

1

2,924,518

## ZIRCONIUM ALLOYS

Thomas Raine, Bramhall, and James Alan Robinson, Bolton, England, assignors to Metropolitan-Vickers Electrical Company Limited, London, England, a British company

No Drawing. Application July 7, 1958  
Serial No. 746,605

Claims priority, application Great Britain July 26, 1957

5 Claims. (Cl. 75-177)

This invention relates to alloys suitable, inter alia, for use at high temperatures in an atmosphere of carbon dioxide.

Conditions arise, in the core of graphite moderated nuclear reactors in which carbon dioxide is used for cooling and heat extraction, where metallic parts are brought, under operating conditions, into contact with carbon dioxide at a high temperature. Normal structural materials, such as steel cannot be employed in these conditions because of their high neutron absorption.

Consideration has been given to the use of alloys of zirconium in such reactors. A known alloy of zirconium, "Zircaloy-2" which contains 1.3-1.6% tin, 0.07-0.2% iron, 0.05-0.15% chromium and 0.03-0.08% nickel, possesses good strength, and has a low neutron cross-section. But in the temperature range above 400 C. its resistance to corrosion by carbon dioxide is inadequate.

It has now been discovered, however, that when used in contact with carbon dioxide at temperatures up to 600° C. an alloy of zirconium with copper and molybdenum or chromium is both resistant to corrosion and has improved resistance to creep.

Zirconium alloys in accordance with the present invention contain 0.5-1.5% by weight of copper, and from 0.25-1.5% by weight of molybdenum or chromium, the remainder consisting wholly of zirconium, except for unavoidable impurities which are normally found in the commercial material, known as sponge zirconium, which is preferably used as the source of zirconium in the alloy.

Two alloys which constitute preferred embodiments of the invention are:

Example 1—Cu, 0.5%; Mo, 0.5%; remainder Zr

Example 2—Cu, 1.0%; Mo, 1.5%; remainder Zr

The following mechanical properties of the improved alloys in comparison with zirconium and "Zircaloy-2" are as follows:

### Hardness tests at room temperature

Alloy	Arc Melted, V.P.N.	Hot Rolled, V.P.N.	Cold Rolled, 40% Reduction	Cold Rolled, 40% Reduction and Annealed at 800° C.
Zirconium		138	190	140
Zircaloy-2	146	176	220	170
Example (1)	156	169	195	160
Example (2)	214	220	230	185

V.P.N. represents "Vickers Pyramid Number."

These tests showed the improved hardness of the alloys of the invention over zirconium and "Zircaloy-2."

Hardness tests at a temperature of 500° C. with in-

2

creasing times of load application and compared with "Zircaloy-2" showed the following results:

Alloy	V.P.N.			
	3 secs.	30 secs.	300 secs.	3,000 secs.
Zircaloy-2	60	52	38	30
Example (2)	66	61	59	56

The specimens of both alloys were annealed at 820° C. in vacuo prior to testing.

Tests made at 475° C. indicated that Example 1 alloy was slightly harder for the longest period of load application, and slightly less hard for the shorter periods of load application than "Zircaloy-2."

The tensile strength of the improved zirconium alloys of the invention at room temperature, after annealing at 820° C. showed increases over that of "Zircaloy-2." Specimens of Example 1 alloy were about 20% better, and of Example 2 alloy about 80% better than those of "Zircaloy-2," the percentage elongation of specimens of Example 1 was about the same as that of "Zircaloy-2," while that of Example 2 was about two-thirds that of "Zircaloy 2." This improvement was increased when the specimens were tested at 375° C.

Tensile creep tests at 6,000 p.s.i. the specimens being tested in an atmosphere of argon, showed the following results:

Alloy	Condition	Temp. of Test, ° C.	Time in hours to reach a strain of—			
			0.2%	0.3%	0.5%	1.0%
Zircaloy-2	Annealed at 830° C.	450	800	1,500	3,300	6,600
Do	do	475	300	600	1,040	2,240
Do	do	500	120	275	480	810
Example (1)	Annealed at 820° C.	450	860	1,960	5,500	-----
Example (2)	do	475	500	900	1,700	3,800

The increase in creep resistance of the improved alloys over that of "Zircaloy-2" was greater the higher the percentage strain.

The reaction to corrosion by CO<sub>2</sub> is illustrated by results given below of tests at 700° C. and one atmosphere gas pressure.

Alloy	Time to reach 50 mg./cm. <sup>2</sup> gain in weight, hours	Post transition Corrosion rate, mg./cm. <sup>2</sup> /hr.
Zirconium	1,200	50.1×10 <sup>-3</sup>
Zircaloy-2	150	370×10 <sup>-3</sup>
Example (1)	5,000	11.4×10 <sup>-3</sup>
Example (2)	5,000	9.4×10 <sup>-3</sup>

At a temperature of 600° C., with the same gas pressure, the improvement indicated at 700° C. was even more marked. These trends are also followed at both lower temperatures and higher gas pressures.

The work hardening properties of the improved alloys showed an improvement over "Zircaloy-2."

The thermal neutron absorption cross-section of zirconium with a low hafnium content is only slightly affected by additions of copper and molybdenum within the specified range, for example, if the macroscopic cross-section of reactor grade zirconium is taken as 0.010428

cm.<sup>-1</sup> relative to a cross-section in barns/atom of 0.20, then the corresponding cross-sections of Example 1 and Example 2 are 0.012386 cm.<sup>-1</sup> and 0.015126 cm.<sup>-1</sup> respectively.

The high temperature mechanical properties of zirconium-copper-molybdenum and zirconium-copper-chromium alloys mentioned above can be further improved by heat treatment, which consists of heating the alloy to a temperature of 850° C. to 950° C. and maintaining the temperature for a specified time before quenching to reduce the temperature of the alloy rapidly. This treatment may then be followed by a tempering treatment which consists of reheating the alloy for a specified time at a temperature below 850° C.

Arising from the ability of zirconium to oxidise and to absorb atmospheric and other impurities readily at elevated temperatures, the constituents of the alloy should be melted in a vacuum arc furnace. Apart from this restriction the alloys of the invention can be readily fabricated by conventional methods.

Impurities in the base zirconium sponge should be kept to a minimum. The most deleterious impurities from the corrosion resistance point of view are aluminium, silicon, hydrogen, oxygen, nitrogen and titanium. Aluminium should be kept below 150 parts per million, whilst nitrogen and titanium are not so injurious, and in the latter case, and titanium content may be as high as 1,000

parts per million without appreciably affecting the corrosion resistance of the alloys.

What we claim is:

1. An alloy consisting of 0.5 to 1.5% by weight of copper, 0.25 to 1.5% by weight of a metal selected from the group consisting of chromium and molybdenum, and the remainder zirconium except for unavoidable impurities.
2. An alloy as claimed in claim 1 and intended to be employed at a high temperature in contact with carbon dioxide, in which impurities, such as aluminium and titanium are restricted to the order of 100 parts per million, by weight.
3. An alloy as claimed in claim 1, in which the source of zirconium used in making the alloy is that commercially known as sponge zirconium.
4. An alloy consisting of 0.5% by weight, of copper, 0.5% by weight, of molybdenum and the remainder zirconium except for unavoidable impurities.
5. An alloy of 1.0% by weight copper, 1.5% by weight of molybdenum, and the remainder zirconium except for unavoidable impurities.

#### References Cited in the file of this patent

#### UNITED STATES PATENTS

2,705,674 Chubb ----- Apr. 5, 1955