Zirconium alloys in nuclear technology

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Abstract. This paper describes the historical development of zirconium and its alloys as structural materials for nuclear reactors. The various problems encountered in the early stages of the development of zircaloys and their performance in reactors operating presently are described in detail. The development of Zr-2·5% Nb alloys for pressure tube applications is discussed. The paper concludes with a detailed discussion on the development potential of zirconium alloys for high temperature applications and a brief account of the work carried out at Trombay in this field.

Keywords. Zirconium; zirconium alloys; structural materials; nuclear reactors; corrosion; high strength alloys.

1. Introduction

The development of zirconium metallurgy is essentially due to the nuclear industry, where zirconium alloys have come to be regarded as the proven structural material. This is primarily because of their unique combination of good corrosion resistance in water near 300°C and low capture cross-section for thermal neutrons (Douglass 1971). It is quite likely that the application of zirconium in the nuclear industry will remain its dominant use. This paper begins with an account of the present day use of zirconium alloys in the nuclear industry mainly to acquaint non-nuclear technologists with the various sizes, shapes and functions of such structural materials. Then the history of the development of presently accepted zirconium alloys—zircaloy-2 and zircaloy-4—is given some consideration. A discussion on the development of high-strength zirconium alloys follows and the paper concludes with a brief account of the work being done at Trombay.

2. Current applications

There are two types of water-cooled power reactors. In the first, the whole reactor core is enclosed in a large steel pressure vessel in which one fluid, usually ordinary water, is both the heat transfer medium and neutron moderator. Such a reactor is based on the pressurised water reactor (PWR) and boiling water reactor (BWR) concepts, where zirconium is used for the cladding tubes which encase the uranium dioxide fuel pellets. The reactor operating at Tarapur near Bombay is an example of the BWR reactor.

In the second, the pressure vessel is replaced by a large number of tubes each conveying either light or heavy water coolant over an individual fuel element. These

pressure tubes pass through a calandria tank containing cool, heavy water moderator. The pressure tube is separated from the surrounding calandria tube by a gas gap which insulates the moderator from the hot coolant. Operating reactors of this type are the pressurised heavy water-cooled CANDU-PHW and the boiling light water-cooled CANDU-BLW and the British steam-generating heavy water reactor SGHWR. The nuclear power station at Rana Pratap Sagar at Kota in Rajasthan is an example of the CANDU-PHW system. In these reactor systems, the fuel-cladding tubes, the pressure tubes and sometimes the calandria tubes are all made of zirconium alloy.

Fuel-cladding tubes are thin-walled (0·4 to 0·8 mm) and experience a complex sequence of heterogeneous tensile, creep and recovery strains during their operating life of 15,000 to 30,000 hr. The pressure tubes in CANDU reactors are 103 mm ID and the minimum wall thickness is in the range of 2·4 to 5·1 mm depending on the strength of the alloy and the operating conditions (Ross-Ross 1968). Tubes for the SGHWR are of 130 mm ID and a minimum wall thickness of 5 mm (Watkins & Cockady 1965). These pressure tubes are subjected to the full coolant pressure (55–60 bar in SGHWR, CANDU-BLW and 85–90 bar in CANDU-PHW) and coolant temperature of 200–300°C. Unlike the fuel-cladding tubes, these tubes experience a simple biaxial stress system with a hoop-to-axial stress ratio of approximately 2:1. The tubes must have very high integrity throughout a plant life perhaps exceeding 200,000 hr. Although failure can be tolerated and faulty tubes replaced, it is very expensive.

The zircaloy calandria tubes typically have a wall thickness of 1·24 mm and 107·7 mm ID, in a CANDU-PHW system. These tubes are generally fabricated from rolled sheets by seam welding. The demands made on zircaloy calandria tubes are less exacting than those made on fuel or pressure tubes (Cheadle 1977).

3. Historical development

The decision to use zirconium in a nuclear reactor was essentially due to Admiral Rickover of the US Navy (Rickover 1975). He was in charge of the development of nuclear-propelled ships and submarines. The reactor for navigation had necessarily to be compact and had to operate when the ship was rolling or pitching or at an angle, when the submarine was diving or surfacing. Thus a pressurised water reactor (PWR) was envisaged, and hence a metal which would withstand corrosion at high temperatures for long periods of time, which would maintain its integrity in an environment of intense radiation and which would not absorb neutrons required for the nuclear reaction, was needed. The availability of the metal in sufficient quantities and at reasonable cost would be the additional consideration. Stainless steel, beryllium and aluminium all had disadvantages which weighed against their use. Zirconium also did not appear promising as it was expensive and not produced in quantity. Initial tests with zirconium showed that it absorbed neutrons needed for the fission process. It was discovered later that naturally-occurring zirconium contained about 2% by weight of hafnium, which gave zirconium the high level of absorption cross-section for neutrons. Kaufman at MIT and Pomerance at Oak-Ridge came out with laboratory successes in separating hafnium from zirconium and showed that zirconium in its pure form absorbed only a few neutrons. These early promises

led Admiral Rickover to decide that zirconium would be the reference core structural material for the Mark I PWR in the Idaho prototype and for the Mark II reactor being built for the nuclear submarine, Nautilus.

Though the decision was taken by the U. S. Navy to use zirconium as the reactor structural material, no technical specifications had been elaborated. The only thing they knew was that the metal should be 'as pure as possible' and the minimum strength limits were to be 'as strong as possible without increasing the hardness'.

Naturally, the choice fell on the crystal-bar process (also called the Van-Arkel-DeBoer Process) for the production of high-purity zirconium. This process is essentially a refining rather than a metal reduction technique. In this process zirconium tetra-iodide is formed at the surface of a bed of impure metallic zirconium maintained at low temperature (approximately 400°C) by reaction with free iodine and is decomposed at the surface of a hot (approximately 1400°C) filament, depositing pure zirconium on the filament and liberating iodine vapour to react again with the impure zirconium. The end product was designated as the 'crystal bar' because of the bright surface and the external shape of the grains that grew on the filament.

When crystal bar zirconium was corrosion-tested in high temperature water autoclaves, it was found that corrosion-resistant material became black after testing, while non-corrosion resistant samples became white, the different appearances being related to the thickness and physical nature of the zirconium oxide corrosion product film. Initial experiments with crystal bar zirconium showed a bewildering variety of corrosion test behaviour. This led to the problem of detecting and measuring the culprit impurity elements in zirconium. It was found that if the refining process could be carried out under sufficiently 'antiseptic' conditions, a reproducible high level of corrosion resistance could be obtained.

At this stage, the decision was taken to use a purer grade of sponge zirconium as the raw material (for crystal bar), which had then become possible by the Kroll process. In the Kroll process, zirconium tetrachloride vapour, prepurified by sublimation, is brought into contact with the reductant, molten magnesium, using precautions to exclude air during all critical operations. The use of this high-purity raw material coupled with improved operating practices and procedures resulted in an improved yield of corrosion-resistant product.

Every one connected with zirconium technology knew that continued purification of the product was not necessarily the correct path. In fact, it was then observed that the crystal bar stock received from two different sources did not behave in a similar manner. Contrary to expectations, it was found that the corrosion resistance of the purer material was lower than that of the impure crystal bar. It was argued that the pick-up of impurity elements like iron, chromium and nickel might be helpful in imparting corrosion resistance to zirconium. Even with intentional additives, zirconium showed poor corrosion resistance in the presence of nitrogen. It was ultimately decided that refining the Kroll sponge into crystal bar zirconium might not be the right step and thus the programme of development of Kroll-process sponge-base alloys was started.

4. Development of zircaloys

The first stage in the development of zirconium alloys was to identify those elements which improved the corrosion behaviour of Kroll sponge zirconium to a level apparently equivalent to that of the good quality crystal bar. These elements were tin, tantalum and niobium, which, in decreasing order of effectiveness, circumvented the damaging effect of the impurities present in the sponge then available. Tin as an alloying addition was selected for intensive investigation because it was most effective in imparting corrosion resistance without seriously affecting the neutron economy. The level of addition which at one time was as high as 5 wt% was reduced to 2·5 wt%, as a good compromise between corrosion resistance, strength and fabricability. This alloy was designated as zircaloy-1. Samples of zircaloy-1 were subjected to long-term high temperature water corrosion testing and soon a disturbing trend became noticeable. Instead of continuing to corrode at a decreasing rate with increasing time, the corrosion rate at a specific time (breakaway or transition time) increased and remained essentially constant thereafter. This transition time for zircaloy-1 was not much greater than the time at which unalloyed sponge would begin to show white non-adherent oxide corrosion product. Thus an immediate halt was called to the processing of zircaloy-1 and an urgent search for an alternative was started.

Around that period, the important effect of iron additives on the corrosion behaviour of zirconium had been established. In fact a melter in the Bettis fabrication shops had melted a zircaloy-1 ingot which had become contaminated with stainless steel and the resultant material proved to have an outstanding corrosion resistance. Subsequent experiments with nickel additives also confirmed its beneficial effect. Thus the next step was to choose an alloy composition that would confer major corrosion resistance and permit the use of the fabrication experience gained with zircaloy-1. Thus in selecting the composition, the iron content was nominally set at 0·15% mainly because of the range of iron present in the then available Kroll sponge. A nominal nickel level of 0·05% was chosen because of the beneficial effect of nickel on high temperature corrosion resistance. Chromium is picked up as an impurity from the stainless steel reacting vessels and thus its content was kept at 0·10%. For tin, unlike in zircaloy-1, a nominal level of 1·5%, which was found to be adequate to counteract the deleterious effects of nitrogen, was suggested. This new alloy composition, designated zircaloy-2, was found to have tensile properties equal to those of zircaloy-1 but much better high temperature corrosion resistance. Table 1 gives the alloying additions in zircaloys.

Table 1. Compositions of zircaloys

Alloy	Mean composition in weight %			
	Sn	Fe	Cr	Ni
Zircaloy-1	2·5	—	—	—
Zircaloy-2	1·5	0·12	0·10	0·05
Zircaloy-3	0·25	0·25	—	—
Zircaloy-4	1·50	0·22	0·10	—

Though zircaloy-2 performed satisfactorily, there was a fear that with increase in reactor core lifetimes, the detrimental effect of the high tin content of zircaloy-2 would reveal itself. In fact tin was originally added in zircaloy-1 with the belief that it was a good corrosion inhibitor, but this belief proved ill-founded. Thus it was decided to limit the tin content to the amount just necessary to counteract the nitrogen levels present in the sponge, as well as to tramp nitrogen levels picked up during melting. So Zr with 0·25% Sn and 0·25% Fe was recommended as the most corrosion resistant composition in the family of zirconium alloys. This alloy was designated as zircaloy-3.

During corrosion testing, zircaloy-3 showed a network of fine white corrosion indications, which were identified as stringers of Fe-Cr intermetallic compounds. The stringers formed as a result of the fabrication of the material in the two-phase alpha plus beta region which exaggerated the agglomeration of the intermetallic phases. Though the formation of stringers could be avoided by altering the fabrication temperatures, it was found that with the introduction of the vacuum arc melting of zirconium (as compared to the induction melting practised earlier), the stringers vanished totally. However, the lower mechanical properties of this alloy compared to zircaloy-2 contributed to its abandonment.

Right at that time, the far-reaching effect of hydrogen on the mechanical properties of zirconium and its alloys became more evident, when notched bar impact testing was initiated. Samples that yielded low impact values showed the presence of crystallographically-oriented zirconium hydride platelets which were absent in normally behaving samples. Analysis of zircaloy specimens showed the inter-relations between hydrogen content and embrittlement in notched impact tests. It was estimated that the tolerance level of hydrogen in zirconium could be around 250 ppm. During investigations on eutectic diffusion bonding techniques for the development of plate type fuel elements, it was found that when zircaloy-2 sheets were coated with nickel, hydrogen absorption increased considerably. A suggestion was then made to eliminate the 0·05% nickel addition in zircaloy-2 and this alloy then came to be referred to as 'nickel-free zircaloy-2'. This alloy was however found to have inadequate corrosion resistance. The choice was then to increase the iron content. Thus a new composition of the alloy with 0·18 to 0·24% Fe, 0·10% Cr and 1·5% Sn was arrived at and this was designated as zircaloy-4. It was found to retain almost as good steam corrosion resistance as zircaloy-2 while exhibiting one-half of the hydrogen absorption.

5. Performance of zircaloys

The zirconium alloys—zircaloy-2 and zircaloy-4 have become the widely accepted structural material in operating reactors at present. Typical properties of zircaloy-2 at 300°C are shown in table 2 (McDonald 1971). The differences in the ratios of yield-to-tensile, transverse-to-longitudinal, and transverse-to-biaxial strengths partly reflect differences in the crystallographic textures of these alloys. The highly anisotropic deformation behaviour of zirconium leads to pronounced textures in fabricated components, depending on the alloy and the fabrication and heat-treatment history. For zircaloy tubes, the texture is such as to inhibit wall-thinning during biaxial stressing, resulting in large circumferential expansion and some axial contraction prior to

Table 2. Typical tensile and burst properties of zircaloy-2 pressure tube material at 300°C

Alloy autoclaved 72 hr, 400°C	Test	0·2% yield stress 10^3 psi	UTS 10^3 psi	Elongation %
15–20% cold drawn zircaloy-2 103 mm diameter	Long.	45	54	26
	Trans.	50	52	23
	Burst	60	63	26–36
30% cold drawn zircaloy-2 130 mm diameter	Long	51	54	20
	Trans.	48	50	20
	Burst	—	67	20

failure. Thus the texture developed in zircaloys is beneficial to biaxial ductility and to biaxial relative to uniaxial strength. This implies that the fuel tube with such a texture will bulge considerably before it fails. As a result, considerable progress has been made in elucidating the formation of textures and their role in deformation behaviour. However, the desired degree of control of texture formation appears to be difficult.

The major problem in the use of zirconium alloys is hydrogen absorption (from the metal/water reaction) and consequent embrittlement (Ells 1968). It was believed that this could impose the main design limit on zirconium alloys. However, it is now clear that severe embrittlement under tensile loading conditions is observed mainly near room temperature and when the hydride plates are oriented near normal to the applied stress. The conditions producing preferential orientation of plates have been identified and can be controlled. In tubes, circumferential alignment of plates parallel to the operating hoop stress is ensured by avoiding unsupported sinking operations during fabrication. However, a desire to limit the total hydrogen uptake to 300–400 ppm is still a consideration in the selection and processing of zirconium alloys. In this context, it should be stated that stress-assisted hydride precipitation (in service) may lead to severe embrittlement problems at room temperature.

Zirconium alloys harden under irradiation and the extent of hardening depends on the prior metallurgical structure, including dislocation arrangements and the nature and distribution of second-phase precipitates (Williams 1970). The main manifestation of embrittlement by hydride and irradiation, is in a loss of fracture toughness of notched, impacted specimens. The transition temperature from low to high energy absorption is shifted from below room temperature to 200–300°C.

The most important effect of fast neutron irradiation on zircaloys is the increase of the secondary creep rate at 220–350°C by 5 to 10 times. This phenomenon had not been recognised in the PWR pressure tube design but has been studied in great detail in recent years (Nicohls & Watkins 1968; Watkins 1970; Ibrahim 1969).

6. Development of Zr-Nb alloys

In the development of improved alloys for 300°C application, a fair amount of success has been achieved with Zr-2·5 wt% Nb alloy, particularly for pressure tube

applications. It has been used in two conditions (Douglass 1971; Watkins & Cockady 1965), hot extruded at 840°C, then cold-drawn 15–20% or hot extruded, quenched from 880°C, cold-drawn 3–15% and aged for 24 hr at 500°C. In the latter form, it is the strongest of the established zirconium alloys. However, unlike zircaloy-2, in which texture strengthening has played a decisive role by increasing circumferential ductility under biaxially stressed conditions, in Zr-2·5 Nb alloys, the texutres developed in the two conditions appear less attractive and in fact can nullify some of the gain from their higher uniaxial strengths. In this case, wall-thinning is enhanced during biaxial stressing and failure occurs at low circumferential strain. Further, Zr-2·5 Nb solution treated and quenched from the beta phase field is particularly susceptible to irradiation embrittlement (Ells & Williams 1969). Another observation is that the heat-treated Zr-2·5 Nb tubes creep in-pile almost twice as fast as the cold-worked material, in spite of higher uniaxial and biaxial strengths and slower out-of-pile uniaxial creep. This is an important consideration in alloy development. This observation is explained on the basis of texture in these tubes (Ibrahim 1969): grains have basal plane poles parallel to the tube axis, which is absent in the cold-worked tubes. In addition to the texture effect, the neutron flux appears to have a greater effect on heat-treated as compared to cold-worked Zr-2·5 Nb. Since deformation by irradiation creep and growth is known to be dependent on the metallurgical structure (texture, dislocation density and grain structure) of the pressure tubes, ways of altering the structure by modifying the fabrication route and heat treatment schedules have to be found, to improve the stability of the alloy under irradiation (Fleck 1969).

7. High temperature applications

Considering the performance of zircaloy-2 and 4, and Zr-2·5Nb, in presently operating reactors, it is very unlikely that these alloys can be surpassed in either corrosion resistance or neutron capture cross-section at 300°C. The creep strength of these alloys however diminishes rather rapidly with increasing temperature and above 350°C becomes the criterion for selecting a design stress. To improve the station efficiency and the capital cost, the temperature of the coolant tube must be raised significantly to temperatures above 450°C. The prospects for development of zirconium alloys for high temperature applications are quite promising and attempts are being made in several laboratories to develop such high temperature alloys both for cladding and pressure tube applications.

For pressure tube applications, it is necessary to have an alloy which has the following properties at a temperature of at least 450°C (Thomas 1969)

  (i) a minimum stress of 210 to 280 MPa (34 to 45 kpsi) as one third of the UTS,
 (ii) a maximum creep rate of 10^{-7} hr^{-1} after 5000 hr at a stress of 62 to 74 MPa (10 to 12 kpsi),
(iii) a minimum of 155 MPa (25 kpsi) as the stress to rupture in 100,000 hr,
 (iv) a neutron capture cross-section not significantly greater than that of zircaloy-2.

However, most of the high-strength zirconium alloys have poor corrosion resistance and it would be necessary to clad these with a corrosion resistant alloy. This

would obviously mean complex production processes and costs but then this would have to be balanced against the rewards of higher efficiency.

There are many similarities between the physical properties and metallurgy of titanium and zirconium and their alloys. Alpha titanium has a higher shear modulus than alpha zirconium. The Young's modulus values also show an advantage over titanium. These differences indicate that titanium alloys may develop slightly higher tensile and creep strengths than zirconium alloys. The other important parameter to be considered is the self-diffusion coefficient. Calculated diffusivities suggest that alpha zirconium may have a higher creep resistance than alpha titanium in the temperature range where steady-state creep occurs by dislocation climb, a diffusion-controlled process. However, such comparisons are only of limited value when alloying additions are made to the metal, and structural differences are introduced by fabrication processes. However, the data support the view that zirconium alloys should be capable of providing mechanical properties similar to those of titanium alloys.

Initial experiments on the effect of several alloying additions on the properties of zirconium have shown that to achieve high yield strength at 500°C, the most effective additives are the alpha stabilisers Al and Sn and the beta stabilisers Mo and Nb. Al and Sn are reasonably soluble in zirconium compared with other alloying elements and provide solution strengthening upto about 850°C. Mo and Nb have only a limited solubility in zirconium and their strengthening effect is due to a dispersion of fine precipitates which can be achieved by quenching and ageing treatments. Increased strengthening is obtained in ternary alloys containing combinations of alpha+beta stabilizing additions so that both solution and precipitation hardening contribute. Table 3 gives the tensile properties of some selected ternary and quarternary alloys of zirconium and indicates the systems worth studying (Thomas 1969). It appears that the required objectives may be reached by the ones containing 3 to 4 wt% Sn and 1 to 2 wt% Mo or the ones containing 1 to 2 wt% Al and 0·5 to 1·5 wt% Mo. The creep behaviour of these will have to be taken into account in the final selection.

The alloying additions that can be made to zirconium have to face the constraint of not increasing the neutron capture cross-section. The increment in cross-section for each 1% of alloying addition (Thomas 1969) indicates the penalty in neutrons associated with each element (table 4).

In the development of a new alloy, in addition to strength requirements, one major concern is corrosion resistance. Thus even though Al is a more effective strengthener

Table 3. Tensile properties of various zirconium alloys, normalised to 450°C

Alloy composition wt%	Treatment	UTS kpsi	% Elongation
Zr-3 Al-3 Sn	Annealed at 650°C	82	10
Zr-3 Sn-1·5 Mo	Air cooled from 900°C	96	10
Zr-3·7 Sn-2 Mo	β-quenched/aged	110	10
Zr-5Nb-2 Sn	(α+β) quenched/aged 8 hr at 482°C	130	5
Zr-1·5 Al-1·5 Mo	Hot worked and annealed at 790°C	70	20
Zr-3 Al-1·5 Sn-1·5 Mo	Hot worked and annealed at 790°C	90	20
Zr-1·5 Al-0·5 Mo	(α+β) quenched	112	2

Table 4. Increase in thermal neutron capture cross-sections of zirconium due to 1 wt% alloy addition

Element	Cross-section increase Σ_c cm^2 per cm^3
Sn	0·00019
Mo	0·00089
Nb	0·00037
V	0·00335
Sb	0·00174
Si	0·00114
Al	0·00012

than Sn, zirconium alloys containing Al have extremely poor corrosion resistance. (In fact, the composition specifications of zircaloys indicate a maximum permissible level of 75 ppm for aluminium). Thus a Zr-Sn alloy could be a preferred base. Further, limits set by neutron capture cross-section, solubility limits of the individual elements and the prospect that good creep strength would be promoted by a combination of alloying elements that give rise to intermetallic compounds, has led the Canadian Group to suggest the following range of alloys for testing as pressure tube materials: Zr with 2 to 4 wt% Sn, 0·5 to 1·5 wt% Mo, 0·5 to 2 wt% Nb, 0·5 to 1·5 wt% Al and 0·5 wt% Si. The precaution to be taken in this case is that such alloys cannot be used unclad.

It would be appropriate at this stage to refer to the work of scientists from UK and Scandinavia on the development of new zirconium cladding alloys (the ' SCANUK ' alloys) (Tyzack *et al* 1977). The reasons given by them for their choice of alloy composition and the results obtained by them can be stated as follows:

Improvements in corrosion resistance and mechanical properties would be obtained by alloying zirconium with elements selected from group V A and VI A and possibly group VIII A of the Periodic Table. Another alloying element of proven worth in the context of 300°C fuel element operation is tin, particularly in counteracting the effects of nitrogen. Tin appears to maintain a mildly beneficial influence on corrosion upto ~350°C but in 450°C steam and at higher temperatures, particularly at high pressures, its presence becomes significantly detrimental. The binary alloy systems of zirconium with the elements of the above 3 groups are either of the form in which the β phase extends over the whole composition range with no intermetallic phases (*e.g.* Nb, Ta) or of the eutectoid type including intermetallic phases (*e.g.* V, Cr, Mo, W, Fe, Co, Ni, Cu). The solubility of these elements in alpha zirconium is very limited and the likelihood of appreciable solid solution hardening is very small. However, one could take advantage of the possibility of dispersion strengthening by eutectoid decomposition since both the tensile strength and creep resistance can be improved at temperatures $\leqslant 500$°C by precipitation of finely-dispersed intermetallic phases. The hardening introduced in this way can be greater than that due to solid solution. A further approach would be to base the strengthening process upon a martensitic transformation. It is thus possible to produce the desired tensile or creep strength by controlling the range of alloying additions, but designing for ductility is much more difficult and a reasonable balance between tensile strength and ductility is to be made. Another aspect which should be borne in mind is that any high

temperature homogenising treatments followed by quenching and tempering should be done at the billet stage rather than on the tubing to avoid distortions in the finished product.

The 'Scanuk' alloy compositions are shown in table 5. The texture of the Scanuk alloy tubes was similar to that of commercial zircaloy-2 tubes. The UTS values at 25°C for the different alloys are also given in table 5. One can see that the mechanical properties of 'Scanuk' alloys compared favourably with those of zircaloy-2 and in some respects represented an improvement. These alloys had higher strengths than zircaloy-2 in the temperature range of 250–400°C and the decrease in strength with increase in temperature was much less severe—alloys 3 and 4 were the best in the sense that their strength at 300–400°C exceeded that of zircaloy-2 by some 15–25%. Alloy 4 showed more resistance to hydrogen absorption than zircaloy-2. The hydride precipitates were very small and were found to be circumferentially oriented. All these alloys showed markedly lower oxidation rates than zircaloy-2. It may be possible to improve the 'Scanuk' alloys with further study and optimisation.

8. Zirconium metallurgy at Trombay

The Metallurgy Division, Bhabha Atomic Research Centre, Trombay, Bombay has been carrying out programmes on zirconium and its alloys, mainly to understand the physical and mechanical properties of pure zirconium and its alloys, which would lead to the development of newer alloys with improved properties for nuclear applications (Asundi 1973). A brief resume of the work carried out at Trombay is given below.

In zirconium alloys, microstructural control by thermal and mechanical processing is of particular importance since the selection of alloy composition is severely restricted by neutron absorption considerations. In general, the most suitable mode of strengthening for a given alloy system is dictated largely by the relevant phase diagram. Thus age hardening could be employed in systems where the solid solubility is strongly temperature-dependent, martensitic strengthening in alloys which undergo an allotropic transformation, hardening through the creation of the numerous interfaces associated with a two-phase lamellar aggregate in eutectoid systems, and order hardening in systems where an ordering reaction occurs. Fortunately, it is possible to invoke one or the other of the known methods of microstructural strengthening in

Table 5.   Scanuk alloy compositions and UTS values at 25°C

Alloy	Nb	Fe	Sn	Cr	Mo	Ni	Oxygen	UTS at 25°C kg/mm^2
1	0·91	0·026	—	0·01	0·005	0·005	0·100	47
2	0·93	0·038	0·073	0·01	0·005	0·005	0·096	45
3	1·12	0·045	0·060	0·49	0·005	0·005	0·126	50
4	0·52	0·036	0·060	0·49	0·004	0·005	0·134	47
5	0·49	0·037	0·047	0·01	0·280	0·005	0·097	47
6	0·58	0·044	0·060	0·32	0·220	0·005	0·125	48

dilute zirconium alloys of compositions compatible with nuclear applications. The wide variety of microstructures that can be produced in a number of zirconium base systems has been examined in our laboratory and the influence of these structures on the mechanical properties has also been investigated.

Zirconium-rich alloys undergo a martensitic transformation during quenching from the high temperature beta phase. The morphology and the fine structure of the martensite has been found to be strongly dependent on the alloy composition and the transformation temperature. In our laboratory, the microstructure associated (figures 1 and 2, plate 1) with the martensitic transformation has been analysed for zirconium of different levels of purity and of a host of binary systems like Zr-Nb (Banerjee & Krishnan 1971), Zr-Ti (Banerjee & Krishnan 1973), Zr-Ta (Mukhopadhyay *et al* 1978), Zr-Al (Mukhopadhyay *et al* 1979a) Zr-Cu (Wadekar *et al* 1979) and Zr-Cr (Mukhopadhyay *et al* 1979 b). These studies have revealed that the M_s temperature is the most important parameter in determining the nature of the martensite product in terms of morphology and substructure. It has been possible, on the basis of the extensive work carried out in our laboratory, to propose a generalisation that in zirconium base alloys a lath morphology and a dislocated substructure result when the M_s temperature exceeds 650–700°C, while lower M_s temperatures lead to the formation of internally-twinned acicular martensites. The amount of a particular alloying addition necessary to bring about the transition naturally depends on the effectiveness of that particular element in depressing the M_s temperature. Mechanical property investigations have revealed that though both types of martensites are characterised by high densities of interfaces, only the internally twinned plate martensite could lead to a very substantial strengthening due to the martensite microstructure *per se* (Banerjee *et al* 1978). This is because in lath martensites, the lath boundaries are small angle boundaries which do not act as effective barriers to the propagation of deformation fronts.

Even when a martensitic structure enhances the strength of an alloy, it is important to examine the temperature regime over which this strengthening is effective. To test this, the martensites obtained in the various alloys studied have been tempered at different temperatures, including those pertinent to reactor operation. It has been found that in most cases, the martensite structure remains more or less unaltered upto about 500°C and contributes to the strength of the alloy (Banerjee *et al* 1976). Moreover, precipitation (whether of an intermetallic phase or of the beta phase) occurs preferentially along the martensitic interfaces during tempering so that even when the martensite undergoes recovery and recrystallisation, the distribution of closely spaced precipitates continues to act as a barrier to the propagation of slip and twinning (figures 3 and 4, plate 1).

While studying the precipitation of the beta phase in Zr-Nb martensites during tempering, an anomaly has been observed in that at temperatures close to but below the monotectoid temperature, a non-equilibrium zirconium-rich, bcc phase precipitates in preference to the equilibrium, niobium-rich bcc phase. A similar observation has also been made in the Zr-Ta system which also shows a monotectoid reaction. To resolve this anomaly, extensive computer calculations have been made to generate free energy versus composition data (Menon *et al* 1979). With the aid of these, a thermodynamic rationale has been arrived at for explaining the apparently anomalous precipitation behaviour. In fact it has been possible, on the basis of these calculations, to predict the complete sequence of phase transformations, over the entire

composition range, for Zr-Nb alloys (Menon *et al* 1978). The correctness of these predictions has been verified by experiments conducted here and elsewhere.

It has been mentioned earlier that apart from producing a martensitic structure, another promising method of generating-numerous closely spaced interfaces in zirconium alloys would involve the occurrence of the eutectoid transformation on a fine scale. The eutectoid reaction has been studied in the Zr-Cu (Mukhopadhyay *et al* 1979c) and the Zr-Cr systems (Mukhopadhyay *et al* 1979d). The former, where a phase separation cannot be prevented even during rapid beta quenching, is the prototype of a class of eutectoid systems known as active eutectoids (figure 5, plate 2). These are quite prevalent in zirconium and titanium alloy systems. On the basis of the work carried out in our laboratory, a viable mechanism for the active eutectoid decomposition, invoking the formation of an ordered transient phase, has been proposed.

There has been strong emphasis recently on considering the feasibility of alloys based on the intermetallic phase Zr_3 Al for reactor applications. The microstructural features associated with Zr_3 Al formation in Zr-Al alloys have been studied in our laboratory (Mukhopadhyay *et al* 1979e). In the course of these investigations, it has been possible to establish that the formation of equilibrium Zr_3Al in hypostoichiometric alloys is preceded by the formation of a metastable ordered phase which has a hexagonal crystal structure. The precipitation mode of the equilibrium Zr_3Al phase in beta quenched and aged alloys has been found to be of the discontinuous type (figure 6a–c, plate 2). The mechanical properties associated with different types of matrix-precipitate aggregates have been examined and analysed (Raman *et al* 1978).

Zirconium alloys have been investigated extensively by internal friction studies mainly to understand the behaviour of interstitial and substitutional solutes in the lattice (Mishra & Asundi 1972). These studies have shown that the activation energy for the jump of an oxygen atom from one octahedral position to the other is dependent upon the size of the substitutional solute. The larger the difference in size between the solute and the solvent atom, the smaller the activation energy. This indicates that the elastic interactions between the various species of atoms are far more predominant than the electronic interactions. It also suggests that oxygen, though easily soluble in zirconium, has a tendency to cluster around the substitutional solute, presumably to minimise the local elastic distortions accompanying such point defects (Mishra & Asundi 1970). The behaviour of nitrogen is rather interesting. Only substitutional solute atoms which are larger than the zirconium atom can cause internal friction peaks. This again shows that clustering around the substitutional solutes occurs because the nitrogen atom is larger than the oxygen atom. It is apparent that those solute atoms which are larger than the zirconium atom have a tendency to attract nitrogen atoms for the minimisation of the elastic distortion. By a purely elastic interaction phenomenon, one can explain the role of tin in zirconium, in counteracting the deleterious effect of nitrogen on corrosion by a scavenging mechanism.

Irradiation-hardening studies have been conducted on an experimental alloy, Zr-0·5% Nb-1·0% Cr upto a fluence of 10^{18} to 18^{19} n/cm^2. The recovery of radiation hardening has been found to take place in the range of 200–400°C in well-annealed specimens, while for the quenched and aged alloy, this range was pushed upto 500–700°C. The microstructure of the quenched and aged alloy showed precipitation of chromium (Ray & Sharma 1967).

9. Conclusion

Zircaloy-2 has proved its worth as an excellent structural material particularly in pressurised reducing conditions. Under oxygenated boiling conditions, however, it appears to be susceptible to localised accelerated attack particularly in regions of flow discontinuity. Considering the excellent performance of zircaloy-2 is it possible to develop an alternate material which would find ready adoption? This might happen if some major improvements in alloy properties are achieved. On the other hand, it seems more likely that a change could be based on a study of some serious operational shortcomings in the properties of zircaloy-2.

Efforts have been made to develop high temperature zirconium alloys; but it appears now that all ideas of using nuclear superheated steam appear to have been abandoned. As such, R & D activities in this area do not find much support.

Finally, fibre reinforcement is the subject of active materials research but has not yet made a significant impression on zirconium metallurgy. Efforts in this direction may prove useful.

If one looks at the research being carried out by material scientists in areas like ion-implantation and laser glazing, it appears that it may be possible to develop high-strength zirconium alloys which could be laser-treated to have an outer amorphous layer which could lead to improved corrosion resistance. However, it may be necessary to restrict the operating temperature to say less than 550°C, to avoid crystallisation of the amorphous layer.

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Plate 1
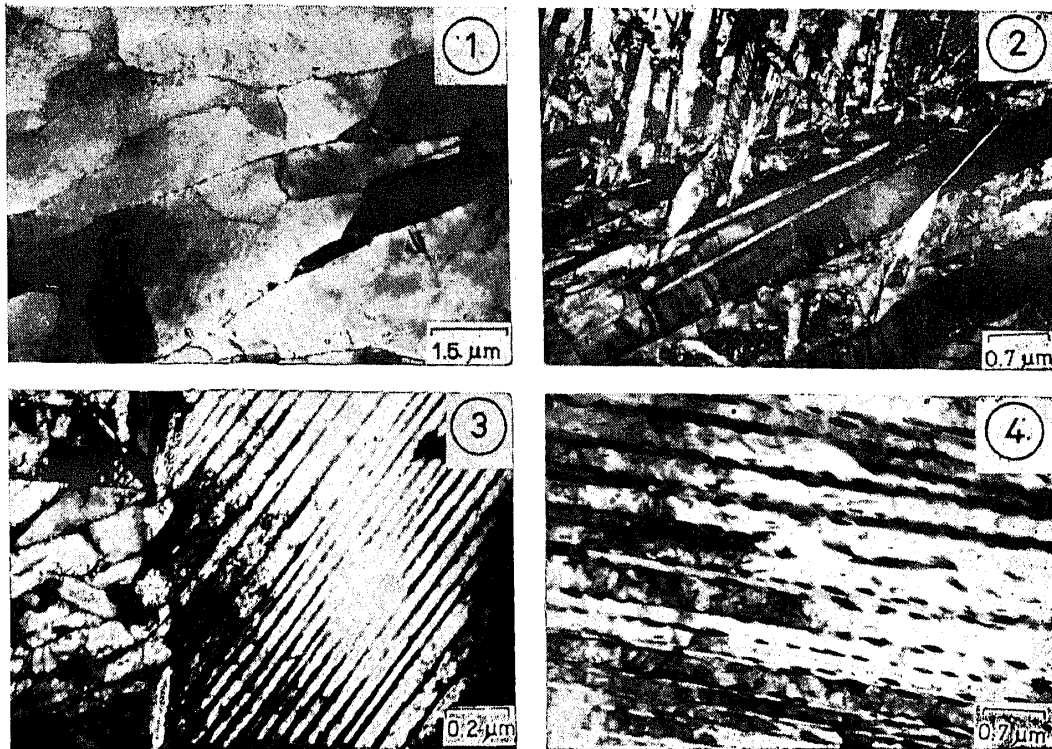
Figures 1 to 4. 1. Lath martensite structure in β quenched Zr-0·1 Cu alloy. 2. Acicular martensite structure in β quenched Zr-15 Ti alloy. 3. Internally twinned plate martensite in β quenched Zr-2·5 Nb alloy. 4. Precipitation along twin boundaries in tempered Zr-2·5 Nb alloy martensite.

Plate 2
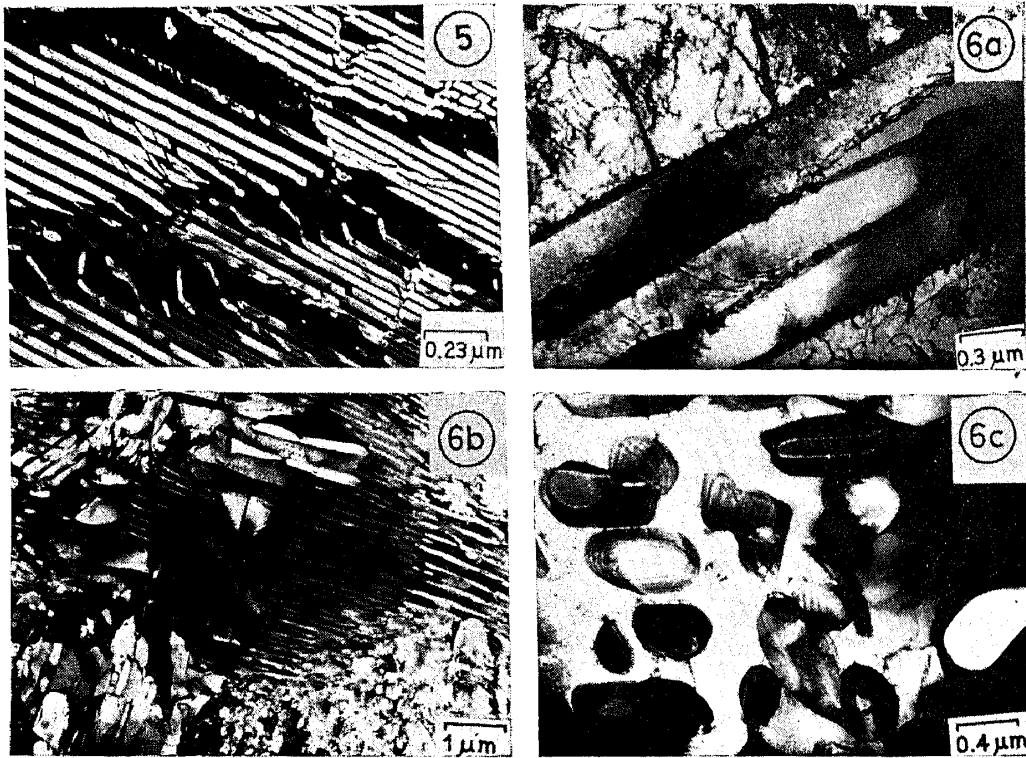
Figures 5 and 6.   5. Lamellar two phase structure in β quenched Zr-1·6 Cu alloy (dark field).   6. (a) Dislocated lath martensite in β quenched Zr-4·6 Al Alloy.   (b) Lamellar structure comprising α and Zr_3 Al lamellae in Zr-4·6 Al alloy after ageing.   (c) Two-phase structure comprising α grains and spheriodised Zr_3 Al crystals in Zr-4·6 Al alloy after prolonged ageing.