CURRENT TRENDS IN THE USE OF ZIRCONIUM ALLOYS(*)

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The development of zirconium and its alloys for use in nuclear reactors began in the United States in 1948 when it was found that hafnium-free zirconium had a much lower neutron-absorption cross-section than had previously been suspected. Structural materials for use in water cooled Power Reactors must possess a combination of high strength, corrosion resistance, and low neutron capture cross-section. Zirconium alloys alone have the required combination of these. It will be fruitful to trace very briefly, the history of development of the Zirconium alloys.

Zirconium:

The first zirconium base cladding material used was iodide zirconium. It consists of zirconium metal in its purest commercial state, and consequently is very expensive. Furthermore, the corrosion characteristics of this material, although certainly adequate, are sensitive to handling and pickling operations.

Zircaloy-1:

The tin addition was found to counteract the deleterious corrosion effects of nitrogen, carbon and other impurities. This alloy, zirconium sponge plus 2.5 w/o Sn was known as zircaloy-1 (Table I). Experience showed that zircaloy-1 did not possess completely adequate corrosion resistance in water and steam, in that, rate of adherent oxide film build up was high and cast doubt as to adequate heat removal from zircaloy-1 clad fuel elements.

Zircaloy-2:

The next development was zircaloy-2 whose composition is given in Table I. This is a sponge base material to which has been added 1.5 w/o Sn for reasons outlined earlier, with small additions of Fe and Cr for improved

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corrosion resistance in water and steam, and a small amount of nickel for enhancing corrosion resistance in steam. This is the alloy which has seen an extensive use in the nuclear power reactors.

Zircaloy-3:

Development of zircaloy-3 (Table I) was another step and it contains 0.25% Sn and 0.25% Fe and this alloy never saw an extensive application because of its inferior corrosion characteristics.

Nickel Free Zircaloy-2:

The nickel free zircaloy-2 (Table I) was developed to counteract the bad effects of possibility of hydriding and even this alloy does not possess any significant improvement over that of zircaloy-2.

Zircaloy-4:

Bearing the above considerations in mind, zircaloy-4 containing 0.24 w/o Fe is developed (Table I) for yielding the same volume of intermetallic phases present in zircaloy-2 and also to recapture some of the steam corrosion resistance that might be lost by removal of nickel. The hydrogen absorption characteristics of modified zircaloy-4 is observed to be definitely superior to Zircaloy-2.

Zirconium-Niobium alloy

The Russian work reported at the second Geneva Conference strongly suggested that an alloy of zirconium containing 1 to 5 weight per cent niobium would have superior mechanical strength and adequate corrosion resistance. From the Russian work and early studies at AECL, an alloy containing 2.4 - 2.8% Nb and 900-1300 ppm oxygen was chosen as representing satisfactory combination of properties and is compatable with the manufacturing requirements.

a) Fabrication & Mechanical Properties:

Zirconium-niobium tubes can be produced in two ways and possess higher mechanical properties than zircaloy-2. Pressure tubes with 3.25" ID(Candu type) have been extruded and cold drawn to about 23% R.A. and the tubes produced by this route will have a minimum tensile strength of 70,000 psi (at 300^{o}C) which is about 30-40% greater than that of zircaloy-2 tube.

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An alternate method of production is to extrude, quench from about 880°C (depending on oxygen content) into water, draw to size and age at 500°C. This route will produce a tube with an UTS of 90,000 psi (at 300°C) which is about 70% greater than that of zircaloy-2.

b) Corrosion

The data reported so far indicates that the heat treated Zr-Nb is considerably better than the coldworked material and can give oxidation rates similar to zircaloy-2. From the present evidence it appears that heat-treated zirconium-niobium tubes will oxidize no more in reactor than zircaloy-2 and hydrogen pick up per unit area will be less than that of zircaloy-2.

c) Creep:

From the creep point, coldworked zircaloy-2 is definitely considered to be inferior to either coldworked or heat treated zirconium-2.5wt% Niobium.

Zirconium-Niobium-Copper Alloy

Addition of small quantities of copper to the binary Zr-2.5wt% Nb alloy gives a useful reduction to the corrosion rate in air and carbon dioxide. By suitable choice of solution heat-treatment and aging temperatures, tensile properties of the ternary alloy can be made nearly identical to those considered as optimum for the binary alloy.

Other Zirconium alloys:

Alloys such as Zr-1% Cu-1.5% Mo, Zr-1.25% Al-1% Sn-1% Mo, Zr-0.5% Nb-1%Cr have been investigated for special environment and also as possible substitutes for the Zircaloys and they are yet to gain prominence for the large scale applications in a reactor.

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TABLE I - CHEMICAL COMPOSITION OF SOME ZIRCONIUM ALLOYS

(in weight %)

Alloy type	Sn	Fe	Cr	Ni	Nb	Cu	Oxygen	Total Fe+Cr+Ni	Zirconium + permitted impurities
Zircaloy-1	2.5	-	-	-	-	-	-	-	Balance
Zircaloy-2	1.20-1.70	0.07-0.20	0.05-0.15	0.03-0.08	-	-	1000-1400 PPM	0.18-0.38	-do-
Zircaloy-3	0.2 -0.3	0.2 -0.3	500 PPM	500 PPM	-	-	-	-	-do-
Ni-Free Zircaloy-2	1.2 -1.7	0.12-0.18	0.05-0.15	70 PPM	-	-	-	-	-do-
Zircaloy-4	1.2 -1.7	0.18-0.24	0.07-0.13	70 PPM	-	-	1000-1400 PPM	0.28 min.	-do-
Zr-Nb	100 PPM	1500 PPM	200 PPM	70 PPM	2.40-2.8	-	900-1300 PPM	-	-do-
Zr-Nb-Cu	-	-	-	-	2.4 -2.8	0.5	-	-	-do-

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