# The present status and the projected programme of zirconium development in India

### N. SARATCHANDRAN, R. K. GARG, C. V. SUNDARAM and H. C. KATIYAR

THE nuclear power industry continues to be the major consumer of zirconium metal production in the world today. On the basis of neutron economy, corrosion resistance and mechanical strength, zirconium alloys have been the ideal choice for the fuel-cladding and other core components in watercooled nuclear power systems. In the United States alone, the current annual requirement of zircaloy tubing for nuclear fuel cladding has been placed at 250 tons, which will grow to 600 tons by 1970 and 900 tons by 1973. In India, for the 1200 MW(e) nuclear power programme envisaged for the IV Plan period, zircaloy tube requirements have been estimated at 50 tons per year and will increase to 75 tons and more during the V Plan period.

There is also a small but growing market for commercial grade zirconium in the form of very fine powder for 'gettering', photo-flash and detonator applications, and in the form of thin foils in flash-bulbs.

The raw material for the production of both nuclear grade and commercial grade zirconium metal is the mineral zircon  $(ZrSiO_4)$ , of which India has abundant reserves in the Kerala beach sands.

## The present status and the projected programme of zirconium development in India

To the nuclear engineer, the metal zirconium offers many attractions. When free from its natural contamination of hafnium, it has a very low thermal neutron absorption cross-section ( $\sigma a = 0.18$  barns). With strict control on the interstitial impurity content, the metal has good ductility, permitting extrusion into thin-walled tubing as required for fuel canning. And when appropriately alloyed, the metal shows vastly improved corrosion resistance and good mechanical strength, qualifying it for the rigours of reactory service.

In two of the major reactor types that are now accepted as economical—namely the pressurised water reactor (PWR) and the boiling water reactor (BWR) zirconium alloys are widely used for the cladding of

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#### SYNOPSIS

The paper surveys the current world situation with respect to zirconium development and highlights the achievements in the Indian programme. Pilot plant work carried out at the Bhabha Atomic Research Centre, Trombay, on (i) the processing of Indian zircon for the removal of hafnium and other impurities by solventextraction and the production of nuclear grade ZrO<sub>2</sub>, (ii) the conversion of the pure oxide to ductile sponge metal via the chloride route by magnesium (or sodiummagnesium) reduction of  $ZrCl_4$  followed by vacuum separation of the by-products, and (iii) the production of homogeneous zirconium alloys by consumable electrode arc-melting is described. Based on the know-how generated at Trombay, a zirconium plant with a capacity to produce initially 50 tons/year of zircaloy tubing has been designed and will be commissioned at Hyderabad, Andhra Pradesh, in about two years. It is also proposed to locate, at the same site, a small facility for the production of commercial grade micron-size zirconium metal powder to meet the local demand.

uranium dioxide fuel and for the permanent reactorcore components. It has been estimated that by 1971, over 65% of the commercial nuclear electricity (~25 000 MWe) generated in the world will be from the PWR's and the BWR's—thus placing zirconium on a firm footing in nuclear engineering.<sup>1</sup>

#### Zirconium alloys for nuclear service

Major zirconium minerals—baddeleyite  $(ZrO_2)$  and zircon  $(ZrSiO_4)$ —are always associated with hafnium to the extent of 1 to 3 per cent of the zirconium content. Whereas zirconium, as stated at the outset, has a low absorption cross-section for thermal neutrons, pure hafnium is a strong neutron-absorber ( $\sigma a = 115$  barns). In the interests of strict neutron economy aimed at in the pressurised and boiling water reactors, zirconium has to be substantially free from the natural

hafnium contamination. The tolerance limit for hafnium in nuclear grade zirconium metal is specified at 200 ppm.<sup>4</sup>

Unalloyed zirconium metal (even in its purest form) has been known to be unpredictable in its corrosion behaviour which is greatly influenced by even very small amounts of nitrogen, carbon and other impurities. For improved corrosion resistance in hot water and steam and better mechanical strength for nuclear service, the metal requires to be toned up by alloying. The development of the zircaloys with tin as the major alloving addition and minor amounts of Cr, Fe, and Ni was a break-through in this context.<sup>5</sup> In particular, zircaloy-2 has come to be universally accepted for fuel-canning and for structurals in the pressurised and boiling water reactors. Addition of 1.2-1.7% of tin as in zircaloy-2 effectively counteracts the deleterious effects of nitrogen, enhancing the corrosion resistance and mechanical strength. The addition of small amounts of chromium, iron, and nickel (Fe+Cr+Ni=0.18 - 0.38%) reduces the hydrogen pick-up in the metal, contributing to the stability of the oxide film and thereby preventing further corrosion.

A zirconium  $-2.5^{\circ}_{0}$  Nb alloy has been mentioned as a potential competitor to zircaloy-2. The niobium alloy possesses about 40% higher tensile strength in the cold-worked condition, 90% higher tensile strength in the heat-treated condition, greatly enhanced creep strength, associated with good ductility. Since the neutron capture cross-section of the Zr-2.5 wt.% Nb alloy is nearly identical with that of zircaloy-2, significant gain in power reactor neutron economy is possible by using thinner sections of the niobium-alloy for the stressed in-reactor components like the pressure tubes.<sup>5</sup>

The purity specifications of nuclear grade zirconium sponge and zircaloy-2 are given in Table I.<sup>4,6</sup> The stringent specifications on impurity limits will emphasize the importance of strict quality control in the various stages of the production of zirconium and its alloys. In Table II, the tensile properties of zirconium metal and its alloys are compared.<sup>7-9</sup>

#### Zirconium in the Indian nuclear power programme

The first three power stations in the Indian Nuclear Power Programme, Tarapur (Maharashtra),  $190 \times 2$ MWe and Kalpakkam (Madras) 400 MWe, are designed to use zircaloy-2 for the fuel-tubes, end-plugs, wire pads and for other structural components such as fuel channels,\* pressure tubes and calandria tubes. The initial zircaloy inventory for the Tarapur reactor has been around 38 tons and the annual replacement requirements are estimated at 5-10 tons. For each of the 200 MWe pressurised heavy water reactors (Rajasthan), the initial inventory of zircaloy-2 will be around 22 tons and the annual replacement around 3 tons. To meet the immediate requirements of the above three stations and the additional demands for other stations to follow, it has been decided to set up a zirconium

\*The fuel channels in the Tarapur reactors will be of zircaloy-4 (which, but for its much lower nickel content specified at 40 ppm, essentially corresponds to the zircaloy-2 composition).

 
 TABLE I Purity specifications for nuclear grade zirconium sponge and zircaloy-2 ingot 4, 6

				1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1
Nuclear grade zirconium sponge 99 <sup>.</sup> 5%		Zircaloy-2 ingot		
		97% 1·20-1·70% 0·05-0·15% 0·07-0·20% 0·03-0·08% 0·18-0·38%		Alloying element Sn Cr Fe Ni Fe+Cr H Ni 0
		0100	1 1/0	
500	PPM	500	PP	М
1300	,,	-		
25	3.2	25	32	
50	3.7	70	, ,	
1400	2.8	*		
75	7.5	75	22	
0.2	2.2	0.2	,,	
0.5	. 2	0.2	23	
20	13	20	,,	
200	" 5	*		
50	33	20	13	
1500	,,	*		
200	5.5	200	13	
600	3.5	20	,,,	
100	23	130	,,,	
50	3 9	50	>>	
50	> >	50	",	
	3.2			
	3.3			
	33			
	5.9		23	
	33		3 y	
50	33	100	. 5.9	
	2irconiu 99.5% 500 1300 25 50 1400 75 0.5 20 200 50 1500 200 50 1500 200 600 100 50 50 70 100 100 50 3.5 50	zirconium sponge         99.5%         500       PPM         1300       ,,         25       ,,         50       ,,         1400       ,,         75       ,,         0.5       ,,         0.5       ,,         200       ,,         200       ,,         50       ,,         1500       ,,         100       ,,         50       ,,         100       ,,         50       ,,         100       ,,         50       ,,         3.5       ,,         50       ,,         50       ,,         50       ,,         50       ,,         50       ,,         50       ,,         50       ,,         3.5       ,	zirconium spongeingot $99.5\%$ $97\%$ $1.20-1$ $0.05-0$ $0.05-0$ $0.05-0$ $0.05-0$ $0.05-0$ $0.05-0$ $0.07-0$ $0.03-0$ $0.18-0$ $0.10-0$ $500$ PPM $500$ 1300 $1.25$ $.$ $50$ $.$ $25$ $.$ $50$ $.$ $1400$ $.$ $.$ $.$ $75$ $.$ $0.5$	zirconium sponge         ingot           99.5%         97%           1·20-1·70%           0:05-0:15%           0:07-0:20%           0:03-0:08%           0:10-0:14%           500         PPM           500         PPM           1:20            25         .           50         .           75         .           50         .           75         .           0:5         .           0:5         .           0:5         .           0:5         .           0:5         .           0:5         .           0:5         .           0:5         .           0:5         .           0:5         .           0:5         .           0:5         .           20         .           200         .           100         .           100         .           100         .           0.00         .           0.00         .           0.00         .

\* Listed as alloying elements

plant at Moula Ali, near Hyderabad (Andhra Pradesh). This plant will have an initial capacity to produce 50 tonnes of zircaloy-2 mill-products, mainly in the form of tubing. The integrated process flow-sheet selected for use in the above plant, has been based on the extensive development work carried out in the various pilotplants operating at Trombay. Provision has also been

Alloys	Test temperature	Mechanical properties				
		UTS (psi)	0.2% Yield stress (psi)	% Elongation on 1 inch gauge length	Creep rate	
Nuclear grade zirconium metal	300°C	15 000-20 000	9 000–14 000	30	5×10-3%/hr at 38 000 psi and 200°C in air	
Zircaloy-2 (cold-worked 19%)	300°C	47 000	42 000	12	2×10-4%/hr at 40 000 psi in air	
Zirconium-2 <sup>.5</sup> w% Niobium (heat-treated)	300°C	89 000	76 000	15.3	1.8×10-4%/hr at 60 000 psi in air	

TABLE II Mechanical properties of nuclear grade zirconium metal and its alloys7-9

made for the reprocessing of off-grade zircaloy millscrap for reconversion to nuclear grade sponge.<sup>10</sup>

#### Zirconium development programme at Trombay

The economics of production of nuclear grade zirconium metal from the mineral zircon and its conversion into zircaloy-2 mill-products, is governed by the following factors : (1) The close similarity in the chemistry of zirconium and hafnium requires the application of complex and expensive techniques for their separation. (2) Zirconium metal is prone to react with oxygen and nitrogen even at moderately elevated temperatures and contamination with these gases results in loss of ductility of the metal, rendering its fabrication difficult. Tolerance limits for oxygen and nitrogen in zirconium metal are specified at 1 400 ppm and 50 ppm, as in Table I. The stringent limits on gas content in the metal call for scrupulous control of the reaction atmosphere during metal reduction. (3) Molten zirconium is highly reactive and a universal solvent. There are no known refractories that can hold the molten metal without introducing contamination. The melting and casting of zirconium thus necessitate the use of exotic and unconventional techniques. The seizing characteristics of zirconium billets during extrusion and forming operations at plastic temperatures (750°-850°C) require special billet-sheathing and lubrication procedures.

The process of conversion of zircon sand into zircaloy-2 mill-products can be conveniently split into three major stages, bringing into play some sophisticated chemical and metallurgical engineering : (1) the production of hafnium-free zirconium oxide from zircon ; (2) the conversion of zirconium oxide into ductile nuclear grade zirconium sponge; and (3) the production of zircaloy-2 mill-products from the sponge metal.

#### Production of hafnium-free zirconium oxide

The beach sands of South India contain about 5-9%zircon, associated with other minerals like ilmenite, monazite, rutile and sillimanite. The zircon concentrate that is made available from the beach sand beneficiation plants correspond to the following typical analysis:

 $ZrO_2 + HfO_265.5 - 66.5\%$ ;  $SiO_2.31 - 32\%$ ;  $Al_2O_3.0.7\%$ ;  $Fe_2O_3.0.1\%$ ;  $TiO_2.0.3 - 2.5\%$ ;  $ThO_2.0.02\%$ ,  $U_3O_8.0.035\%$ ; and  $P_2O_5.0.1\%$ .

(The hafnium content expressed as.

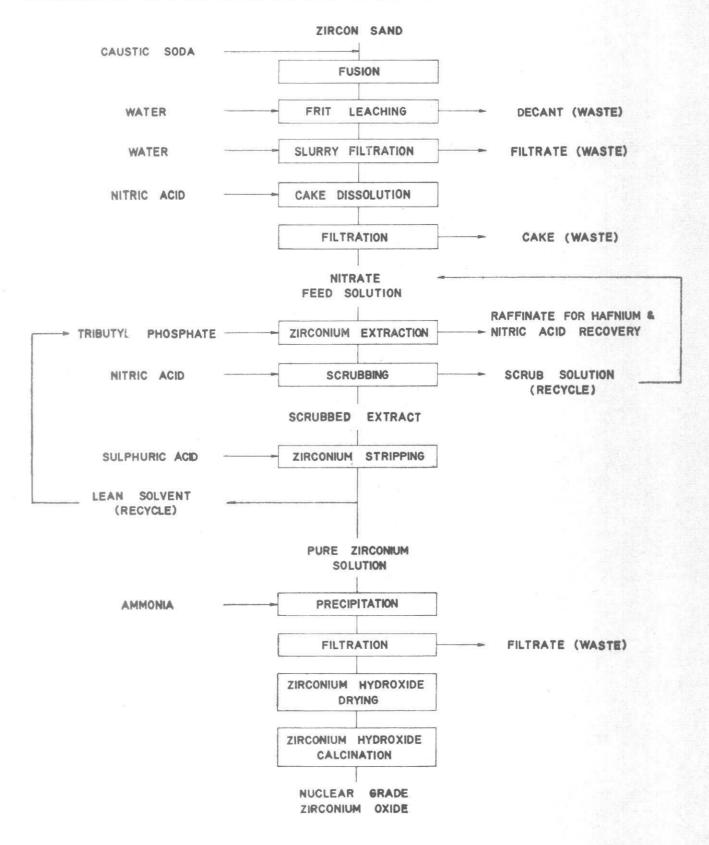
$$\frac{\text{HtO}_2}{\text{ZrO}_2 + \text{HfO}_2} \times 100 = 2.5$$

The process of obtaining hafnium-free zirconium oxide from zircon involves three main steps :

- (1) Opening up of zircon sand to bring zirconium and hafnium values to a soluble form;
- (2) Separation of hafnium and other impurities from zirconium to obtain pure zirconium intermediate; and
- (3) Conversion of the zirconium intermediate into zirconia.

The available methods for the opening up of zircon and the separation of hafnium and zirconium have been extensively reviewed in the literature.<sup>11,12</sup> Out of these, two processes have been examined in detail at Trombay for the production of hafnium-free zirconium oxide.

In the first process<sup>13</sup> —based on the fractional crystallisation of double fluorides—zircon is fused with  $K_2SiF_6$ around 650°—700°C whereby the zirconium and hafnium values are converted into water-soluble  $K_2ZrF_6$  and



1 Flow-sheet for the production of nuclear grade zirconium oxide

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 $K_2$ HfF<sub>6</sub>. A 12-stage fractional crystallisation of the double fluorides simultaneously removes the hafnium and other impurities yielding pure  $K_2$ ZrF<sub>6</sub>, which can be further converted to zirconia by ammonia precipitation.

The alternate process<sup>14</sup> —based on solvent extraction -involves the fusion of zircon sand with about 1.5 times its weight of caustic soda flakes in a pot furnace at about 600°C. The friable frit is leached with water and filtered. The sodium zirconate cake is dissolved in nitric acid to give a nitrate feed solution. Zirconium is extracted from this feed by contacting with tributyl-phosphate diluted with kerosene. The loaded organic is then scrubbed with nitric acid for the removal of any associated hafnium and finally pure zirconium is stripped from the organic by contacting with sulphuric acid. These sequential operations are carried out in a counter-current multiple-stage mixer-settler system. The pure zirconium solution is then precipitated with ammonia and filtered; the filter cake is to dried and calcined to pure zirconium oxide. Hafnium left in the raffinate after zirconium extraction is processed to give pure HfO<sub>2</sub> by similar techniques.

An evaluation, of the two processes with regard to capital cost, cost of production, ease of operation, hafnium recovery, problems of materials of construction and availability of chemicals, has been made and the solvent extraction process using TBP has been selected for the Hyderabad plant. A flow-sheet showing the various steps in this process is outlined in Fig. 1. The spectrochemical analysis giving the purity of zirconium oxide as produced in the pilot-plant solvent extraction experiments is shown in Table III.

#### Production of nuclear grade zirconium sponge

Nuclear grade zirconium sponge of consistent quality and the required purity can be produced in large scale by the Kroll process of controlled magnesium reduction of anhydrous zirconium tetrachloride vapours (in an atmosphere of argon) followed by high-vacuun treatment of the products at 900°C for the removal of MgCl<sub>2</sub> and excess magnesium.<sup>15</sup> This process yields zirconium metal as a partially sintered sponge-like product containing very low amounts of oxygen and other interstitials. The sponge after crushing and grading is well-suited for further compaction and fabrication of consumable electrodes for arc-melting.

The detailed process flowsheet for the conversion of hafnium-free zircon into nuclear grade zirconium sponge is presented in Fig. 2. Pilot-plant equipment for experimenting the processes have been specially designed, fabricated, and tested at Trombay to facilitate the design and commissioning of large-scale productiontype units. The major unit processes involved in the production of the sponge are summarised below :

1. Zirconium tetrachloride required as intermediate in the production of the metal, is produced by the direct chlorination of zirconia-carbon briquettes (prepared by the wet-extrusion method) at 750°C in a silica brick-lined furnace. The briquettes are heated by impressing three-phase voltage across graphite electrodes

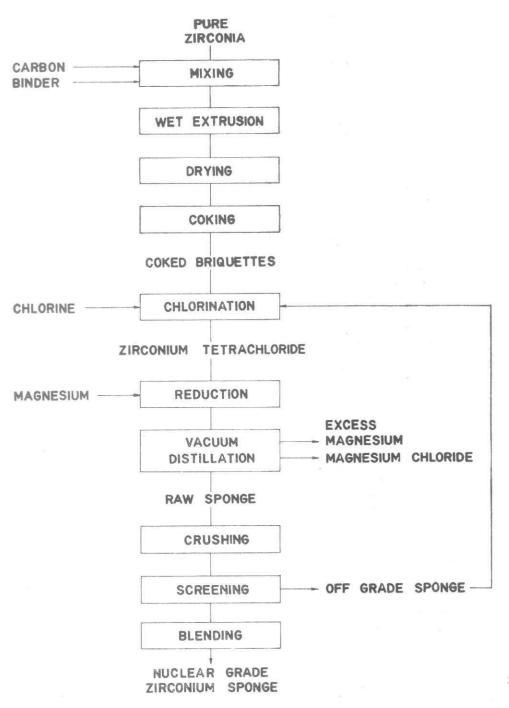
TABLE III Cnemical purities of typical hafnium-free zirconium oxide and zirconium sponge batches produced in the pilot-plant

Impurities	Hafnium-free zirconium oxide		Magnesium reduced zirco- nium sponge		Magnesium- sodium reduced zirconium sponge	
O N Al B Cd Co Cu Cr Fe Hf Mg Mn Mo Ni Pb Sb Si Sn V W	$\begin{array}{c} 25 \\ 6 \cdot 8 \\ 0 \cdot 5 \\ 10 \\ 25 \\ 25 \\ 195 \\ 100 \\ 60 \\ 10 \\ 10 \\ 10 \\ 10 \\ 10 \\ 50 \\ 460 \\ 10 \\ 25 \\ 50 \end{array}$	РРМ	$\begin{array}{r} 990\\ 31\\ 25\\ 0.5\\ 10\\ 25\\ 120\\ 1000\\ 100\\ 10\\ 45\\ 10\\ 10\\ 45\\ 10\\ 10\\ 50\\ 10\\ 50\\ 25\\ 50\\ \end{array}$	PPM	990 54 25 0·5 10 25 15 50 100 10 50 10 50 10 50 10 50 10 50 10 50 10 50 10 50 10 50 10 50 50 10 50 50 50 50 50 50 50 50 50 5	РРМ
Hardness Arc-melted button)			135	VPN	132	VPN

embedded in the charge. The chloride vapours from the furnace are condensed in a double-walled inconel condenser at  $150-200^{\circ}C$  as dense crystals suitable for metal reduction.

2. Magnesium reduction of zirconium tetrachloride is carried out in a specially designed stainless steel retort under slight positive pressure of argon. The chloride and the metal-reductant are loaded in separate containers into the retort. After in-situ purification of the chloride by out-gassing the volatile impurities at 150-200°C prior to melting the magnesium, the chloride is distilled in a controlled fashion to react at the surface of molten magnesium. The system is provided with adequate controls to guard against any large temperature excursion in the reduction crucible or excessive pressure rises. There are provisions for automatic and manual bleeding of the chloride vapours from the retort and admitting argon as and when necessary. At the end of the reduction, the crucible contains the zirconium sponge covered with magnesium chloride.

3. The distillation-separation of  $MgCl_2$  and excess magnesium from zirconium sponge are carried out in another heavy-walled inconel retort, capable of evacuation down to 1 micron Hg at 900°C. The top section of the retort is heated with an evacuated bell-type nichrome furnace, and the bottom section jacketed for water cooling. Magnesium chloride and excess magnesium are recovered by condensation in the cooler portions of the retort. The entire system is equipped with essential safety features for the protection of the

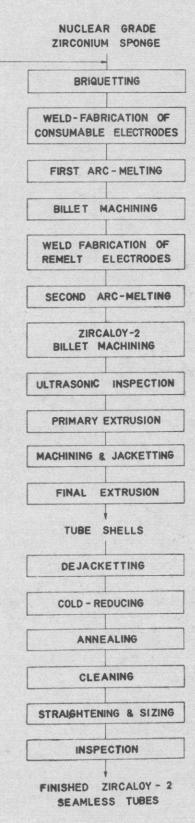


2 Flow-sheet for the production of nuclear grade zirconium sponge

equipment and the charge in the event of power failures during operation.

4. The sponge (that is pyrophoric when fresh) is conditioned prior to discharge from the vacuum distillation retort. The lumps are carefully chiselled from the crucible, crushed and graded. Metal from different reduction batches is blended on the basis of evaluation reports and then sent for melting.

In an attempt to upgrade the quality of the magnesium-reduced sponge, the use of a small percentage of liquid sodium along with magnesium during the initial stages of reduction has been found to substantially lower the metallic impurities in the sponge and also improve its crushability.<sup>16</sup> The effectiveness is attributed to the gettering action of sodium in the initial stage and the scavenging action of sodium chloride during



ALLOYING

ADDITIONS

3 Flow-sheet for the production of zircaloy-2 tubes

magnesium reduction. The use of sodium does not introduce any special problems during the vacuumdistillation step. The purities of the magnesium reduced sponge and the bi-metal reduced sponge are compared in Table III.

#### Production of zircaloy-2 mill products

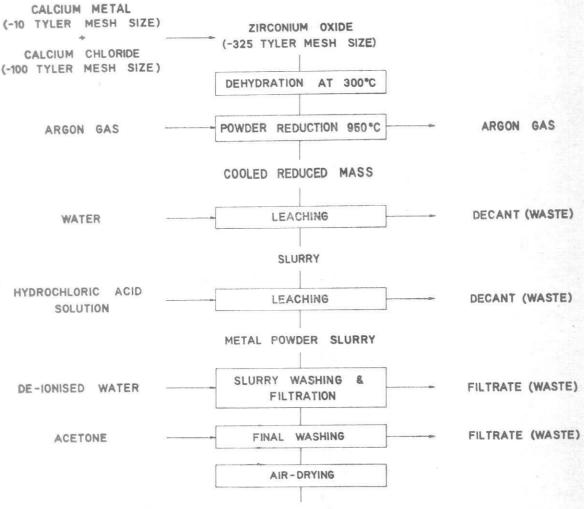
Zircaloy-2 tubes and other components meant for service in nuclear reactors have to be fabricated to close dimensional tolerances and should possess sound structural integrity and good corrosion resistance. Unlike other metals and alloys in normal engineering use, zirconium and its alloys are prone to severe attack by air at normal plastic working temperatures (around 800°C). The oxides and nitrides formed on the surface tend to diffuse into the main body of the alloy seriously affecting the ductility and corrosion resistance. The alloy is also succeptible to seizing during frictional plastic working operations like extrusion and drawing. To overcome these handicaps during fabrication, pro-tective sheathing of the ingot with copper or glass during extrusion and the extensive use of special lubricants to avoid contact with the tools are recommended. To preserve the corrosion resistance of the alloy, careful cleaning of the surface of the finished component is also mandatory.

The operations involved in the production of the various zircaloy-2 components can be broadly divided into the following four groups:

- 1. Compaction of zirconium sponge with alloying elements, weld-fabrication of consumable electrodes and double arc-melting of the electrodes to obtain homogeneous zircaloy ingots;
- 2. Break-down of the cast ingots by forging or  $\beta$ extrusion into intermediate size billets and further extrusion of these billets into tubes and other sections as desired :
- 3. Finishing to size of the various components by cold-reducing with intermediate annealing, final pickling and cleaning; and
- 4. Quality control.

The flow-sheet evolved for the conversion of nuclear grade zirconium sponge into zircaloy-2 seamless tubes which form the major requirement for the reactors (compared to other structural components) is presented in Fig. 3.

Conventional induction melting in graphite crucibles is unsuitable for the production of zircaloy ingots due to prohibitive carbon pick-up. Non-consumable electrode arc-melting with tungsten electrodes is acceptable for very small batches, but on production scale, the melting is handicapped by splattering due to arc-instability and the process consumes about 7 to 13 KWH power per kilogram of the melt.<sup>17</sup> Consumable electrode arcmelting with water-cooled copper molds is the only process successfully employed today for tonnage melting of zircaloy. The high thermal conductivity of copper permits chilling of molten zirconium at the mold wall to avoid alloying with copper. The splattering of the



ZIRCONIUM METAL POWDER

4 Flow-sheet for the production of zirconium metal powder

melt is absent in this process and the power consumed is only about 1.25 KWH/kg.

In the extensive small scale consumable electrode arcmelting experiments performed at the Atomic Fuels Division, procedures have been evolved and conditions optimised for the compaction of sponge briquettes with alloying additions, fabrication of consumable electrodes by argon arc-welding of a number of sponge briquettes inside an argon-filled chamber and controlled vacuum arc-melting. A double vacuum arc-melting sequence has been found necessary for homogenising the alloy composition of the billet in order to meet reactor specifications and for the effective removal of volatile impurities and elimination of porosity.

After machining and ultrasonic inspection, the castbillet is heated—preferably in an induction furnace to avoid excessive atmospheric contamination—and subjected to a break-down operation either by extrusion in the  $\beta$ -phase (using glass or other special lubricants) or by forging to produce intermediate-size billets. Jacketting of the cast-billet is not considered necessary during primary extrusion as the machining involved in the preparation of the secondary extrusion billets will remove any small surface defects.

The shells needed for the tubular blank extrusion are prepared by trepanning or boring of the intermediate size billets. Depending on the capacity of the extrusion press available (which determines the extrusion temperature), the shells are jacketted prior to extrusion either with mild steel and copper or with copper alone. With an intermediate layer of mild steel, the extrusion can be conveniently carried out at temperatures as high as 900°C (zirconium-iron eutectic forms at about 934°C), and with lower thrust. If copper alone is used for jacketting, the extrusion has to be necessarily restricted to below 800°C (zirconium copper eutectic forms at 822°C), thus calling for the use of high extrusion pressures. Values of extrusion constants for zircaloy-2 at 700°C and 870°C are 30 kg/mm<sup>2</sup> and 24.5 kg/mm<sup>2</sup> respectively. For the range of the products to be produced at Hyderabad, a 3000 ton extrusion press has been provided for in the proposed zirconium plant.

Finished size zircaloy tubes are manufactured from the extruded tube stock either by conventional colddrawing on draw-benches or by the Pilger coldreduction process. The Pilger process reduces simultaneously both the diameter and wall thickness of tubes by employing a mandrel and a pair of rotating grooved rolls on a rocking stand. The Pilger process also permits a reduction of 50 to 60 per cent (maximum being about 80 per cent) per pass, whereas only about 10 to 20 per cent reduction per pass is possible on the draw-benches.

One of the critical factors governing the performance of zircaloy tubing in reactors is the orientation of the hydride precipitates. Whereas a circumferential distribution of the hydrides does not adversely affect the tube life in the reactor, a radial distribution of the hydrides can contribute to cracking-failure under stress. It has been generally observed that the proper orientation of hydride precipitates in the finished tubes can be better achieved in the Pilger cold-reduction process, than in conventional drawing.

With a view towards understanding the special problems associated with the fabrication of zircaloy tubing and working out a detailed flow-sheet, extensive development efforts have been undertaken at Trombay. The investigations have been concerned with the design of copper-jacketted extrusion billets, extrusion behaviour of zircaloy at different temperatures and choice of proper lubricants.

Rigid quality control and inspection procedures in the various stages of fabrication of each of the components are mandatory to ensure lower percentages of rejections of the end-products. Both non-destructive tests and destructive tests are employed for this purpose. The range of non-destructive tests include visual inspection, ultrasonic inspection, eddy-current test for wires, dimensional checks and radiography when necessary. The destructive tests comprise chemical analysis,<sup>18</sup> metallography, corrosion, burst and mechanical tests.

#### Other applications of zirconium and its alloys

Zirconium wool or shreddings and finely divided zirconium metal powder are widely used in the manufacture of photo-flash bulbs. The shreddings burn rapidly in an oxygen-rich atmosphere to 3500°K in 2 milliseconds. The cumbustion is triggered by igniting a bead made from zirconium metal powder and an oxidizing agent like potassium chlorate. Zirconium metal powder used in this trigger has to be pure and particularly low in volatile impurities and should have an average particle size of 3-5 microns ensuring a flash point around 200°C. Micron-size zirconium metal powder is also used as getter in the manufacture of vacuum tubes due to its high reactivity with oxygen and nitrogen.

In response to requests received from Indian manufacturers of photo-flash and electric bulbs, a process flow-sheet (Fig. 4) has been developed at Trombay for the production of micron-size zirconium metal powder. The process involves the calcium reduction of zirconium oxide at 950°C in the presence of a heat sink like calcium chloride, followed by acid leaching of the reduced mass.<sup>19</sup> Presently a pilot-plant with a capacity to produce up to 20 kg powder per month is operating at Trombay for making supplies to the local industries. To meet the gradually growing demand for the powder and also keeping in view the potential export market, the setting up of tonnage production of the metal powder is under consideration.

The addition of zirconium to steels accounts for a large portion of the consumption of the metal in the non-nuclear industries. Zirconium is added in the form of a zirconium-silicon-iron electric furnace alloy. The effect of zirconium is the same as that of aluminium and titanium in fixing up nitrogen and thus avoiding strain-ageing and also helping to improve the deepdrawing properties. The addition of zirconium also refines the grain-size and improves the tensile and impact strengths.

The effectiveness of zirconium in refining the grainsize and controlling grain-coarsening is even better recognised in the production of special magnesium alloys. Light-weight Mg-Zr, Mg-Zn-Zr, Mg-Th-Zr, and Mg-Rare Earths-Zr alloys have superior strengths at elevated temperatures and are extensively used in the aircraft industry. At Trombay, a process has been developed for the preparation of zirconium-bearing magnesium-zinc alloys.<sup>20</sup> The process consists of the reduction of zirconium oxide by zinc-magnesium alloy in a fused-salt medium. A loading of up to 15 w% zirconium in zinc-magnesium has been obtained by this process.

Zirconium is resistant to a number of chemicals and this coupled with its high mechanical strength and amenability to fabrication commends it as a potential constructional material in the chemical process industries. The prospective areas of application are in the manufacture of heat exchanger valves and pumps for use in urea production and handling of nitric acid, hydrochloric acid, caustics, and as spinnerets for the manufacture of rayon fibres.21 However, the prevailing high cost of zirconium mill-products is a key deterrent for the immediate acceptance of the metal in the chemical process industries. The situation is expected to improve when new cladding techniques like metalliding and explosion-cladding are fully developed, so that thinner zirconium sections can be clad on base metals like steel.

To conclude, the zirconium development programme at Trombay has given an insight into the various problems associated with production of this highly reactive metal and its alloys. With the setting up of the zirconium production plant at Hyderabad, it is expected that apart from meeting the commitments for the nuclear industry, there will be enough impetus for the full exploitation of the potentialities of zirconium in other industries.

#### References

1. Brahm Prakash and Sundaram, C. V. : 'Materials for nuclear power—the present status', Paper presented in the Symposium on the 'Use of non-ferrous metals in Engineering Industries', Nov. 15 (1967), Rourkela, under the auspices of the Indian Institute of Metals.

- 2 Feature Article, 'Zirconium producers respond to nuclear
- 3.
- 4.
- Feature Article, 'Zirconium producers respond to huclear growth', Chemical and Engineering News, July 17, (1967).
  Gran and Jeffery : 'A 'boomlet' in Zircaloy', Nucleonics, Vol. 25, No. 3, pp. 66-70, March, (1967).
  Wessel, F. W. : Zirconium Chapter in 'Minerals Facts and Problems', Bureau of mines, Bull. 585, p. 996, (1960).
  Balaramamurthy, K. : Current Trends in the Use of Zirconium Alloys, Atomic Fuels Division, Bhabha Atomic Research Centre (1968). Bombav-74 5 Centre, (1968), Bombay-74, Specification No. Met/52 for reactor grade zircaloy-2 ingots,
- 6. Atomic Energy of Canada Limited.
- Placid Rodriguez, Private Communication, Metallurgy Division, Bhabha Atomic Research Centre, Bombay-74, (1968).
- Ray, S. and Mehta, M. L.: The creep behaviour of Zr 0.5 8 w% Nb-1.0 w% Cr alloy, Bhabha Atomic Research Centre, Bombay-74, Report No. B.A.R.C./308 (1967). Ray, S., Mukherjee, J. L. and Mehta, M. L.: Effect of
- thermal treatment on hardness and tensile properties of Zr-0.5 w% Nb-1.5 w% Cr alloy, Bhabha Atomic Research Centre, Bombay-74, Report No B.A.R.C./295, (1967). Saratchandran, N. and Sundaram, C. V.: Reclamation of off-grade zircaloy mill-scrap Part I, Transactions of the Indian Lastitute of Mathematica and 212 & December (1966).
- Indian Institute of Metals, pp. 213–8, December, (1966). Brahm Prakash and Sundaram. C. V. : The present status
- of zirconium metallurgy. Symp. on Rare Metals, pp. 95-113,
- Ind. Inst. of Metals, Calcutta (1958). Brahm Prakash and Sundaram, C. V. : 'Separation of hafnium from zirconium by vapor phase dechlorination', United Nations' Conference on the Peaceful Uses of Atomic Energy, Vol. 8, Paper No. p/876, pp. 554-8, (1955).

- 13. Subramanyam, R. B. and Sundaram, C. V.: 'Pilot-plant production of nuclear grade zirconium sponge from Indian zircon', Transactions of the Indian Institute of Metals, pp.
- 9-20, March, (1966). Sundaram, C. V. and Garg, R. K.: 'Production and Indus-trial applications of zirconium', Paper presented at the Con-ference on 'Research and Industry', December 20-21, (1965). Miller, G. L.: Zirconium, Butterworths Publications,
- 15. London, (1957).
- Semi-annual Report, Jan-June, (1968), Extractive Metallurgy 16. Section, Metallurgy Division, Bhabha Atomic Research Centre, Bombay-74, (To be published).
- Gordon, R. B.: Chap. 6 Melting and Shaping of zirconium and its alloys, in 'The Meltallurgy of Zirconium' edited by Benjamin Lustman and Frank Kerze, Jr., McGraw-Hill Book Company, Inc. New York, (1955). Krishnan, T. S.: Analytical quality control in the produc-
- 18. tion of nuclear grade zirconium and its alloys, Paper to be presented at the Symposium on 'Recent Developments in Non-ferrous Metals' Technology', National Metallurgical Laboratory, Jamshedpur, December 4-7, (1968).
  19. Sundaram, C. V., Ray Chaudhuri, P. K., Raman, L. V. P. and Krishnan, T. S.: Production of zirconium metal powder
- by calcie-thermic reduction, Transactions of the Indian Institute of Metals, pp. 187-190, December, (1967).
- Garg, S. P., Paul, C. M., Subramanyam, R. B., Sood, D. D. and Hariharan, A. V. : 'Reduction of zirconium oxide with 20. zinc-magnesium alloy under molten flux media', Paper to be presented at the 22nd Annual Meeting of the Indian Institute of Metals, Calcutta, Jan. 13-15, (1969).
- Feature Article : CPI's reactive metal use to double by 1970, 21. Chemical and Engineering News, July 8, (1968).