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ZIRCONIUM ALLOY

Ulrich Rösler, Erlangen, Germany, assignor to Siemens-Schuckertwerke Aktiengesellschaft, Berlin-Siemensstadt, Germany, a corporation of Germany

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My invention relates to zirconium alloys and, in a more particular aspect, to alloys suitable as structural material for use in nuclear reactors, such as for the envelopes or cans of nuclear fuel elements.

Structural materials in the interior of nuclear reactors, particularly canning materials for fuel elements, are required to meet essentially the following four requirements:

(1) Lowest feasible absorption cross section for thermal neutrons,
(2) High corrosion resistance relative to liquid or gaseuos reactor coolants,
(3) Sufficient mechanical strength and ductility, and
(4) Insensitivity to neutron irradiation.

As regards these requirements, zirconium alloys have been found to be well suitable, particularly in reactors using water as coolant. Preferably employed has been the alloy known under the trade name Zircaloy-2 which, aside from zirconium, contains about 1.5% tin, 0.15% iron, 0.1% chromium and 0.05% nickel. (All percentages given in this specification are by weight.) These alloying additions counteract the impairment in corrosion resistance of pure zirconium due to contaminating traces of other elements, mainly nitrogen.

Nuclear reactors equipped with fuel-element cans and structural parts of Zircaloy-2 or Zircaloy-4, the latter being nickel-free Zircaloy-2, can be operated with water temperatures only up to about 350° C. above which the materials are no longer sufficiently corrosion resistant. These temperatures do not afford employing in the reactor plant the improved, modern turbines of increased efficiency, because these turbines would make it desirable to convert to operation with superheated steam at temperatures between 400 and 500° C. and more. Recently there have become known zirconium-columbium (niobium) alloys with promising improved corrosion resistance in the just-mentioned temperature range as compared with Zircaloy-2 and Zircaloy-4.

It is an object of my invention to provide zirconium alloys, preferably for the above-mentioned use in nuclear reactor plants, which afford achieving a considerably higher corrosion resistance than heretofore attained with the known zirconium-columbium alloys.

I have discovered, and it is a feature of my invention, that such improvement is achieved by providing a zirconium-base alloy with an amount of 0.005 to 1.0%, preferably 0.01 to 0.5%, calcium, as well as one or more of the elements columbium (niobium), tin, iron, chromium, nickel, molybdenum, copper, tungsten, vanadium, tantalum and palladium, each in a quantity of 0.01 up to about 5%, the remainder of the alloy being zirconium, inclusive of impurities. However, in order to obtain most favorable properties, the above-mentioned additional elements are preferably present in a total quantity of less than about 10% so that the remainder consists

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of more than 90% zirconium. In the most favorable alloys according to the invention, the zirconium remainder was not less than about 95% and contained 0.1 to 5%, preferably 0.3 to 2.5%, columbium in addition to the above-mentioned amount of calcium.

For best results, therefore, the zirconium alloy contains columbium as well as calcium and it may also contain the alloying addition known for this type of alloy, namely tin, iron, chromium, nickel, molybdenum, copper, tungsten, vanadium, tantalum and palladium which have been found to afford a further improvement in corrosion resistance and/or the mechanical properties of zirconium-base alloys. In this respect, reference may be had to the following literature:

R. S. Ambartsumyan et al.: "Mechanical Properties and Corrosion Resistance of Zirconium and its Alloys in Water, Steam and Gases at Elevated Temperatures," 2nd Geneva Conference (1958), 15/P/2044.

J. P. Pemsler: "The Corrosion of Zirconium Alloys in 900° F. Steam," NMI–1208 (1958).

S.B. Dalgaard: "The Corrosion Resistance of Zr-Nb and Zr-Nb-Sn Alloys in High-Temperature Water and Steam," AECL–993 (1960).

J. N. Wanklyn, J. T. Demant and D. Jones: "The Corrosion of Zirconium and its Alloys by High Temperature Steam. Part I: The Effect of Alloy Composition," AERE–R3655 (1961).

In general, the preferred alloys according to the invention, aside from containing 0.1 to 5%, preferably 0.3 to 2.5% columbium and 0.005 to 1.9%, preferably 0.01 to 0.5%, calcium, may contain at least one of the above-mentioned additions within the following quantity ranges:

0.2 to 1% Sn
0.1 to 1.5% Fe
0.1 to 1.5% Cr
0.1 to 1.5% Ni
0.5 to 1% Mo
0.5 to 1.5% Cu
0.5 to 1% W
0.2 to 1% V

As mentioned, however, the remainder of zirconium should constitute the greatly preponderant proportion, namely more than 90% and preferably more than 95% of the total alloy.

The improved corrosion properties of the alloys according to the invention are exemplified by test results reported in the following tables. The zircon alloys investigated were produced from zirconium sponge (reactor grade) and the alloying elements, by melting them together in an electric arc furnace under argon at a pressure of about 200 mm. Hg. For securing homogeneous concentration of the alloy, each alloy was twice re-melted. The alloy was subjected to cold rolling down to a sheet thickness of 0.7 mm. Specimens were produced of about 3 cm.^{2} size. These were etched in the usual manner. Employed as etching agent was the following composition: 45 volumetric percent HNO_3 (65% concentration) + 10 volumetric percent HF (40% concentration) + 45 volumetric percent H_2O. Approximately 25 microns thickness were eliminated by etching. The specimens were then subjected for respective periods of 8, 32 and 64 days to the effect of hot steam at 500° C. under a pressure of 1 atmosphere absolute. The results are listed in the following Table I:

Table I

No.	Cb, Percent	Cu, Percent	Fe, Percent	Ca, Percent	Zr	Weight increase after 8 days, mg./dm.^{2}
1		0.5			Remainder	57.2
2		0.5		0.1	do	53.2
3		1			do	60.1
4		1		0.02	do	55.2
5		1		0.1	do	57.0
6		1		0.5	do	54.1
7		0.5	0.5		do	60.5
8		0.5	0.5	0.02	do	58.9
9	1	1		0.02	do	70.0
10	1	1		0.1	do	71.8
11	1	1		0.5	do	68.3

The last column in Table I indicates the increase in weight after 8 days of steam treatment as a measure of the amount of corrosion. A comparison of alloy specimens 1 and 2 shows that the calcium-containing alloy 2 exhibited a reduction in corrosion relative to the calcium-free alloy 1. The other series of tests exhibited analogous results.

The specimens 12 to 17 listed in the following Table II and the comparative specimens 18, 19 listed in Table III were subjected simultaneously to the same tests.

Table II

No.	Composition of alloy			Weight increase after—	
	Cb, percent	Ca, percent	Zr	32 days, mg./dm.^{2}	64 days, mg./dm.^{2}
12	0.5	0.02	Remainder	305	579
13	0.5	0.1	do	312	600
14	0.5	0.5	do	187	349
15	1.0	0.02	do	200	467
16	1.0	0.1	do	230	513
17	1.0	0.5	do	305	638

Table III

No.	Composition		Weight increase after—		
	Cb, percent	Zr	8 days, mg./dm.^{2}	32 days, mg./dm.^{2}	64 days, mg./dm.^{2}
18	1	Remainder	218	760	1,345
19		Zircaloy-2	238	1,110	2,460

It will be noted that the calcium-free specimens according to Table III, tested together with the calcium-containing specimens 12 to 17 of Table II exhibited considerably higher increases in weight due to corrosion.

A comparison of the values for the alloy 18 (1% Cb, remainder Zr) with alloy 15 (1.0% Cb and 0.02% Ca, remainder Zr) shows that very slight additions of calcium can effect a reduction of the weight increase down to approximately one-fourth of the original value, the particular composition at which minimum weight increase is achieved being also determined by the other constituents of the alloy. A similar behavior with respect to corrosion is also observable with heat-treated zirconium alloys.

It has also been found that the addition of calcium considerably increases the mechanical strength of the zirconium alloys. It is known that zirconium and zirconium alloys embrittle due to ingress of hydrogen with corrosion caused by water or steam. Such impairment is counteracted to a great extent by the calcium additions. The bending angles listed in Table IV were determined up to occurrence of the first fissures after bending the identified specimens over a bending mandrel of 3.5 mm. diameter. The specimens were previously subjected to corrosion in steam at 500° C. for 32 days.

Table IV

No.	Composition			Binding angle, degrees
	Cu, percent	Ca, percent	Zr	
21	0.5		Remainder	72
22	0.5	0.02	do	91
23	0.5	.1	do	180
24	0.5	0.5	do	100

As mentioned, alloys according to my invention, and especially those of the above-listed compositions that exhibit minimum susceptibility to corrosion, are well suitable as canning or envelope material for nuclear fuel elements or generally for use as structural materials in the interior of nuclear reactors, particularly those that operate with super-heated steam as coolant.

I claim:

1. A zirconium alloy consisting substantially of 0.005 to 1.0% calcium and at least one element selected from the group consisting of columbium, tin, vanadium, tantalum, palladium, copper, chromium, molybdenum, tungsten, iron and nickel in a quantity up to about 5% for each but amounting to a total less than 10%, the remainder being substantially all of zirconium.

2. A zirconium alloy containing 0.01 to 0.5% calcium and at least one element selected from the group consisting of Cb, Sn, V, Ta, Pd, Cu, Cr, Mo, W, Fe and Ni in a total quantity between about 0.1 and about 5%, the remainder being substantially all of zirconium.

3. A zirconium alloy consisting substantially of 0.1 to 5% columbium, 0.005 to 1.0% calcium, and a remainder substantially all of zirconium.

4. A zirconium alloy consisting substantially of 0.3 to 2.5% columbium, 0.01 to 0.5% calcium, and a remainder substantially all of zirconium.

5. A zirconium alloy containing 0.1 to 5% columbium, 0.005 to 1.0% calcium, and at least one of the following additions:

0.2 to 1% Sn	0.5 to 1% Mo
0.1 to 1.5% Fe	0.5 to 1.5% Cu
0.1 to 1.5% Cr	0.5 to 1% W
0.1 to 1.5% Ni	0.2 to 1% V

and a remainder substantially all of zirconium.

6. A zirconium alloy for use as structural material in nuclear reactors, comprising 0.3 to 2.5% columbium, 0.01 to 0.5% calcium, and at least one of the following additions:

0.2 to 1% Sn	0.5 to 1% Mo
0.1 to 1.5% Fe	0.5 to 1.5% Cu
0.1 to 1.5% Cr	0.5 to 1% W
0.1 to 1.5% Ni	0.2 to 1% V

the maximum amount of said additions being about 5%, and the remainder of the alloy being substantially all of zirconium.

7. A zirconium alloy consisting substantially of copper and calcium each in an amount of about 0.5 to about 1%, the remainder being substantially zirconium.

8. A zirconium alloy consisting substantially of about 0.5% copper, about 0.5% iron, about 0.02 to about 0.5% calcium, the remainder being substantially zirconium.

9. A zirconium alloy consisting substantially of about 1% columbium, about 1% copper, 0.002% up to about 0.5% calcium, the remainder being substantially zirconium.

10. A zirconium alloy consisting substantially of about 0.5 to about 1% of columbium, more than 0.002% up to about 0.5% calcium, the remainder being substantially zirconium.

No references cited.