore, it can be confirmed that the addition of P in even a small amount is effective at exhibiting creep resistance and also that creep resistance is considerably enhanced with an increase in the amount of Ta.

[0084] 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 of the invention as disclosed in the accompanying claims.

Claims

1. A zirconium alloy, comprising:

1.1 to 1.2 wt% of Nb,
0.01 to 0.2 wt% of P,
0.2 to 0.3 wt% of Fe,
optionally 0.01 to 0.15 wt% of Ta,
and a balance of Zr.

2. The zirconium alloy of claim 1, wherein P is added in an amount of 0.02 to 0.07 wt%.

3. The zirconium alloy of claim 1, wherein Ta is added in an amount 0.01 to 0.15 wt% of Ta.

4. The zirconium alloy of claim 3, wherein Ta is added in an amount of 0.03 to 0.1 wt%.

5. A method of manufacturing a zirconium alloy, comprising steps of:

- (1) melting a mixture comprising 1.1 to 1.2 wt% of Nb, 0.01 to 0.2 wt% of P, 0.2 to 0.3 wt% of Fe, optionally 0.01 to 0.15 wt% of Ta, and a balance of Zr, thus preparing an ingot;
- (2) subjecting the ingot prepared in step (1) to solution heat treatment at 1,000 to 1,050°C (β -phase range) for 30 to 40 min and then to β -quenching using water;
- (3) preheating the ingot treated in step (2) at 630 to 650°C for 20 to 30 min and subjecting the ingot to hot rolling at a reduction ratio of 60 to 65%;
- (4) subjecting the material hot-rolled in step (3), to primary intermediate vacuum annealing at 570 to 590°C for 3 to 4 hr and then to primarily cold-rolled at a reduction ratio of 30 to 40%;
- (5) subjecting the material primarily cold-rolled in step (4), to secondary intermediate vacuum annealing at 560 to 580°C for 2 to 3 hr and then to secondarily cold-rolled at a reduction ratio of 50 to 60%;
- (6) subjecting the material secondarily cold-rolled in step (5), to tertiary intermediate vacuum annealing at 560 to 580°C for 2 to 3 hr and then to tertiarily cold-rolled at a reduction ratio of 30 to 40%; and
- (7) subjecting the material tertiarily cold-rolled in step (6), to final vacuum annealing at 440 to 650°C for 7 to 9 hr.

6. The method of claim 5, wherein in step (1), P is added in an amount of 0.02 to 0.07 wt%, and in step (7), the final vacuum annealing temperature is 460 to 600°C.

7. The method of claim 5, wherein in step (1), the mixture comprises 0.01 to 0.15 wt% of Ta.
8. The method of claim 7, wherein Ta is added in an amount of 0.03 to 0.1 wt%, and in step (7), the final vacuum annealing temperature is 460 to 530°C.
9. The method of any one of claims 5 to 8, wherein P is compacted before melting the mixture in step (1).

Patentansprüche

1. Zirkoniumlegierung, umfassend:

1,1 bis 1,2 Gew.% Nb,
0,01 bis 0,2 Gew.% P,
0,2 bis 0,3 Gew.% Fe,
gegebenenfalls 0,01 bis 0,15 Gew.% Ta, und
Zr als restlichen Bestandteil.

2. Zirkoniumlegierung nach Anspruch 1, wobei P in einer Menge von 0,02 bis 0,07 Gew.% zugegeben wird.

3. Zirkoniumlegierung nach Anspruch 1, wobei Ta in einer Menge von 0,01 bis 0,15 Gew.% Ta zugegeben wird.

4. Zirkoniumlegierung nach Anspruch 3, wobei Ta in einer Menge von 0,03 bis 0,1 Gew.% zugegeben wird.

5. Verfahren zum Fertigen einer Zirkoniumlegierung, umfassend die Schritte:

(1) Schmelzen einer Mischung, die 1,1 bis 1,2 Gew.% Nb, 0,01 bis 0,2 Gew.% P, 0,2 bis 0,3 Gew.% Fe, gegebenenfalls 0,01 bis 0,15 Gew.% Ta, und Zr als restlichen Bestandteil umfasst, wodurch ein Barren hergestellt wird;
(2) Unterziehen des in Schritt (1) hergestellten Barrens einer Lösungswärmebehandlung bei 1.000 bis 1.050 °C (β -Phasenbereich) für 30 bis 40 Minuten und dann β -Quenchen unter Verwendung von Wasser;
(3) Vorheizen des in Schritt (2) behandelten Barrens auf 630 bis 650 °C für 20 bis 30 Minuten, und Unterziehen des Barrens Heißwalzen mit einem Reduktionsverhältnis von 60 bis 65 %;
(4) Unterziehen des in Schritt (3) heißgewalzten Materials primärem Zwischenglühen im Vakuum bei 570 bis 590 °C für 3 bis 4 Stunden und dann primärem Kaltwalzen mit einem Reduktionsverhältnis von 30 bis 40 %;
(5) Unterziehen des in Schritt (4) primär heißgewalzten Materials sekundärem Zwischenglühen im Vakuum bei 560 bis 580 °C für 2 bis 3 Stunden und dann sekundärem Kaltwalzen mit einem Reduktionsverhältnis von 50 bis 60 %;
(6) Unterziehen des in Schritt (5) sekundär kaltgewalzten Materials tertiärem Zwischenglühen im Vakuum bei 560 bis 580 °C für 2 bis 3 Stunden und dann tertiärem Kaltwalzen mit einem Reduktionsverhältnis von 30 bis 40 %; und
(7) Unterziehen des in Schritt (6) tertiär kaltgewalzten Materials letztem Glühen im Vakuum bei 440 bis 650 °C für 7 bis 9 Stunden.

6. Verfahren nach Anspruch 5, wobei in Schritt (1) P in einer Menge von 0,02 bis 0,07 Gew.% zugegeben wird und in Schritt (7) die letzte Glühtemperatur im Vakuum 460 bis 600 °C beträgt.

7. Verfahren nach Anspruch 5, wobei in Schritt (1) die Mischung 0,01 bis 0,15 Gew.% Ta umfasst.

8. Verfahren nach Anspruch 7, wobei Ta in einer Menge von 0,03 bis 0,1 Gew.% zugegeben wird und in Schritt (7) die letzte Glühtemperatur im Vakuum 460 bis 530 °C beträgt.

9. Verfahren nach einem der Ansprüche 5 bis 8, wobei P verdichtet wird, bevor die Mischung in Schritt (1) geschmolzen wird.

Revendications

1. Alliage de zirconium, comprenant :

1,1 à 1,2 % en poids de Nb,
0,01 à 0,2 % en poids de P,
0,2 à 0,3 % en poids de Fe,
éventuellement 0,01 à 0,15 % en poids de Ta,
et le reste étant du Zr.

2. Alliage de zirconium selon la revendication 1, P étant ajouté en une quantité de 0,02 à 0,07 % en poids.

3. Alliage de zirconium selon la revendication 1, Ta étant ajouté en une quantité de 0,01 à 0,15 % en poids de Ta.

4. Alliage de zirconium selon la revendication 3, Ta étant ajouté en une quantité de 0,03 à 0,1 % en poids.

5. Procédé de fabrication d'un alliage de zirconium, comprenant les étapes de :

(1) fusion d'un mélange comprenant 1,1 à 1,2 % en poids de Nb, 0,01 à 0,2 % en poids de P, 0,2 à 0,3 % en poids de Fe, éventuellement 0,01 à 0,15 % en poids de Ta, et le reste étant du Zr, préparant ainsi un lingot ;
(2) soumission du lingot préparé dans l'étape (1) à un traitement thermique par solution à une température de 1 000 à 1 050 °C (plage de la phase β) pendant 30 à 40 min et ensuite à une trempe β à l'aide d'eau ;
(3) préchauffage du lingot traité dans l'étape (2) à une température de 630 à 650 °C pendant 20 à 30 min et soumission du lingot à laminage à chaud à un rapport de réduction de 60 à 65 % ;
(4) soumission du matériau laminé à chaud dans l'étape (3), à un recuit sous vide intermédiaire primaire à une température de 570 à 590 °C pendant 3 à 4 h et ensuite à un laminage à froid de manière primaire à un rapport de réduction de 30 à 40 % ;
(5) soumission du matériau laminé à froid de manière primaire dans l'étape (4), à un recuit sous vide intermédiaire secondaire à une température de 560 à 580 °C pendant 2 à 3 h et ensuite un laminage à froid de manière secondaire à un rapport de réduction de 50 à 60 % ;
(6) soumission du matériau laminé à froid de manière secondaire dans l'étape (5), à un recuit sous vide intermédiaire tertiaire à une température de 560 à 580 °C pendant 2 à 3 h et ensuite un laminage à froid de manière tertiaire à un rapport de réduction de 30 à 40 % ; et
(7) soumission du matériau laminé à froid de manière tertiaire dans l'étape (6), à un recuit sous vide final à une température de 440 à 650 °C pendant 7 à 9 h.

6. Procédé selon la revendication 5, dans l'étape (1), P étant ajouté en une quantité de 0,02 à 0,07 % en poids, et dans l'étape (7), la température du recuit sous vide final étant de 460 à 600 °C.

7. Procédé selon la revendication 5, dans l'étape (1), le mélange comprenant 0,01 à 0,15 % en poids de Ta.

8. Procédé selon la revendication 7, Ta étant ajouté en une quantité de 0,03 à 0,1 % en poids, et dans l'étape (7), la température du recuit sous vide final étant de 460 à 530 °C.

9. Procédé selon l'une quelconque des revendications 5 à 8, P étant compacté avant la fusion du mélange dans l'étape (1).

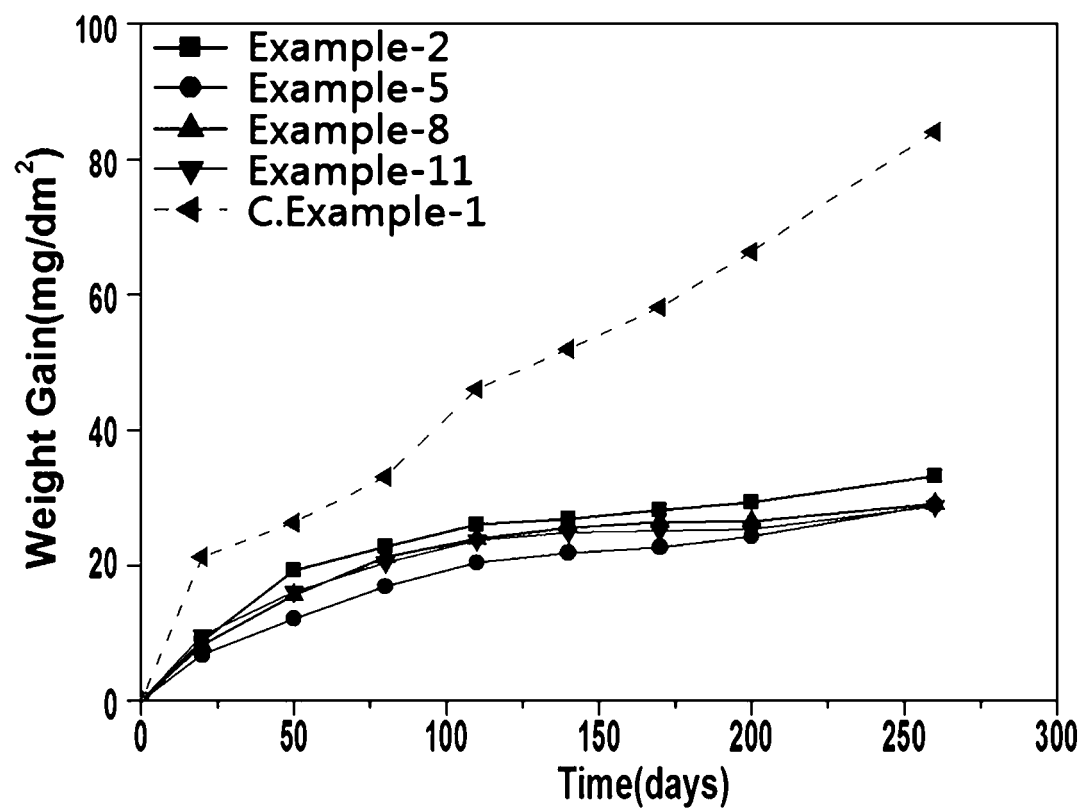


FIG. 1

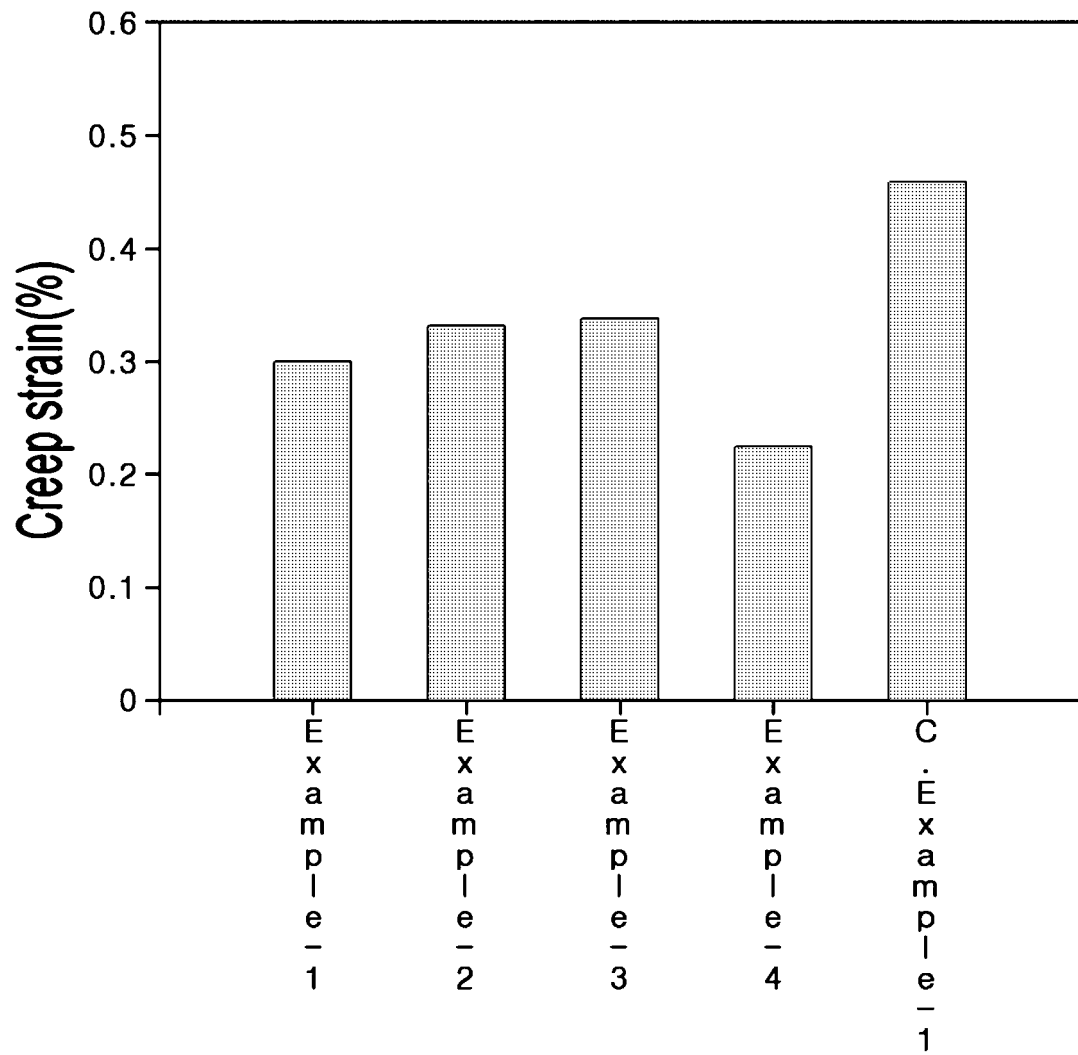


FIG. 2

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 4649023 A [0006] [0014]
- US 5648995 A [0007] [0015]
- US 6325966 B [0010] [0016]
- US 2012145287 A1 [0017]
- KR 20120126205 A [0018]