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ZIRCONIUM BASE ALLOY

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ABSTRACT OF THE DISCLOSURE

The disclosure is directed to a zirconium based alloy having a high resistance to corrosion in superheated steam at 400° to 650° C. and having a high resistance to hydrogen absorption and low susceptibility to hydrogen embrittlement. The alloy consists essentially of a copper content in the range of about 1.5 to 1.7 at. percent, an iron content in the range of about 0.35 to 0.55 at. percent, with the remainder zirconium. In addition, a structure can be produced from the alloy having even greater improved corrosion resistance by treating, working and fabricating the alloy at temperatures below 765° C.

The invention described herein was made in the course of, or under, Contract No. AT(04–3)–189, Project Agreement No. 24, with the United States Atomic Energy Commission.

This invention relates to alloys of zirconium, and in particular to alloys having low neutron absorption properties, together with unique low corrosion and hydrogen embrittlement and absorption properties in an atmosphere of superheated steam, between 400° C. and 650° C. as well as to methods employing such alloy in a superheated steam nuclear environment.

In nuclear reactors designed to generate superheated steam, and in which a zirconium alloy is used, two basic problems exist: (1) a corrosion process occurs between the steam and zirconium according to the reaction $Zr+2H_2O \rightarrow ZrO_2+2H_2$; and (2) the hydrogen produced by the above reaction, in addition to the free hydrogen produced by radiolytic dissociation of the water or steam when exposed to fast neutrons or gamma rays within the reactor, is readily absorbed by the zirconium alloys of the prior art to create zirconium hydride which precipitates as a brittle second phase in the alloy matrix and causes severe embrittlement of the alloy, thus making it unusable as a structural material such as cladding for fissile fuel or in structural non-heat transfer applications such as pressure tube thermal liners. For example, existing alloys of zirconium such as Zircaloy–2 contain 1.5 weight percent tin, 0.12 weight percent iron, 0.10 weight percent chromium, and 0.05 weight percent nickel; Zircaloy–3, containing 0.25 to 0.50 weight percent tin, 0.25 to 0.10 weight percent iron, and 0.20 weight percent nickel; and Zircaloy–4, containing 1.2 to 1.7 weight percent tin, 0.18 to 0.20 weight percent iron, 0.07 to 0.13 weight percent chromium, and 0.007 weight percent maximum nickel have been found to deteriorate rapidly at the elevated temperatures encountered with superheated steam. These alloys are better applied to applications in low temperature water reactors.

The superiority of the alloy of the present invention is dependent upon a critical composition range of alloying elements and upon critical fabrication treatments which provide a zirconium alloy having a low hydrogen absorption and low hydrogen embrittlement, coupled with a high corrosion resistance and good fabricability for use in a superheated steam nuclear reactor operating in the temperature range between 400° C. and 650° C.

It is therefore an object of this invention to provide

an alloy of zirconium having a low corrosion rate at temperatures of the order of 650° C. in steam.

It is a further object of this invention to provide an alloy of zirconium having a low susceptibility to hydrogen embrittlement at elevated temperatures.

It is a still further object of this invention to provide an alloy of zirconium having a low rate of hydrogen absorption at elevated temperatures.

It is a further object of this invention to provide an alloy of zirconium having a neutron absorption cross section substantially the same as, or less than, existing alloys of zirconium currently used in nuclear reactors.

Other and more particular objects of this invention will be manifest upon study of the following detailed description.

The alloy of the present invention is distinguished from the alloys of the prior art in that by addition of only small, but quite critical, amounts of copper and iron within a narrow range of composition to reactor grade zirconium having only traces of other elements present, an alloy is produced having low hydrogen absorption and embrittlement characteristics, along with high corrosion resistance, moderately high strength and good fabricability, and in which the beneficial properties are developed to a superior degree by certain specified heat and working treatments.

In general, a study of corrosion and hydrogen absorption and embrittlement effects on zirconium indicate that the process is dependent upon the solid state properties of the zirconium oxide film forced on the surface of the metal. Thus, the chemical, electrical and mechanical properties of the oxide film containing portions of the alloy elements determine the corrosion and hydrogen embrittlement characteristics of the alloy. For example, it has been found that small quantities of copper and iron will tend to cause the oxide film to have a greater ability to adhere to the metallic surface of the alloy, as well as maintain plasticity of the surface oxide, thus preventing further opportunity for corrosion and hydrogen absorption through cracks in the oxide film. It has been found that copper tends to concentrate under the oxide film rather than to be disposed evenly throughout the film. On the other hand, it has been found that yttrium tends to decrease plasticity of the oxide film, resulting in early cracking and spalling of the film, thus exposing the bare metal to further corrosion and materials tending to cause hydrogen embrittlement.

It has been found by experiment that the amount of copper and iron in the alloy, as well as the total amount of alloying material, must be carefully controlled in balanced proportions. If the alloy contains less than 1.8 at. percent total alloy ingredients, it is not as strong as the commonly used Zr-Sn-Fe-Cr-Ni alloys. When the alloy contains more than 2.0 at. percent total alloy ingredient content, its ductility and fabricability declines to less than that of commercial alloys of the prior art. With an alloy containing more than about 2.1 at. percent copper, the neutron absorption cross section becomes significantly or undesirably high. A zirconium alloy which contains more than 0.7 at. percent total Nb+Fe will become brittle at room temperature at a hydrogen content of less than 1000 p.p.m. Moreover, if the alloy contains no iron, it is more expensive because it requires more expensive starting materials to provide the bulk desired. In the case of a zirconium alloy containing both chromium and copper, the corrosion resistance is worse than for copper alone or chromium alone; but remarkably, when the alloy contains about 1.6 at. percent copper, the hydriding rate is lower than for any other heretofore known zirconium alloys. With the foregoing complex factors in mind, the alloy of this invention is a zirconium-base reactor alloy having a minimum of 1.5 at. percent and a maximum of 1.7 at. percent copper, and a minimum of 0.25 at. percent

and a maximum of 0.55 at. percent iron, with the balance zirconium, and with all other impurity elements within the American Society for Testing Materials standard limits for commercial reactor grade zirconium, e.g., the same limits as for Zircaloy–2, Zircaloy–3 and Zircaloy–4, set forth above.

Compared with the existing alloy Zircaloy–2, Table I illustrates the properties of the alloy of the present invention.

TABLE I.—CORROSION AND HYDRIDING BEHAVIOR

	Zr+1.6 at. percent Cu +0.4 at. percent Fe	Zircaloy–2
Long term corrosion rate in mg./dm.²/day:		
500° C.	1.0	9.6
400° C.	0.22	1.4
300° C.	0.02	0.074
Hydriding Rate in p.p.m./day (50 mil thick sample):		
500° C.	1.4	10.6
400° C.	0.4	0.54
Hydrogen Content in p.p.m.[1] (50 mil thick coupon):		
500° C.[2]	26	617
400° C.[2]	25	19

[1] Increase over original hydrogen impurity content of 4 to 27 p.p.m. average in experimental lots.
[2] After 1,500 hours.

It may be noted that the alloy of the invention is inherently superior to reactor zirconium alloys of the prior art, even with conventional heat and working treatments. However, to obtain even further improvements, it is important, in the practice of this invention, to adhere to certain time-temperature parameters during the fabrication and working of the alloy in order to obtain the best corrosion resistance. It has been found that heating and/or working the alloy of thet present invention for any substantial time period in the two-phase alpha plus beta temperature region, 760 to 910° C., will result in a 25 to 30% increase in corrosion weight gain at 500° C. Table II illustrates the effect of temperature during fabrication on the corrosion weight gain.

TABLE II

A. Corrosion Weight Gains (mg./dm.²) at 500° C. for Zr+1.6 at. percent Cu+0.4 at. percent Fe

	After 291 hours	After 1,882 hours
(1) Solution 1 hour 955° C.; quenched; aged 24 hours at—		
765° C.	83	211
895° C.	105	243
730° C.	119	324
865° C.	99	237
895° C.	113	291
(2) No solution or quench; forged 740° C.; hot rolled 540° C.; cold work 40%; annealed 650° C.	82	170

B. Corrosion Weight Gain (mg./dm.²) at 500° C. for Zr+1.1 at. percen Cu+0.34 at. percent Fe

(1) Solution 2 hours 955° C.; quenched; aged 8 hours at 565° C.	82	25

Thus it can be seen that the preferable working and fabrication temperatures are below 765° C. More specifically, the alloy can be subjected to an initial period of heating to an elevated temperature above about 910° C., e.g., 1–2 hours at 955° C. to bring alloy ingredients into equilibrium solution. Then the alloy is quenched or otherwise rapidly cooled. Alternatively, the cast alloy is worked, e.g., forged and/or rolled, annealed as indicated, at temperatures below 740° C. with rather uniform corrosion properties being provided, as well as the hydride resistance being retained. The quenched alloy behaves similarly in the latter type treatments.

TABLE III

Zr+1.6 at. percent Cu+0.4 at. percent Fe

	Room Temperature	400° C.	500°
Yield Strength (kg./mm.²)	39	17	13
Ultimate Tensile Strength (kg./mm.²)	45	19	14
Percent Elongation	31	48	68
Percent Reduction in Area	62	85	96

Although the foregoing embodiment has been described in detail, there are obviously many other embodiments and variations in configuration which can be made by a person skilled in the art without departing from the spirit, scope or principle of this invention. Therefore, this invention is not to be limited except in accordance with the scope of the appended claims.

What is claimed is:

1. A zirconium based alloy having a high resistance to corrosion in superheated steam at 400° to 650° C., high resistance to hydrogen absorption and low susceptibility to hydrogen embrittlement, consisting essentially of a copper content in the range of substantially about 1.5 to 1.7 at. percent, iron content in the range of about 0.35 to 0.55 at. percent, and with the remainder zirconium.

2. A zirconium based alloy as defined in claim 1, wherein said copper content is about 1.6 at. percent and said iron content is about 0.4 at. percent.

3. A zirconium based alloy constituted in accordance with claim 1, further defining a structure having improved corrosion resistance resulting from the steps of: subjecting the thus constituted alloy to an initial period of heating at a temperature of about 955° C. for a period of about ½ hour to bring alloy ingredients into equilibrium solution, quenching the thus heated alloy, and working the thus quenched alloy at temperatures below 765° C. to substantially the final form of the structure.

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