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ZIRCONIUM ALLOYS CONTAINING CERIUM AND YTTRIUM

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9 Claims. (Cl. 75—177)

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 gaseous 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 constitutes an essential feature of my invention, that such improvement in corrosion resistance is achieved by composing a zirconium-base alloy of 0.005 to 1% substance from the group consisting of cerium and yttrium, and one or more of the elements columbium, tin, copper, iron, chromium, nickel, molybdenum, tungsten, vanadium, tantalum and palladium, each in a quantity of up to about 5%, the remainder being substantially all of zirconium, which is understood to include impurities. However, the total amount of the above-mentioned addition elements, aside from cerium or yttrium, is less than 10% and preferably less than 5% so that zirconium constitutes more than 90% and preferably more than 95% of the alloy, all percentages stated in this specification being by weight.

I have found it preferable for best results, particularly with respect to structural materials for use in nuclear reactors, to employ a cerium or yttrium content of 0.01 to 0.5%. For example, a favorable alloy composition

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contains 0.1 to 5%, preferably 0.3 to 2.5% columbium, 0.01 to 0.5% cerium, the remainder being substantially zirconium inclusive of impurities. Also applicable is the same composition if the cerium is substituted by 0.01 to 0.5% yttrium. In both cases the alloy may also contain at least one of the following additions within the stated ranges:

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

As mentioned, however, the total amount of such additions should remain below the limits given above. The just-mentioned additions belong to the group of metals known as constituents in 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 zirconium-base alloys according to the invention, the increase in corrosion resistance under nuclear-reactor operating conditions achieved by the addition of cerium or yttrium is accompanied by the advantage that these additions do not appreciably increase the absorption cross section for thermal neutrons. The absorption cross section of cerium is 0.7 barns/atom. Cerium is the only element from the series of the rare earths having a relatively low absorption cross section. The absorption cross section for thermal neutrons in the case of yttrium is 1.38 barns/atom, which is still rather low. The corresponding absorption cross sections for zirconium and columbium are 0.18 and 1.1 barns/atom respectively. The addition of cerium or yttrium in the small quantities stated has only a negligible effect upon the absorption cross section of the entire Zr-Cb alloy. It will indeed be seen from the following test results that extremely slight quantities of cerium and yttrium additions suffice to secure the desired results.

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 remelted. The alloy was subjected to cold rolling down to a sheet thickness of 0.8 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 subjected for 32 days to a steam atmosphere of 500° C. at a pressure of 1 atmosphere absolute. The increase in weight stated in the last column of Table I was determined as a measure of susceptibility to corrosion.

TABLE I

No.	Cb, percent	Ce, percent	Zr	Increase in weight, mg./dm.^{2}
1	0.5	0.02	Remainder	231
2	0.5	0.1	do	241
3	0.5	0.5	do	347
4	1.0	0.02	do	444
5	1.0	0.1	do	626
6	1.0	0.5	do	538

The following two known zirconium alloys 7 and 8 listed in Table II were subjected to the same tests simultaneously with specimens 1 to 6.

TABLE II

No.	Cb, percent	Zr	Increase in weight, mg./dm.^{2}
7	0.5	Remainder	474
8	1.0	do	731

It will be noted that specimen 1 differs from 7 only by an addition of 0.02% Ce but exhibits a considerably lower sensitivity to corrosive action. Analogously, each of specimens 4, 5 and 6 differs from specimen 8 by an addition of Ce resulting in increased resistance to corrosion. It is apparent that very slight additions of cerium may afford a reduction down to about one-half of the original increase in weight relative to a corresponding Zr-Cb alloy.

The following tables III and IV contain analogous comparative test data relating to yttrium-containing zirconium-base alloys.

TABLE III

No.	Cb, percent	Y, percent	Zr	Increase in weight, mg./dm.^{2}
9	0.5	0.02	Remainder	272
10	0.5	0.1	do	257
11	0.5	0.5	do	448
12	1.0	0.02	do	397
13	1.0	0.1	do	423
14	1.0	0.5	do	457

The yttrium-free alloys 15 and 16 according to the following Table IV were simultaneously subjected to the same tests as the alloys 9 to 14 according to Table III.

TABLE IV

No.	Cb, percent	Zr	Increase in weight, mg./dm.^{2}
15	0.5	Remainder	474
16	1.0	do	731

It will be noted that specimens 15 and 16 exhibit a considerable increase in weight, indicative of lower resistance to corrosion, in comparison with the corresponding yttrium-containing alloys of Table III. As in the case of the cerium addition, very slight amounts of yttrium

may be sufficient for reducing the weight increase down to one-half of its original value.

I claim:

1. A zirconium alloy consisting essentially of 0.1 to 5% columbium, 0.005 to 1.0% cerium, the balance consisting essentially of zirconium.

2. A zirconium alloy consisting essentially of 0.3 to 2.5% columbium, 0.01 to 0.5% cerium, the balance consisting essentially of zirconium.

3. A zirconium alloy consisting essentially of 0.3 to 2.5% columbium, 0.01 to 0.5% cerium, and at least one addition selected from the group consisting of

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

and the balance consisting essentially of zirconium.

4. A zirconium alloy consisting essentially of about 0.5% columbium, about 0.02 to about 0.5% cerium, the balance consisting essentially of zirconium.

5. A zirconium alloy consisting essentially of about 1% columbium, about 0.02% cerium, the balance consisting essentially of zirconium.

6. A zirconium alloy consisting essentially of 0.1 to 5% columbium, 0.005 to 1.0% yttrium, the balance consisting essentially of zirconium.

7. A zirconium alloy consisting essentially of 0.3 to 2.5% columbium, 0.01 to 0.5% yttrium, the balance consisting essentially of zirconium.

8. A zirconium alloy consisting essentially of 0.3 to 2.5% columbium, 0.01 to 0.5% yttrium, and at least one addition selected from the group consisting of

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

and the balance consisting essentially of zirconium.

9. A zirconium alloy consisting essentially of about 0.5 to about 1% columbium, 0.02 to 0.5% yttrium, the balance consisting essentially of zirconium.

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