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METHOD OF IMPARTING CORROSION RESISTANCE TO ZIRCONIUM BASE ALLOYS

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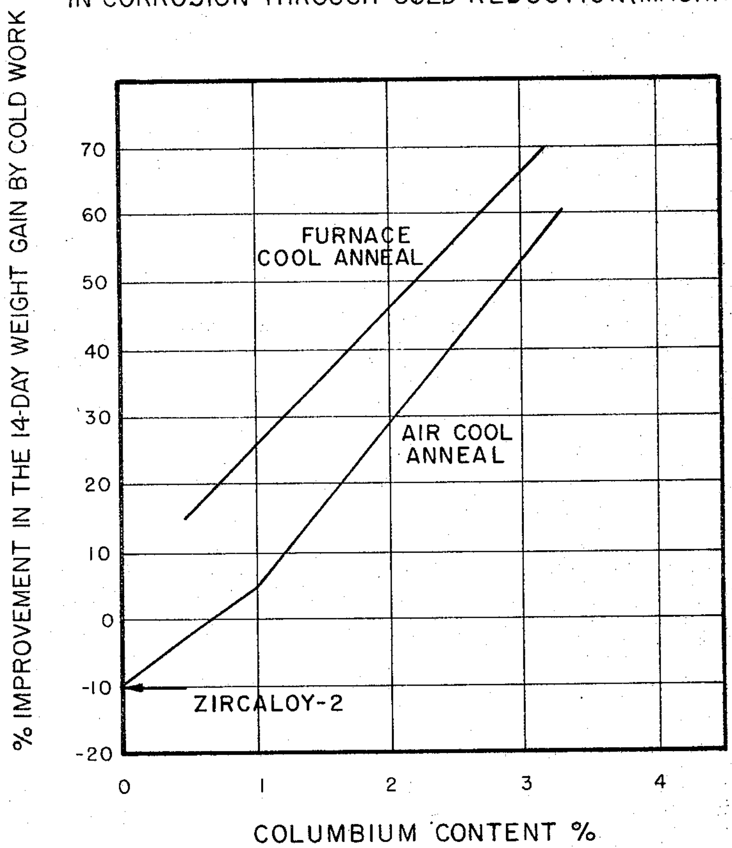
EFFECT OF COLUMBIUM CONTENT ON THE IMPROVEMENT IN CORROSION THROUGH COLD REDUCTION(MACHINING)



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METHOD OF IMPARTING CORROSION RESISTANCE TO ZIRCONIUM BASE ALLOYS

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This application is a continuation-in-part of Serial No. 75,931, filed December 15, 1960, now abandoned.

The invention relates to zirconium base alloys and more particularly to a method or procedure for treating zirconium base alloys having low resistance to corrosion to impart substantially increased corrosion resistance to such alloys.

There is an existing and unsatisfied need for wrought zirconium base alloy products having a combination of high strength and high corrosion resistance for the fabrication of equipment used in nuclear reactor devices such as nuclear steam generator power plant equipment.

One commercial zirconium alloy containing 1.5% tin, 0.10% chromium, 0.05% nickel, 0.12% iron, and a maximum of 60 p.p.m. nitrogen, sometimes known as "Zircaloy-2," has been used somewhat extensively because of its low corrosion rate at elevated temperatures when in the presence of water or steam. The corrosion rate of this alloy, that is, its weight gain during corrosion, is about 37 mg./dm.^{2} in 750° F.–1500 p.s.i.g. steam for 14 days, as compared with a corrosion rate for unalloyed zirconium under the same test conditions of about 31 mg./dm.^{2}. However, the strength of Zircaloy-2 at elevated temperatures (18,000 p.s.i. yield strength at 900° F.) leaves much to be desired.

The unsatisfied need for wrought zirconium base alloy products requires a minimum 35,000 p.s.i. yield strength at 0.2% offset at 900° F. with 10% minimum room temperature tensile elongation in 2 inches, not possessed by Zircaloy-2, combined with a corrosion rate comparable to that of Zircaloy-2; or requires wrought zirconium base alloy products having at least 50% greater strengths than the strengths of Zircaloy-2 at all temperatures accompanied by a comparable corrosion rate.

A number of zirconium base alloys have been developed which satisfy the indicated high strength requirements, but each has a much higher corrosion rate or a much poorer corrosion resistance than required to satisfy the need.

The usual practice for making say ⅝" hot rolled zirconium base alloy bars involves annealing hot rolled bars and then shot-blasting, pickling and straightening the bars. Similarly, hot rolled zirconium base alloy sheet, plate and strip products are usually hot rolled, then annealed and air cooled, then sand-blasted and pickled. Cold rolled zirconium base alloy sheet material normally is fabricated from hot rolled sheets produced in the manner described, the hot rolled sheets then being cold rolled to finished gauge, scrubbed, annealed, sand-blasted, pickled, slit to width, cut to finished length, leveled, inspected, tested and shipped.

All of the indicated procedures thus involve a usual pickling operation as a final metal treatment step following any annealing treatment.

In searching for wrought zirconium base alloy products combining high corrosion resistance and high strength at various temperatures and particularly at elevated temperatures, we observed that a peculiar film was present on the surfaces of some of the wrought products after the described final pickling operation in the manufacture of hot rolled bar and sheet products and cold rolled sheet products, when normal pickling solutions were used.

Although later established to be incorrect, initially it was believed that this peculiar film present on the surfaces of the finished products was the cause of the high corrosion rate characterizing wrought zirconium base alloy products investigated that had strengths high enough to satisfy the existing need.

We then unexpectedly discovered that the intolerable high corrosion rate of the investigated zirconium base alloys that did have the required high strengths could be reduced to a corrosion rate low enough to satisfy the requirements by introducing cold work into the material. Cold work as defined and as used throughout this specification and claims means the "permanent strain produced by an external force in a metal below its recrystallization temperature." Several examples of cold working operations are cold extrusion, machining, cold rolling, drawing, coining, shot blasting, peening, rocking and grinding. The terms "machined" and "machining" mean to plane, shape, turn, mill, etc., by a machine or machines.

Further investigation established that when material having a high or unacceptable corrosion rate, and which was treated by the indicated final cold working operation to reduce the corrosion rate to a low acceptable value, was again treated to remove the effect of cold working as by a stress relief treatment, the corrosion rate again increased to an unacceptable high value. This established that it was critical to use a cold working operation as a final treatment operation to achieve the low corrosion rate characteristic.

Further investigation established that it is not the presence of the peculiar film following pickling which caused the high corrosion rate. Pickled cold work strip was found to have an appreciably lower corrosion rate than pickled strip without cold work, thus indicating the necessity for cold work in the final product.

We have been unable to account for the reason why the introduction or retention of cold work in producing high strength wrought zirconium base alloy products imparts high corrosion resistance or a low corrosion rate to such products. This result is completely contrary to the belief and teachings in the art of manufacture and treatment of metals and alloys. The literature on corrosion resistance of metals and alloys abounds with statements that cold work stimulates or increases corrosion of the cold worked surfaces. There is no known information in any literature, prior to our discovery, that a final cold working step in the manufacture of wrought zirconium base alloy products can be used to increase appreciably the corrosion resistance of such products.

We have made a further discovery that the zirconium base alloys which exhibit decreased corrosion when treated in accordance with the invention by a final cold working operation, are characterized by reduced H_2 pickup as corrosion progresses. This characteristic is of great importance because nuclear reactor applications for zirconium base alloy materials require as little H_2 pickup as possible.

Accordingly, it is an object of the present invention to provide a new method of imparting high corrosion resistance to zirconium base alloys which normally have low corrosion resistance or are characterized by a high corrosion rate.

Furthermore, it is an object of the present invention to provide a new method of making wrought zirconium base alloy products having strengths at all temperatures at least 50% greater than the strengths at the same temperatures of Zircaloy-2, to impart to such products a corrosion rate comparable to the 37 mg./dm.^{2} corrosion rate in 750° F.–1500 p.s.i.g. steam for 14 days, of Zircaloy-2.

Also, it is an object of the present invention to process the high strength zirconium base alloy in such a manner that cold work is retained in the final wrought product, thus achieving improved corrosion resistance.

Also, it is an object of the present invention to provide a particular series of steps or mode of treatment used in the manufacture of wrought zirconium base alloy products which reduces the rate of H_2 pickup as corrosion progresses.

Moreover, it is an object of the present invention to provide for the manufacture of zirconium base alloy products having a desirable and heretofore unobtained combination of high strength and high corrosion resistance.

Finally, it is an object of the present invention to provide new method of treating zirconium base alloy products in the manufacture thereof for obtaining the foregoing desiderata, and which overcomes existing difficulties and problems and satisfies an existing need in the art.

These and other objects and advantages, apparent to those skilled in the art from the following description and claims, may be obtained, the stated results achieved, and the described difficulties overcome, by the methods, steps, procedures and treatments which comprise the present invention, the nature of which is set forth below—illustrative of the best modes in which we have contemplated applying the principles—and which are particularly and distinctly pointed out and set forth in the appended claims forming part hereof.

The critical discovery of the invention is that a cold working operation is used to impart low corrosion rate characteristics to the investigated wrought zirconium base alloy products which have high strengths at all temperatures, but which normally exhibit an intolerable and unacceptable high corrosion rate.

In accordance with the invention, zirconium base alloy material which has high strength at both room and various elevated temperatures is melted and hot rolled in accordance with usual or standard practice for producing bar, plate, sheet or strip products. The hot rolled or hot worked material is then annealed in the usual manner and a cold working operation following annealing is performed to impart a low corrosion rate characteristic to the product.

In the case of cold rolled sheet or strip material, hot rolling may be performed in the usual manner followed by annealing and pickling of the hot rolled material. Then the pickled hot rolled material, in accordance with the invention, is cold rolled to desired gauge in order to impart the low corrosion rate characteristics to the material.

The results of carrying out the treatment of the invention are illustrated in Table I below, for a number of columbium containing zirconium base alloys and Zircaloy-2. The columbium content varies from 0% in Zircaloy-2 to 20% in DM 1374. In general, the alloys of this invention will contain about 1 to 20% by weight of columbium. It will be understood, however, that the amount columbium employed need only be sufficient to achieve the desired high strength properties.

TABLE I.—THE EFFECT OF FINAL METAL TREATMENT ON THE WEIGHT GAIN OF SEVERAL COLUMBIUM CONTAINING ZIRCONIUM BASE ALLOYS AFTER A 14-DAY EXPOSURE TO 750° F. STEAM

Heat No.	Alloy Constituents	Heat Treatment	Final Metal Treatment Step or Steps	Weight Gain, mg./dm.², in 14 Days at 750° F., 1,500 p.s.i.g. Steam	Percent Improvement Thru Cold Work
DM 1383	Zr-1% Sn-1% Cr-1% Cb	1,500° F.-1 hr.-FC	Machined and pickled Machined	51.9 36.4	+29.8
DM 1384	Zr-3% Sn-3% Cr-1% Cb	1,550° F.-1 hr.-FC	Machined and pickled Machined	101.9 78.9	+22.5
		1,550° F.-1 hr.-AC	Machined and pickled Machined	87.8 76.2	+13.2
X-2315	Zr-2% Sn-2% Cr-2% Cb	1,475° F.-1 hr.-FC	Machined and pickled Machined	119.8 64.1	+46.4
		1,475° F.-1 hr.-AC	Machined and pickled Machined	78.0 57.5	+26.3
X-2407	Zr-2% Sn-2% Cr-2.5% Cb	1,500° F.-½ hr.-FC	Machined and pickled Machined	69.1 38.5	+44.3
		1,500° F.-½ hr.-AC	Machined and pickled Machined	69.1 50.7	+26.6
X-2406	Zr-1% Sn-1% Cr-2.5% Cb	1,500° F.-½ hr.-FC	Machined and pickled Machined	113.6 41.2	+63.7
		1,500° F.-½ hr.-AC	Machined and pickled Machined	62.2 37.4	+39.3
		1,500° F.-½ hr.-WQ	Machined and pickled Machined	121.3 51.7	+57.4
X-2404	Zr-3% Sn-1% Cr-2.5% Cb	1,500° F.-½ hr.-FC	Machined and pickled Machined	126.6 44.5	+64.8
		1,500° F.-½ hr.-AC	Machined and pickled Machined	76.5 43.2	+54.8
		1,500° F.-½ hr.-WQ	Machined and pickled Machined	184.4 73.3	+60.2
X-2279	Zr-1% Sn-3% Cr-3% Cb	1,525° F.-1 hr.-FC	Machined and pickled Machined	131.6 47.0	+64.3
		1,525° F.-1 hr.-AC	Machined and pickled Machined	87.3 47.6	+45.5
X-2280	Zr-3% Sn-1% Cr-3% Cb	1,425° F.-1 hr.-FC	Machined and pickled Machined	168.5 41.8	+75.2
		1,425° F.-1 hr.-AC	Machined and pickled Machined	109.3 45.0	+58.8
X-2405	Zr-3% Sn-1% Cr-3% Cb	1,500° F.-½ hr.-FC	Machined and pickled Machined	139.4 62.7	+55.0
		1,500° F.-½ hr.-AC	Machined and pickled Machined	137.7 39.8	+71.1
		1,500° F.-½ hr.-WQ	Machined and pickled Machined	185.3 78.5	+57.6
DM 1271	Zr-0.3% Sn-1% Cr-3% Cb	1,425° F.-1 hr.-FC	Machined and pickled Machined	163.0 48.8	+70.1
		1,425° F.-1 hr.-AC	Machined and pickled Machined	82.5 44.9	+45.6
DM 1376	Zr-0.3% Sn-1% Cr-5% Cb	1,100° F.-96 hrs.-FC	Hot Roll and pickle Hot Roll, pickle, cold roll	103.6 50.0	+51.8
DM 1377	Zr-0.3% Sn-1% Cr-10% Cb	1,100° F.-96 hrs.-FC	Hot Roll and pickle Hot Roll, pickle, cold roll	110.1 70.0	+36.4
DM 1375	Zr-0.3% Sn-1% Cr-15% Cb	1,100° F.-96 hrs.-FC	Hot Roll and pickle Hot Roll, pickle, cold roll	118.5 70.6	+40.4
DM 1374	Zr-0.3% Sn-1% Cr-20% Cb	1,100° F.-96 hrs.-FC	Hot Roll and pickle Hot Roll, pickle, cold roll	126.9 87.0	+31.5
28128	Zircaloy-2	1,550° F.-½ hr.-AC	Machined and pickled Machined	37.0 40.4	—9.2

Specimens of all the compositions in Table I with less than 5% Cb were annealed accomplished by an air cool or a furnace cool. The specimen in the first line for each heat treatment was machined and then pickled, while the specimen in the second line for each heat treatment was machined as a final cold working operation after annealing. The same amount of machining was performed for each specimen either as a final cold working operation or prior to pickling so that the results can be compared, and the machining in the above and in all of the specific embodiments was accomplished by planing, unless otherwise indicated.

In the first line for each heat containing 5% Cb or greater, the specimens were hot rolled and pickled. In the second line for each heat, the specimens were treated in the same manner but were cold rolled to gauge following the pickling operation.

Of the twenty-seven examples of columbium containing zirconium base alloys, all except one showed a significant improvement by cold working. The improvement in one case (X–2280) was as great as 75%, while Zircaloy-2 showed a minus 9.2%.

The percent improvement that can be expected in the 14-day weight gain is dependent on the columbium content and heat treatment. This is illustrated in the accompanying figure, where data from Table I of zirconium base alloys containing 3% or less columbium content were used. The data for zirconium alloys containing 5% or greater columbium were not used, since the improvement in corrosion resistance was obtained by a different cold working process. The graft shows that for both heat treatments the percent improvement becomes greater as the columbium content is increased. For a constant columbium content, specimens furnace cooled from the annealing temperautre showed a greater percentage improvement by cold working than air cooled specimens. However, the improvement noted in air cooled specimens was still appreciable.

The data in Table I show that zirconium base alloys investigated which normally have a high corrosion rate

may be treated in accordance with the invention to impart high corrosion resistance to the material.

Table I illustrated the effect of cold work on the corrosion resistance of zirconium base alloys containing up to 20% Cb. The cold work was obtained by machining. During machining, the depth of cold work is very shallow and can be removed by a pickle operation. The percent of cold deformation is not certain. Table II illustrates, in more quantitative manner, the effect of cold work on the corrosion rate. In these examples, the cold work was obtained by cold rolling. The reductions studied were up to 88%. The corrosion tests were carried out for extended times so that accurate corrosion rates could be established. These results clearly show that the corrosion rate is progressively decreased as the amount of cold work (as measured by cold reduction) is increased.

Also included in the table are results for machined specimens. The post transition corrosion rate would indicate that the cold work introduced during machining is equivalent to the amount of cold work that is obtained in a 50% reduction by cold rolling.

As illustrated in Table I, the cold work introduced during machining is superficial and can easily be removed by a pickle. During cold rolling, the cold work is distributed throughout the cross section with the greatest amount being at the surface and progressively decreasing away from the surface. Therefore, a pickle of a cold rolled product should not completely erase the beneficial effects of the cold working operating since the surface after pickling would have some cold work remaining. Table III illustrates the effect of pickling a cold rolled surface. For example, the Zr-2.5% Cb-1% Cr.-3% Sn alloy without cold work has a post transition corrosion rate of 4.1 mg./dm.²/day. By cold rolling 88%, this rate is decreased to 2.0. Pickling the cold worked specimen does not raise the rate to the original value but to an intermediate value of 2.7. Thus, the pickle removed a highly cold worked surface exposing a new surface which contains slightly less cold work. This example and others in Table III show that the cold work in the material and not the lack of peculiar pickle film is the critical feature of the invention.

TABLE II.—EFFECT OF COLD WORKING ON THE CORROSION RESISTANCE OF Cb CONTAINING ZIRCONIUM BASE ALLOYS

Alloy Composition	Source of Cold Work [1]	Weight Gain, mg./dm.², in Indicated Time at 750° F., 1,500 p.s.i.g., Steam							Post Transition Corrosion Rate mg./dm.²/Day
		14 Days	28 Days	56 Days	84 Days	112 Days	140 Days	168 Days	
Zr-2.5% Cb	None	54	68	100	147	196	245	293	1.7
	4% Red. by cold rolling	51	63	101	143	182	222	260	1.5
	17% Red. by cold rolling	48	60	91	133	177	216	252	1.4
	50% Red. by cold rolling	38	49	88	118	155	188	213	1.1
	88% Red. by cold rolling	38	49	67	100	124	142	166	0.8
	Machined all over	37	46	65	88	119	148	-------	1.0
Zr-2.5% Cb-1% Cr-1% Sn	None	68	112	192	272	357	435	505	2.9
	6% Red. by cold rolling	68	105	194	279	370	449	526	3.0
	16% Red. by cold rolling	54	88	159	238	315	388	457	2.8
	60% Red. by cold rolling	40	72	133	192	253	313	368	2.1
	87% Red. by cold rolling	35	56	97	142	185	230	273	1.6
	Machined all over	35	63	122	215	297	-------	-------	3.1
Zr-2.5% Cb-1%, Cr-3% Sn	None	82	138	258	381	-------	-------	722	4.1
	7% Red. by cold rolling	73	128	255	368	491	597	697	4.1
	16% Red. by cold rolling	63	122	244	361	492	600	-------	4.1
	52% Red. by cold rolling	53	99	195	299	406	506	596	3.5
	88% Red. by cold rolling	37	46	88	142	200	254	318	2.0
	Machined all over	40	80	187	303	411	508	-------	3.6
Zr-3.0% Cb-1%, Cr-3% Sn	None	114	-------	-------	-------	-------	-------	-------	-------
	6% Red. by cold rolling	101	-------	-------	-------	-------	-------	-------	-------
	17% Red. by cold rolling	97	152	281	396	-------	-------	-------	4.3
	50% Red. by cold rolling	47	85	174	270	-------	-------	-------	3.2
	88% Red. by cold rolling	38	47	79	-------	185	242	304	2.0
	Machined all over	41	56	132	220	320	-------	-------	3.3

[1] Vacuum annealed at 1,450° F.—2 hrs. and Furnace Cooled prior to cold working.

TABLE III.—THE EFFECT OF SURFACE REMOVAL ON THE CORROSION RESISTANCE OF COLD WORKED COLUMBIUM CONTAINING ZIRCONIUM BASE ALLOYS

Alloy Composition	Surface Condition	Weight Gain After 168 days in 750° F., 1,500 p.s.i.g. Steam, mg./dm.²	Post Transition Corrosion Rate, mg./dm.²/day
Zr-2.5% Cb	Cold worked 0%	293	1.7
	Cold worked 88%	166	0.8
	Cold worked 88% and pickle	174	0.9
Zr-2.5% Cb-1% Cr-1% Sn	Cold worked 0%	505	2.9
	Cold worked 87%	271	1.6
	Cold worked 87% and pickle	306	1.8
Zr-2.5% Cb-1% Cr-3% Sn	Cold worked 0%	722	4.1
	Cold worked 88%	318	2.0
	Cold worked 88% and pickle	434	2.7
Zr-3.0% Cb-1% Cr-3% Sn	Cold worked 88%	304	2.0
	Cold worked 88% and pickle	418	2.7

An additional experiment was conducted to establish the criticality of the cold work. The result of eliminating the effect of the final cold working operation of the present invention is shown in Table IV, below, which lists corrosion test values for material from Heat No. X–2280 (Zr-3% Sn-1% Cr-3% Cb) with the specimens machined and pickled in the first line, machined in the second line and machined and then subjected to a vacuum annealing operation in the third line.

TABLE IV

Specimen Preparation	750° F., 1,500 p.s.i.g. Steam	
	14 days mg./dm.²	28 days mg./dm.²
Machined and pickled	168.5	258.4
Machined	41.8	55.9
Machined and 1,400° F.—½ hr. in vacuum Anneal	138.3	225.4

The data in Table IV show that when the effect of a cold working operation was removed by annealing the cold worked material (third line), the corrosion is again increased from the low 41.8 mg./dm.² value to the unacceptable high value of 138.3 mg./dm.² for 14 days.

Since the corrosion rate is decreased by cold working, the rate of hydrogen pickup is also decreased. This is shown in Table V.

TABLE V

[Zr-2.5% Cb-1% Cr-3% Sn—1,500° F.-½ hr.-FC]

Cold Reduction, Percent	Final Metal Treatment or Treatments	168 Days Weight Gain, mg./dm.²	168 Days Hydrogen Pickup, p.p.m./0.1″ Thickness
0	Annealed and pickled	816	129
48	As cold rolled	587	91
80	do	427	27

Because of the cold work, the weight gain after 168 days in 750 p.s.i.g. steam is reduced. Because of less corrosion when cold work is present, the hydrogen pickup is less. In this example, the hydrogen pickup during corrosion for a 0.1″ thick specimen with no cold work would be 122 p.p.m. Through the introduction of cold work this has been reduced to 79 p.p.m. for an 80% cold reduction.

Room temperature elongation and yield strength at 900° F. values are given in Table VI, below, for several of the alloys evaluated in Table I. The last line of Table VI and presents values for Zircaloy-2.

TABLE VI

Heat No.	Composition	R.T. Elong., Percent	Y.S. 0.2% Off. 900° F., p.s.i.
DM 1384	Zr-3% Sn-3% Cr-1% Cb	[1] 13.5	33,000
X–2279	Zr-1% Sn-3% Cr-3% Cb	[1] 12.5	29,000
DM 1271	Zr-0.3% Sn-1% Cr-3% Cb	[1] 12.5	33,000
X–2280	Zr-3.0% Sn-1% Cr-3% Cb	[1] 17.0	42,000
DM 1376	Zr-5% Cb	[2] 18.0	28,000
DM 1377	Zr-10% Cb	[2] 11.0	42,000
DM 1375	Zr-15% Cb	[2] 6.5	48,000
DM 1374	Zr-20% Cb	[2] 9.5	53,000
28128	Zircaloy–2	[1] 23.0	18,000

[1] Percent Elongation in 1″.
[2] Percent Elongation in 2″.

The room temperature elongations of the alloys in Table VI, except DM 1375, satisfy the minimum room temperature elongation requirements indicated above. All of the heats have at least 50% greater yield strength at 900° F. than the 18,000 p.s.i. yield strength of Zircaloy-2, meeting the alternate strength requirements specified above.

Referring to both Tables I and IV, treatment in accordance with the invention may be used to obtain wrought zirconium base alloy products which have high corrosion resistance combined with high strength as compared with the high corrosion resistance-low strength properties of Zircaloy-2. Such a combination of properties has not, to our knowledge, ever been achieved in wrought zirconium base alloy products.

Accordingly, the new method of imparting corrosion resistance to zirconium base alloys of the present invention provides for the treatment of zirconium base alloys which may have high strength but low corrosion resistance to impart substantially increased corrosion resistance to such alloys comparable to that of Zircaloy-2; provides a reduced rate of H_2 pickup for high strength zirconium base alloys which have been treated to obtain increased corrosion resistance; and provides a new procedure solving a problem and eliminating difficulties existing in the art which may be carried out economically to produce wrought zirconium base alloy products having a heretofore unobtained combination of high strength and high corrosion resistance.

In the foregoing description, certain terms have been used for brevity, clearness and understanding, but no unnecessary limitations are to be implied therefrom beyond the requirements of the prior art, because such terms are used for descriptive purposes herein, and not for the purpose of limitation, and are intended to be broadly construed.

Having now described the invention, the features, discoveries and principles thereof, the combined characteristics imparted to wrought zirconium base alloy products treated in accordance with the invention, and the new and useful results obtained, the new and useful methods, steps, procedures, treatments, discoveries and principles, and reasonable mechanical equivalents thereof obvious to those skilled in the art, are set forth in the appended claims.

What is claimed is:

1. The method of increasing the corrosion resistance, as evidenced by decreasing the weight gain at least 13.2% when exposed to 750° F.–1500 p.s.i.g. steam for 15 days, of wrought zirconium base alloy products containing about 1 to 20 weight percent columbium having elevated temperature yield strengths at 900° F. between 28,000 and 53,000 p.s.i., which comprises the steps of hot working and annealing the alloy and finally cold working the surface of the alloy.

2. The method of claim 1 wherein said alloy is pickled after annealing but prior to cold working.

3. The method of claim 1 wherein the cold working is machining.

4. The method of claim 1 wherein the cold working is cold rolling.

5. The method of imparting high corrosion resistance of from 41.8 to 87 mg./dm.^{2} when exposed to 750° F.–1500 p.s.i.g. steam for 14 days to wrought zirconium base alloys containing about 1 to 20 weight percent columbium having from 28,000 p.s.i. to 53,000 p.s.i. yield strength at 900° F. and corrosion resistance of 87.3 to 168.5 mg./dm.^{2} when exposed to 750° F.–1500 p.s.i.g. steam for 14 days when produced by hot rolling, annealing and pickling, including the steps of hot rolling the alloy to develop the 28,000 p.s.i. to 53,000 p.s.i. yield strength at 900° F., annealing the hot rolled alloy, and cold working the surface of the alloy.

6. The method of claim 5 wherein the cold working is machining.

7. The method of claim 5 wherein the cold working is cold rolling.

References Cited by the Examiner

UNITED STATES PATENTS

2,772,964 12/1956 Thomas et al. -------- 75—177

OTHER REFERENCES

AECU–3561: "Scaling of Zirconium and Zirconium Alloys," August 1957, Burke et al., pp. 9–13 relied on.

Journal of Metals, September 1955, pp. 1034–1041, "Zirconium-Columbium Diagram," Rogers et al.

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