Current trends in the use of zirconium alloys

K. BALARAMA MOORTHY

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. For almost a decade the standard zirconium alloy for use in water-cooled reactors has been zircaloy-2. A very considerable body of experience in the fabrication and use of zirconium alloys has been built up. It has been demonstrated that zircaloy tubes can be manufactured to specifications far more exacting in their requirements than is the case for standard code specifications for heat exchanger and condenser tubes.

Reactor experience with zircaloy both as pressure tube and fuel cladding material has been excellent. Nevertheless, because of economic incentive to reduce the pressure tube wall thickness, there has been a continuous search to find zirconium alloy of higher strength with a corrosion resistance equal to or slightly inferior to that of zircaloy.

This report will bring together and review the information available on various zirconium alloys which have been in use on a commercial scale.

Application

The most satisfactory cladding material for the uranium dioxide and for the structural material in pressurised and boiling water reactors has been[1] the zirconium alloys from considerations of neutron conservation, corrosion resistance and high temperature strength. Canada's power reactors—CANDU, NPD and PICKERING and the reactors that are being built at KOTA and KALPAKKAM are heavy water moderated and cooled, and fuelled by natural uranium dioxide.

In the case of the above mentioned power reactors, the calandria tubes are seam-welded zircaloy-2, rolled into type 304 SS calandria end plates (Fig. 1).[2] The calandria tube thickness is designed to carry the exter-

Mr. K. Balarama Moorthy, Bhabha Atomic Research Centre, Bombay.

SYNOPSIS

Reactor experience with zircaloy both as pressure tube and fuel cladding material has been excellent. Nevertheless, because of economic incentive to reduce the pressure tube wall thickness for gaining in neutron economy, there has been a continuous search to find zirconium alloy of high strength with an adequate corrosion resistance. An attempt is made in this report to review the information available and to present current thinking in the use of zirconium-niobium alloys. Because of superior properties in general, heat-treated zirconium-2.5wt niobium is gaining much importance for use as a pressure tube material in Candu type and KANUPP reactors. Since the neutron economic gain is slightly offset by extra expense involved in the heat-treated tubes, some reactor designers prefer to use cold-worked zirconium-2.5wt% niobium as a pressure tube material for Pickering type reactors.

nal static head of the moderator. The pressure tubes are seamless zircaloy-2 hot extruded and cold drawn with maximum 30% cold work. The tube thickness was based[2] on a design stress obtained from the minimum of 1/3 UTS, 2/3 YS and a stress to produce a creep rate of $10^{-5}\%$ per hour. The ends of the pressure tube are rolled into type 403 stainless steel end fittings which provide the transition from the pressure tube to the mild steel (A 106) primary circuit piping. As an example the actual requirement of zircaloy for 200 MWe Candu type reactor is given below :

Fuel Bundles	5·20 T
Calandria tubes	4·42 T
Pressure tubes	12·55 T

The ability to obtain low fuel costs in heavy water moderated natural uranium reactors require that parasitic neutron absorption in the fuel channel is minimised. According to the reported figures it is estimated that the average reactor fuelled with the natural uranium will use up about 325 dollars worth of uranium for each pound of zircaloy in reactor. A 1% reduction in the total weight of coolant tubes in the above mentioned reactors represents about 30 MWd/tonne additional burn-up from the fuel ; this is esti-
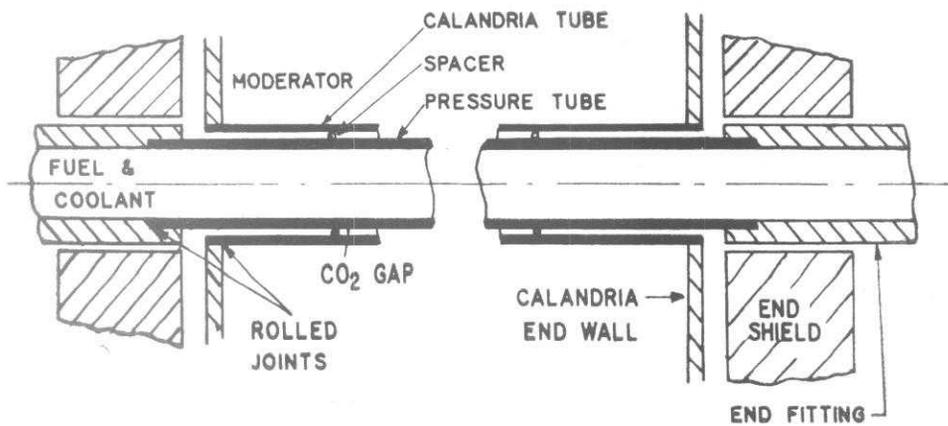
1 *Fuel channel arrangement in Candu type reactors*[2]

mated[3] to be worth about $100 000 equivalent capital. So the developments are aimed at further improvement in neutron economy. The Russian work reported at Geneva Conference suggested that an alloy of zirconium containing 1-5% Nb would have superior mechanical strength and adequate corrosion resistance.

Metallurgy of alloys

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

It was found that additions of 2·5 w/o tin to zirconium sponge metal permitted utilization directly of sponge zirconium of lower cost than iodide zirconium. 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[4] is given in Table I. This is a sponge-base material to which has been added 1·4 w/o Sn for reasons outlined earlier, with small additions of Fe and Cr for improved

TABLE I Chemical composition of some zirconium alloys

Alloy Type	Sn	Fe	Cr	Ni	Nb	Cu	Oxygen	Total Fe + Cr + Ni	Zirconium + permitted impurities
				(in weight %)					
Zircaloy–1	2·5	—	—	—	—	—	—	—	Balance
Zircaloy–2	1·20—1·70	0·07–0·20	0·05–0·15	0·03–0·08	—	—	1000–1400PPM	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	—	—	1000–1400PPM	0·28 min.	do
Zr–Nb	100 PPM	1500 PPM	200 PPM	70 PPM	2·40–2·8	—	900–1300PPM	—	do
Zr–Nb–Cu	—	—	—	—	2·4 –2·8	0·5	—	—	do

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. From the evidence built up over the past years it seems that the factor that is governing to limit the life of zircaloy–2 sheathing is the rate of hydriding. If the hydrogen is in solid solution (at the operating temperatures 300°C–100 ppm) the effect on mechanical properties is negligible, but if it is as hydride even with very small amounts, there are serious effects on the impact properties. During exposure in water-cooled reactors, zircaloy–2 can absorb hydrogen from (i) hydrogen produced in the corrosion reaction, (ii) hydrogen dissolved in the coolant and (iii) hydrogen produced by radiolytic decomposition of the coolant. It has been shown that reducing nickel content in zircaloy–2 to less than 40 parts per million decreases the rate of hydrogen pick up by a factor of about 2 to 3. Mechanical tests have shown that this change in nickel content has no significant effect on the mechanical properties.

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 effects of possibility of hydriding and even this alloy does not possess any significant improvement over that of zircaloy–2. The mechanism by which iron, chromium and nickel enhance corrosion resistance in zircaloy has not been established. It appears[5] as though best corrosion resistance is obtained in structures where the phases containing iron, chromium and nickel are finely and uniformly dispersed.

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. The data obtained clearly indicate that for reactor components exposed to water up to temperature 360°C, zircaloy–4 is superior to zircaloy–2, because of lower hydrogen absorption during hot water corrosion. Investigations showed that desirable corrosion characteristics of zircaloy–4 are retained in steam up to 400°C. For applications in steam at temperatures about 450°C and higher, the use of zircaloy–2 is to be preferred. The latest thinking and experimental results showed that at 300°C in presence of radiation, there is no significant difference in oxidation rates between Zr–2, nickel-free Zr–2 and Zr–4. The nickel-free

material oxidises more than the others at higher temperatures (>400°C). Nickel-free zircaloy–2 and zircaloy–4 pick up less hydrogen for a given amount of oxidation than zircaloy–2.
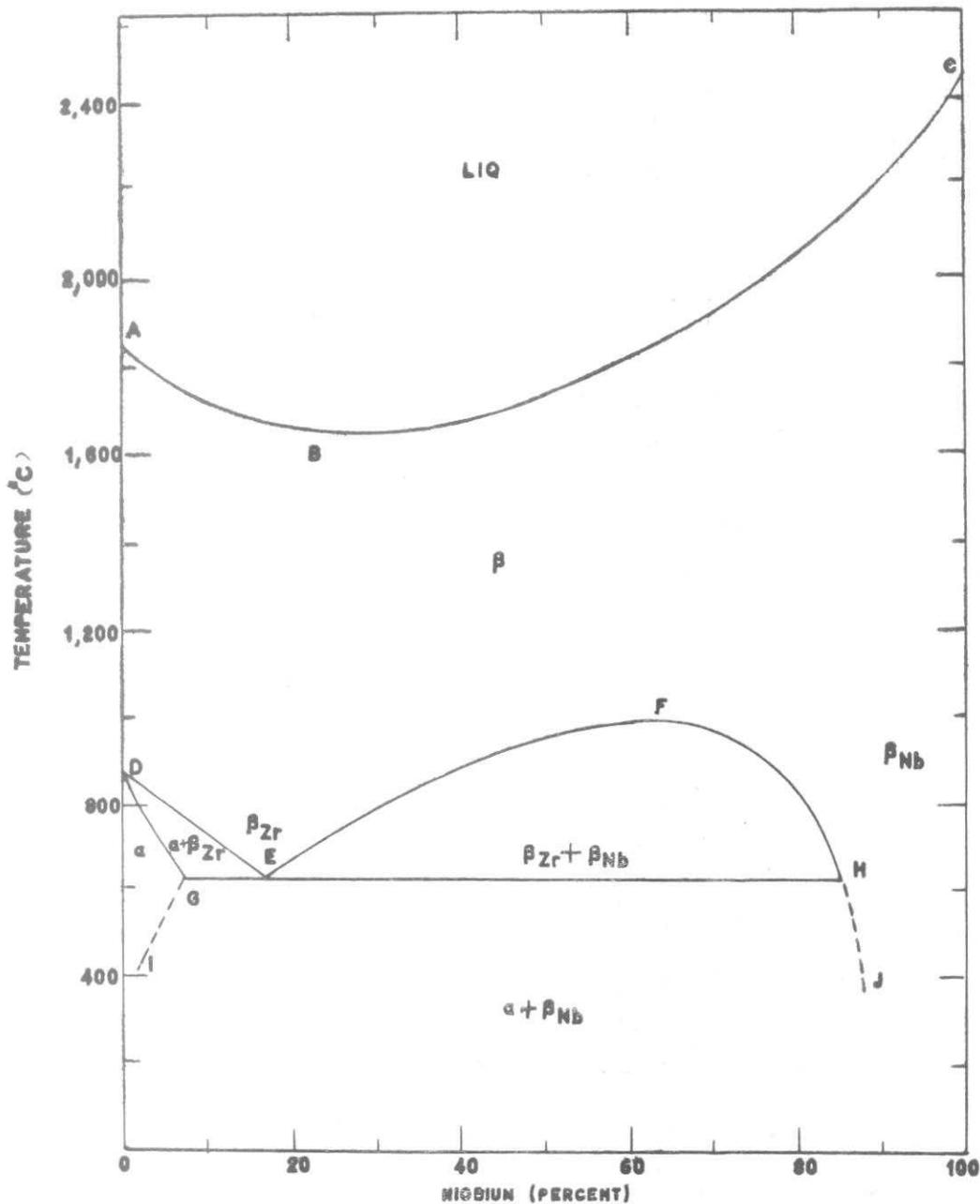
Zirconium-niobium alloy

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. The metallurgy of zirconium-niobium is complex and the generally accepted phase diagram is as given in Figure 2.[6] The zirconium-niobium phase diagram was investigated by Rogers and Atkins. This system is characterised by complete solid solution in the beta phase (B.C.C.) above 1000°C with a monotectoid reaction occurring at 610°C and 17·5% Nb. This reaction yields an alpha zirconium phase (H.C.P) and a niobium-rich beta phase. All conventional zirconium-niobium alloys contain oxygen. Increasing the niobium content increases both as-quenched hardness and the aging response. On the other hand increasing the two constituents decreases the ductility and corrosion resistance. The main effect of oxygen is to increase the alpha plus beta to beta transformation temperature and the effect[7] is as shown in Fig. 3. Experimental work has shown that the transformation temperature is given[8] empirically by the equation

$$T = 871 + 0·8 \ (A - 1000)°C \text{ where A is oxygen content}$$
$$\alpha + \beta + \beta \text{ in ppm.}$$

As such it is important to know the oxygen concentration in the alloy. As is seen from the phase diagram the zirconium-niobium is a heat-treatable alloy with a complex transformation product. 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 compatible with the manufacturing requirements. When an alloy containing 2·5% Nb is rapidly quenched from beta phase, a martensitic type of transformation occurs to alpha zirconium containing niobium in supersaturated solution. This also leads to beta grain growth and a low ductility in the quenched and aged alloy. In addition, the beta quenched alloy is much more susceptible to irradiation embrittlement. It has been observed experimentally that good behaviour is shown by the material which has been quenched from the alpha plus beta phase, cold-worked and aged in high alpha region (500–600°C). Worst behaviour is shown by materials slow-cooled through the alpha plus beta region. The mechanism of the heat treatment is under study and it has been shown that a martensitic transformation during quenching and precipitation during aging are responsible[8] for hardening.

Fabrication and mechanical properties

To date all zirconium niobium alloys have been made

2 *Zirconium-niobium phase diagram*

from reactor grade sponge and no difficulties have been met in meeting the same impurity specifications that exist for zircaloy-2. Zirconium-niobium tubes can be produced in two ways and possess higher mechanical properties than zircaloy–2. Pressure tubes with 3·25″ I.D. (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°C) which is about 30-40% greater than that of zircaloy–2 tube.

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. Average tensile properties of the materials of CW and HT Zr–2·5% Nb and CW Zr–2 are summarised in Table II.

Corrosion

The corrosion rate of cold-worked zirconium-niobium
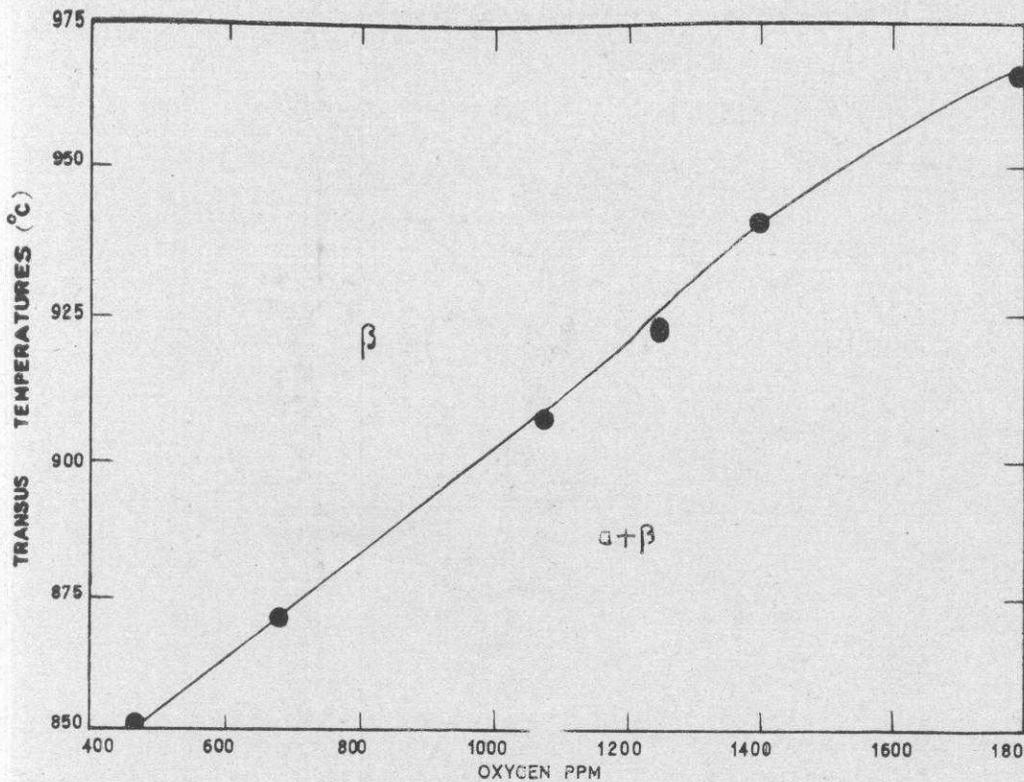
3 *Alpha beta to beta transus temperatures Zr–2·5% Nb*

TABLE II Average tensile properties at 300°C[7]

|	Zircaloy-2*	C.W. Zr-2·5% Nb	H.T. Zr-2·5% Nb
Yield Strength-0·2% offset (PSI)			
Uniaxial longitudinal	45 000	54 000	69 000
,, transverse	47 000	—	85 000
Biaxial	56 000	—	92 000
Ultimate strength (PSI)			
Uniaxial longitudinal	53 000	75 000	88 000
,, transverse	51 000	81 000	98 000
Biaxial	61 000	86 000	1 06 000
Elongation %			
Uniaxial longitudinal	22·5	12–16	16
,, transverse	21	10–14	6–10
Increase in diameter at burst %			
Biaxial	15–20	2–4	2–3
Reduction in area %			
Uniaxial longitudinal	45	53	45
,, transverse	60	52	36
Biaxial	25–30	29	11–19

*Values are at 280°C

at 300°C is 2 to 4 times that of zircaloy-2. The corrosion rate of heat-treated material as mentioned earlier is dependent on the structural condition. It was repor-ted that quenching from beta phase field gave inferior corrosion resistance to quenching from the alpha plus beta field. Cold-working between quenching and aging appears[7] to have an effect on the transformation products which improve the corrosion resistance. The best treatment would be to quench from the alpha plus beta region ; cold-work to 20–30% followed by tempering for 24 hours at 500°C. Unlike zircaloy-2, zircouium-niobium alloys have very poor oxidation resistance in air. In the presence of radiation, the material seems to be resistant to presence of oxygen in the pre-transition oxidation stage. Hydrogen pick up is less than zircaloy-4 for the same amount of oxidation. The data reported so far indicate that the heat-treated Zr-Nb is considerably better than the cold-worked 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.

Creep[7]

At power reactor conditions of 3×10^{13} n/cm² 14000 psi and at 280–300°C the creep rate will be $1·8 \times 10^{-7}$ in./in.hr for zircaloy-2 and the tube can be expected to reach 1% increase in diameter in about 7·5 years. For cold-worked Zr-2·5% Nb at the same operating conditions, 1% would be reached in about 15 years. In fact, it is recently reported[12] on the basis of a few experimental results that the period of 15 years is a pessimistic

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--- Zr-2·5 wt.%Nb, QUENCHED FROM 880°C AND AGED AT 500°C

—— ZIRCALOY-2 15% COLD WORKED
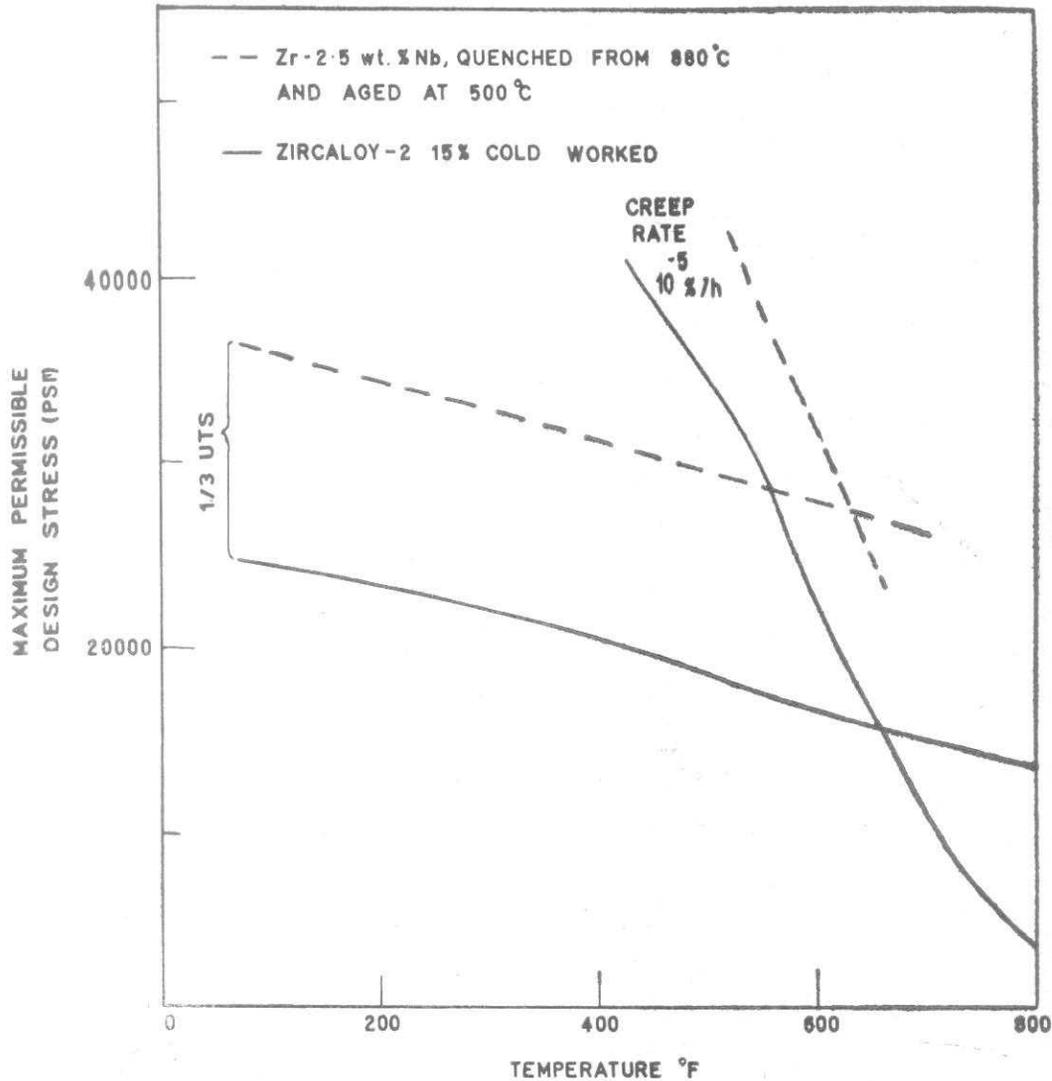
4 *Design stresses for zircaloy-2 and zirconium 2·5 per cent niobium*[2]

figure and it is postulated that 1% increase would only occur in 25–30 years.

It appears from the postulated data that the creep rate would be one half that of cold-worked for heat-treated tubes. That is, 1% increase in diameter would be reached in over 30 years.

From the creep point, cold-worked zircaloy-2 is definitely considered to be inferior to either cold-worked 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. One effect of the copper addition, however, is to give[9] marked changes in the aging kinetics of the alloy. One half weight per cent addition of copper to the binary zirconium-2·5wt% niobium alloys avoids preferred orientation of hydride platelets which is a serious disadvantage of zircaloy-2. In case of Douglas point and RAPP—1

reactors, this ternary alloy has been chosen as the material of 'spacers' between calandria and coolant tubes. This application utilizes both the corrosion resistance to a moist air-carbon dioxide environment and the strength developed by a quench and age heat-treatment. 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

It has been reported[10] that Zr-0·5% Nb-1% Cr alloy exhibits high corrosion resistance and low hydrogen pick up in water at 360°C and also in steam at 400°C. An analysis of the results obtained on this alloy shows that its mechanical properties at room temperature and at elevated temperatures are superior to those of zircaloy-2 and comparable to those of Nr-2·5wt% Nb. The creep rates of Zr-2·5wt% Nb and ternary alloy Zr-0·5% Nb-1% Cr are comparable.

TABLE III Relative merits of C.W. Zr-2. C.W. Zr/Nb and H.T. Zr/Nb[7]

Alloy/ Property	Corrosion	Short term strength	Stress rupture	Fatigue	Out-pile creep	In-pile creep	Energy to fracture unirr. and no hyd.	Energy to fracture irrad. and hyd.
C.W. Zr-2	A	C	C	B	A	C	C	C
C.W. Zr/Nb	C	B	B	B	A	?	C	C
H.T. Zr/Nb	BA	A	A	A	A	BA	B	C

A = Good   B = Medium   C = Poor

Additions of up to 3% V and 3% Cu to zirconium gives[11] an alloy useful in reactors cooled with pressurised CO_2. Corrosion and creep resistance, strength and neutron capture cross-sections are superior to pure zirconium.

Other alloys such as Zr-1% Cu-1·5% Mo ; Zr-1·25% Al-1% Sn-%Mo 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.

Summary and conclusion

Out of the zirconium-base alloys, the binary alloy Zr-2·5wt% Nb presently shows good promise in the power reactor programme. A table can be drawn to compare the various properties of the three alloys—cold-worked Zr-2, cold-worked Zr-2·5wt% Nb and heat-treated Zr-2·5wt% Nb (Table III). On the basis of the survey the heat-treated zirconium-niobium appears to be the best choice for a pressure tube material. Since the neutron capture cross-section of the Zr-2·5wt% Nb alloy is nearly identical to that of zircaloy-2, significant gain in power reactor neutron economy could be obtained by replacing stressed in-reactor components of zircaloy-2 with the heat-treated Zr-Nb alloys. The higher strength of the heat-treated tube offers a reduction in tube wall thickness of nearly 40% which represents a significant improvement in neutron economy. The same can be easily realised from the design considerations (Fig. 4).[2] Because of the aforesaid advantages, heat-treated Zr-2·5wt% Nb is the selected pressure tube material in the Canadian BLW reactors.

Some of this economic gain is offset by extra expense required for the heat-treatment process. Further results on creep experiments on cold-worked Zr-2·5 wt% Nb if conformed to be of same order as that of heat-treated Zr-2·5 wt% Nb, it is quite likely cold-worked zirconium-2·5 wt% niobium will be the choice for pressure tube material for pickering type reactors.

Acknowledgements

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