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SHANTI SWARUP BHATNAGAR MEDAL LECTURE–1979

METALS AND MATERIALS DEVELOPMENT FOR ATOMIC ENERGY AND SPACE PROGRAMMES

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I greatly appreciate the opportunity the Academy has given me to deliver this lecture on the occasion of the Shanti Swarup Bhatnagar Medal presentation. I consider Dr Bhatnagar a great visionary in bringing about the establishment of science and technology in the country at a crucial time when India had to take the responsibility for its own growth in the fast developing world. The Council of Scientific and Industrial Research has played a significant role in fulfilling Dr Bhatnagar's cherished dreams of scientific advancement of India. I had the good fortune of coming in close contact with Dr Bhatnagar as his student during my college and university career. The influence of his colourful and persuasive personality was not confined to the field of science only. His deep interest and active participation in literary pursuits made him a man of great charm and sweetness.

The progress achieved in our country in the fields of atomic energy development and space exploration has already demonstrated that given a sufficiently strong motivation and recognition, it is possible to attain a mature level of technology in a relatively short time, even starting from an under-developed base level. In the brief compass of this talk, I shall dwell upon aspects of special materials development with which I have been associated in both these programmes with my colleagues at Bhabha Atomic Research Centre and at Vikram Sarabhai Space Centre.

METALS AND MATERIALS IN ATOMIC ENERGY PROGRAMME

Nuclear technology is a hybrid technology which involves the constructive interaction of various branches of basic and applied sciences and engineering. Its development requires specifically tailored materials, new concepts of engineering design and practice and suitably trained and oriented personnel. In industrially developed countries, nuclear technology has always been able to lean heavily on a strong base of conventional technology. In contrast, in India, where technological progress has largely been confined to the achievements in the last two to three decades, there have naturally been serious difficulties due to the wide chasm between the targetted objectives of the projects of the nuclear energy programme and the available industrial infrastructure in the country. At the same time, it has been felt that continued dependence on imported expertise and materials is no viable alternative to the attainment of an overall technological self-sufficiency, and that in spite of the initial hardships involved, the evolution of indigenous expertise is the best way by which a growing technology can fit into national programmes.

The availability of materials that can serve as fuel in nuclear reactors is essential for the growth of nuclear technology. In a fission based reactor, the fuel material

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must contain at least one of the three fissile species—uranium-235, uranium-233 and plutonium-239—of which only the first occurs in nature. Natural uranium contains only about 0.7 per cent of this isotope, the remaining fraction being the fertile isotope uranium-238. The latter, however, can be converted to plutonium-239 in a reactor, as a consequence of radiative capture of neutrons. In a similar manner, the naturally occurring fertile nuclide thorium-232 can be converted to the fissile nuclide uranium-233. In India, the known reserves of natural uranium are rather modest while those of thorium are abundant. In view of this, three stages have been envisaged in the country's nuclear power programme. The first stage would involve thermal reactors, fuelled by natural uranium. Efficient reprocessing of the spent fuel from each such reactor would yield plutonium It has been planned that the plutonium obtained from the first generation thermal reactors would be used to fuel the second generation reactors—fast breeder reactors—for power production as well as for the conversion of uranium-238 to plutonium-239 or of thorium-232 to uranium-233. The production of uranium-233 would be very important in view of India's vast thorium reserves. The uranium-233 bred in the second generation reactors would finally be fissioned in third generation reactors, consisting presumably of both fast breeders and thermal near-breeders, which would be optimised to run on the thorium-232–uranium-233 cycle exclusively.

At the present time, India is in the first phase of this programme, so far as the large scale production of nuclear power is concerned. Without exception, this stage of thermal reactors has been the starting point of nuclear energy programmes all over the world using either natural uranium or slightly enriched uranium. Though a large number of reactors of this class have been designed so far, only a few of these designs have been considered suitable for convenient and economic power generation. These systems can be categorised into two groups depending on the choice of the moderator—graphite moderated systems and water moderated systems. The latter employ either light water or heavy water. Table I gives an estimate, on the global basis, of the contribution of water moderated reactors to nuclear power generation. Heavy water, owing to its excellent neutron absorption characteristics, is a very efficient moderator and the neutron economy in heavy water moderated reactors

TABLE I

Nuclear power generation in 1975 and in 1985 (projected) showing the contribution of water moderated reactors

Reactor type	Installed capacity (MWe)	
	1975	1985
Pressurised light water reactor	39000	169000
Boiling light water reactor	25000	85000
Pressurised heavy water reactor	3800	23000
Steam generating heavy water reactor	100	3960
Total nuclear power generation from water moderated reactors	67900	280960
Total nuclear power generation	79840	305100
Contribution from water moderated reactors	85%	92%

can be so good as to permit the use of natural uranium instead of enriched uranium as fuel.

Among the established reactor types, it is difficult to make a comprehensive comparison regarding the relative overall superiority of any given type over any other. Choice in this matter has been guided in different countries by different historical circumstances and by varying selection criteria. The nuclear energy planners in India adopted the Canadian concept of heavy water moderated, natural uranium fuelled reactors, which can use natural uranium very efficiently as the most suitable for the Indian programme. With these reactors, it is possible to attain a high conversion ratio—the generation of approximately 80 atoms of plutonium-239 for every hundred uranium-235 atoms fissioned.

The first stage of the evolution of our nuclear power programme involved the construction of research reactors with a view to gaining experience in their operation and maintenance and also to building up indigenous technologies for the production of the pertinent materials. This stage has been very valuable in gaining the know-how and confidence necessary for embarking on the subsequent power reactor programme. Table II indicates the research reactors that are in operation or are under construction in the country. It is important to note that the list contains not only thermal reactors but also fast reactors. The emphasis in the research reactor programme has been on the attainment of progressively higher levels of self-sufficiency regarding technology, materials and expertise. The same trend has been reflected in the development of power reactors. The degree of success in the quest for technological maturity is reflected in the fact that while the reactors at Tarapur were built entirely with foreign collaboration, the subsequent CANDU-type reactors have far more of indigenously developed technology.

Problems of Nuclear Materials

The development of any technology is intimately linked with the availability of appropriate materials of the desired quality in sufficient quantities. In this manner, technology is largely materials limited. Fortunately, this fact was given due importance very early in the course of our nuclear energy programme and there has been a major emphasis all through on attaining an adequate level of self-sufficiency with regard to nuclear materials. In fact, the growth of our reactor programme and the indigenous development of suitable materials have moved hand in hand with mutual pace setting. Today, the activities in the field of nuclear materials cover a very wide ground in this country. These activities include surveying and prospecting for minerals, development of mines, suitable processing of the relevant ores, production of a number of materials conforming to stringent standards regarding quality, manufacture of reactor components including fuel and structural members, reprocessing of spent fuel and so on. At the same time, the basic research aspect has consistently been stressed with a view to rationalising materials behaviour under reactor service conditions and developing materials with improved properties and performance.

Today, after several years of systematic efforts, India possesses a strong base for the continuation and the future growth of an expanding nuclear power programme.

The property requirements of nuclear materials are severe because a variety of considerations are pertinent. Thus, the materials used in many of the components

TABLE II

Indian research reactors in operation/under construction

Reactor	Location	Type	Power	Reactor core materials				
				Fuel	Clad	Moderator/Reflector	Coolant	Control
APSARA	BARC	Thermal	400 KW	Enriched uranium metal as uranium-aluminium alloy	Aluminium	Light water	Light water	Level control
ZERLINA (1961)	BARC	Thermal	100 KW	Natural uranium metal	Aluminium	Heavy water	Heavy water	—
CIRUS (1963)	BARC	Thermal	40 MW	Natural uranium metal	Aluminium	Heavy water	Light water	Boron carbide
PURNIMA (1972)	BARC	Fast (Pulse)	—	Plutonium dioxide	Stainless steel	Copper and steel reflectors	—	Molybdenum
R-5 (under construction)	BARC	Thermal	100 MW	Natural uranium metal	Aluminium	Heavy water	Light water	Boron carbide
FBTR (under construction)	RRC	Fast (Breeder)	15 MWe	Mixed plutonium uranium dioxide	Stainless steel	—	Liquid sodium	Enriched Boron carbide
PFR (under construction)	RRC	Fast (Pulse)	—	Plutonium dioxide	Stainless steel	—	—	—

should possess not only satisfactory physical and chemical properties but also desirable nuclear properties. This consideration rules out the use, in reactors, of many established high strength, high temperature engineering materials and warrants the development of special materials. Again, the chosen materials have to survive in a uniquely hostile environment. The conventional aggressive factors like high temperature and pressure and corrosive atmosphere are all present in the reactor. In addition, there is the hazard of intense nuclear radiations. Radiation damage of materials can result in drastic changes in their physical, mechanical and chemical properties and therefore, it is necessary that reactor materials should have inbuilt resistance against such damage. Because of all these considerations, the list of materials that are suitable for in-reactor applications is a severely truncated one. Of these, many are extremely reactive and are thus difficult to process and fabricate. In this context, one has also to bear in mind that the safety standards required of nuclear technology are very severe. This fact, coupled with the stringent demands on materials properties, has engendered a meticulous quality control procedure which is unprecedented in its thoroughness. No chance can be taken with reactor components since instances of failure can have catastrophic consequences.

The essential materials in a nuclear reactor pertain mainly to the fuel, the fuel cladding, the pressure tubes (or pressure vessel), the coolant, the moderator (in thermal reactors), the control and the shielding assemblies and the steam generator components. The specific property requirements of the materials used in different parts of a reactor are diverse. Some of these materials will be discussed briefly in the remaining part of this talk, with special reference to the context of the Indian programme.

Fuel Materials

The fuel constitutes the heart of the reactor. A suitable fuel material should possess several desirable properties like high fissile atom density, high thermal conductivity, resistance to irradiation induced dimensional instability and disintegration, chemical stability with respect to the coolant, relatively easy fabricability and reliable performance.

Uranium: Uranium metal was the first fuel to be used in nuclear reactors. This fuel has the advantages of maximum fissile atom density, excellent heat transfer characteristics and amenability to conventional fabrication processes. There are, however, certain difficulties which preclude the attainment of a high level of burn up with this fuel. Uranium, in the solid state, shows three allotropic forms over different temperature ranges (Table III). The crystallographic anisotropy of alpha uranium, which is the stable phase over the temperature regime normally pertinent to reactor operation, leads to growth and wrinkling on thermal cycling and on irradiation. The solution to the problem of growth lies in the avoidance of preferred orientation while wrinkling can be minimised by producing a fine grain size. Reliable methods for obtaining such structural characteristics involve either quenching from the beta phase or stabilising the isotropic gamma phase by appropriate alloying. Irradiation has another deleterious effect on metallic uranium: gaseous fission products like xenon and krypton tend to accumulate in it in the form of very small bubbles. The tendency of these bubbles to coalesce leads to swelling. This effect can be minimised by minute

TABLE III

Allotropic forms of uranium

Property	Alpha phase	Beta phase	Gamma phase
Range of stability	Upto 668 °C	668–775 °C	775–1132 °C
Crystal structure	Orthorhombic	Tetragonal	Cubic (bcc)
Atoms per unit cell	4	30	2
Density (gm/cm^3)	19.04	18.11	18.06
Fabrication	Soft and plastic. Forging, rolling, etc. can be done in the range 300–600 °C	Hard and brittle. Not suitable for working.	Soft and offers low resistance to deformation. Usually worked by extrusion.

additions of some elements. However, even with possible improvements through alloying and heat treatments, the attainable fuel temperature and fuel burn up are not high when the metallic fuel is used.

In India, the initial experience with nuclear fuels involved the metallic uranium fuel which was used in the thermal research reactors, ZERLINA (zero energy) and CIRUS (40 MWt). In CIRUS research reactor operating only slightly above the ambient temperature, the fuel element is in the form of a 3.45 cm dia uranium metal rod and about 3.10 metres long, hermetically sealed in a tight-fitting aluminium jacket. As uranium is a highly reactive metal, the melting of uranium ingots is carried out in a vacuum induction furnace and the metal cast in graphite moulds to 7.6 cm dia billets. The billet, after ultrasonic inspection, is hot-rolled around 600 °C to near final diameter. As rolled uranium is heavily textured and on account of the anisotropy of the metal, it will be, as such, unsuitable for reactor service. The rolled bar is hence heat treated by quenching from the beta range (670–770°C), to arrive at a randomly oriented fine grained structure and then machined to the final dimension, prior to jacketing in aluminium, on a cold draw bench. The first fuel element was made in 1960 and two of the CIRUS fuel elements made at Trombay were irradiated in Canada using a similar reactor there. Their performance was as good as the Canadian made fuel elements. The fuel fabrication plant at Trombay has been in operation for the past over a decade and a half.

The fuel burn-up attainable with metal as fuel is in the region of 3,000 MWd/tonne of uranium. The search for a more suitable fuel than metallic uranium for power reactors led to the development of ceramic fuels, particularly uranium dioxide. At the present time, this is the most widely used fuel in thermal power reactors.

In comparison with metallic uranium, uranium dioxide has a much higher melting point (2800 °C) and superior irradiation stability. Also, by virtue of its isotropic structure and its capacity to accommodate a large amount of fission gases in the sintered compacts, it has a much better resistance to radiation damage than uranium metal. As a consequence, much higher levels of burn up can be obtained with uranium dioxide fuel. Again in water cooled systems, this fuel has good compatibility with the coolant—a very important factor in the event of clad failure. However, the use of uranium dioxide has some disadvantages too. This material has a low thermal conductivity, a poor thermal shock resistance and a low fissile atom density. The poor thermal conductivity of uranium dioxide causes large radial temperature gradients to be set up across the fuel pellets; the centre of the pellet can attain very high temperatures and can even melt. In view of this, efficient heat transfer from the fuel requires that the cross section of the pellets is kept small. For CANDU type reactors like the RAPP reactors, the dimensions of each sintered fuel pellet are: 14.20–14.42 mm diameter and 20.30 mm length. Twenty-four such pellets, stacked axially inside a fuel tube, constitute a fuel element and nineteen such fuel elements are assembled to produce one fuel bundle. Each bundle is 49.53 cm long and 8.17 cm in diameter and weighs approximately 17 kg. For the 200 MWe reactors, it may be mentioned that a complete fuel charge consists of 3,672 fuel bundles. The assembly of the bundle has to be carried out with meticulous care so that the 1000 and odd spot welds on each fuel bundle meet the specified requirements. The end welds are absolutely leak-tight and scrupulous surface cleanliness of the fuel tubes is maintained throughout, to ensure corrosion resistance during service. The burn-up of uranium dioxide fuel is of the order of 9000 MWd per tonne of uranium.

In India, conforming to the global trend, uranium dioxide fuel has been used in the thermal power reactors and a change over to any other alternative fuel system is not likely in the near future.

The indigenous uranium supply in this country has so far depended mainly on the uraninite deposits in the Singhbhum district in Bihar. The processing of uranium begins with concentration processes which can yield a satisfactory feed for subsequent refining to nuclear grade specifications. These concentration processes essentially involve acid leaching of uranium from the associated gangue materials, separation of the dissolved uranium from other soluble and insoluble constituents and subsequent precipitation, filtration and drying to produce a magnesium di-uranate concentrate.

The di-uranate cake is the starting material for the production of nuclear grade uranium or uranium dioxide at the facilities at Trombay and at the Nuclear Fuel Complex, Hyderabad. The cake is dissolved in nitric acid and purified by solvent extraction to produce pure uranyl nitrate solution. The production of nuclear pure uranium dioxide from this solution is accomplished by precipitation of ammonium diuranate, calcination and hydrogen reduction. For producing metallic uranium, reduction of uranium tetrafluoride by calcium or by magnesium is the accepted procedure at Trombay.

Thorium: The principal source of thorium is the mineral monazite occurring in Kerala and Tamil Nadu coasts. The thorium content of the Indian monazite is close to 8–9 per cent. Thorium salts are produced by Indian Rare Earths Ltd. at Trombay.

Unlike uranium, thorium has no fissile isotopes. However, as mentioned earlier, it can be transmuted to fissile uranium–233 by the radiative capture of fission neutrons. Thorium possesses a face centred cubic structure upto about 1400 °C and because of the absence of crystallographic anisotropy, has excellent forming properties as well as radiation stability.

It is planned to neutron irradiate thorium in the FBTR in order to generate

U-233. BARC has developed technology of thorium fabrication and a number of thorium-bearing elements in the so-called J-rods form a part of the core-charge of CIRUS. The separation of U-233 from the irradiated fuel has been achieved.

Plutonium: Plutonium, which does not occur in nature, can be obtained from the spent fuel of reactors burning either natural or enriched uranium. Plutonium has many isotopes of which not all are fissile and the extent of irradiation decides which of these isotopes are likely to be abundant in the spent uranium fuel. Fuel elements that have had a prolonged stay in the core of a power reactor contain a mixture of many of these isotopes while elements with a brief residence time show a predominance of the isotope plutonium-239. However, it appears that plutonium obtained from either of these sources is satisfactory as a nuclear fuel. The high neutronic yield of plutonium fission (about 3 neutrons per atom of plutonium-239) makes the use of this element very attractive as a fast breeder reactor fuel. Plutonium has a low melting point (640 °C) and undergoes phase changes (Table IV). For these reasons, plutonium is more commonly used in the form of its oxide in nuclear reactors and in a diluted form in uranium oxide. Plutonium dioxide is mixed with uranium dioxide to form the mixed oxide fuel for fast reactors. This mixture, essentially a solid solution of one oxide in the other, has the inherent advantages and characteristics of ceramic fuels with regard to high temperature operation in an irradiation environment and is capable of withstanding high levels of burn up. As in the case of uranium dioxide fuel, the mixed oxide fuel is used in the form of short cylindrical rods. Since plutonium is a highly toxic and radioactive element, processing and fabrication of plutonium bearing materials have to be carried out by remote handling in alpha tight glove boxes. Plutonium dioxide produced at Trombay has been used in fuelling the research reactor PŪRNIMĀ. The technology for the fabrication of mixed ceramic fuels for the fast breeder test reactor has been developed at Trombay.

TABLE IV

Allotropic forms of plutonium

Property	Phase					
	Alpha	Beta	Gamma	Delta	Delta Prime	Epsilon
Range of stability	Upto 122 °C	122–206 °C	206–319 °C	319–452 °C	452–480 °C	480–640 °C
Crystal structure	Simple monoclinic	Body centred monoclinic	Face centred orthorhombic	Face centred cubic	Body centred tetragonal	Body centred cubic
Calculated density (gm/cm^3)	19.8	17.8	17.1	15.9	16.0	16.5
Volume change on transformation (per cent)	—	10	2.5	7	—0.5	—3.0
Thermal expansion coefficient (per °C x 10^6)	48	38	35	—9	—120	36

In a fast reactor, the coolant and the fuel surface temperature as well as the power density are higher than those in a thermal reactor of the same capacity. Thus the fuel pellets have to be smaller here in order to avoid central melting. Fast reactor fuel shows an enhanced tendency to exhibit swelling and growth due to solid and gaseous fission product accumulation and is, therefore, required to have a high porosity so that swelling could be accommodated internally. In the Kalpakkam fast reactor which will have an output of 40 MW (15 MWe), the sintered pellet size is about 4.23 mm dia and 8 to 10 mm height. The reactor will demonstrate the feasibility of generating power from a plutonium-fuelled, sodium-cooled fast breeder and will serve as a test facility for, among others, fuel development for future breeders.

Although oxide fuels have been found satisfactory and are being widely used both in thermal and in-fast reactors, there is a persistent interest in the development of alternative fuels like carbides, nitrides, carbo-nitrides and silicides. These have much higher thermal conductivities *vis-a-vis* the oxides and thus can permit reactor operation at higher power levels. However, a number of problems are still to be solved before a large scale change over from the oxides can be contemplated.

Structural Materials

In a nuclear reactor, structural materials are necessary both for in-reactor and ex-reactor components. The property requirements involved are quite varied, depending on the functions of the components. Inside the reactor, suitable structural materials are needed for containing the fuel, the moderator, the control rods and the coolant. Development of suitable materials for fuel cladding and for high temperature, high pressure coolant containment has been an important achievement of nuclear metallurgy. The properties that these materials should possess include good fatigue, creep and tensile strength at elevated temperatures, adequate weldability, satisfactory heat transfer characteristics, compatibility with the fuel as well as with the coolant, resistance against oxidation, stress corrosion and radiation damage and favourable nuclear properties like a reasonably low neutron absorption cross section. The last mentioned property is of great significance for thermal reactors, particularly those using natural uranium fuel. Some of the important reactor structural materials will be discussed in this talk.

Zirconium and Niobium: In water moderated thermal reactors, certain alloys based on the metal zirconium are the most suitable structural materials from considerations of neutron economy, high temperature strength, corrosion resistance and resistance to radiation damage.

The element zirconium, which had only very limited application before the development of nuclear reactor technology, is quite abundant in the earth's crust. Of the zirconium bearing minerals, the most important is zircon which is essentially zirconium silicate. The beach sands of the southern coasts of India contain about five per cent zircon. Zirconium occurs in nature in association with hafnium. Since the latter has a high neutron absorption cross section, all zirconium based in-reactor structural components have to be free from this element (<100 ppm). On the other hand, hafnium is a suitable material for reactor control applications. Starting from zircon concentrate obtained by suitable beneficiation of the ore, the production of hafnium-free zirconium metal involves the following steps: caustic soda fusion for opening up of zircon and removal of silica followed by nitric acid dissolution to obtain a feed solution containing zirconium and hafnium nitrates; separation of zirconium from hafnium and other impurities and obtainment of the former as an oxide intermediate by solvent extraction; chlorination of this hafnium free oxide to yield zirconium tetrachloride; and finally, magnesio-thermic reduction of the chloride to produce hafnium free zirconium metal. In the magnesium reduction process, the metal is obtained in the sponge form which is separated from the reacted charge by pyro-vacuum distillation. The sponge is consolidated by melting before subjecting it to any fabrication step. The extreme reactivity of the metal necessitates its melting

TABLE V

Flowsheet depicting the Indian practice for the production of nuclear grade zirconium sponge from zircon

	Zircon sand ($Zr(Hf)SiO_4$) ↓	
Sodium hydroxide →	Fusion ↓	
Water →	Water leaching ↓	
	Filtration ↓	→ Filtrate (sodium silicate)
	Cake ↓	
Nitric acid →	Dissolution in nitric acid ↓	
	Zirconium nitrate feed ↓	
	Solvent extraction ↓	→ Raffinate for hafnium recovery
	Pure zirconium nitrate ↓	
	Precipitation ↓	
	Zirconium oxide hydrate ↓	
	Calcination ↓	
	Zirconium dioxide ↓	
Carbon →	Wet extrusion with carbon ↓	
	Coking (in nitrogen atmosphere) ↓	
Chlorine →	Chlorination ↓	
	Zirconium tetrachloride ↓	
	Purification ↓	
Magnesium →	Reduction ↓	
	Vacuum distillation ↓	→ Magnesium chloride and excess magnesium
	Raw zirconium sponge ↓	
	Crushing, grading ↓	
	Reactor grade zirconium sponge.	

in an inert atmosphere or under high vacuum. Many of the conventional melting techniques have been found inapplicable in the cases of these reactive metals and consumable vacuum arc melting is the method most widely practised at present.

The flow sheet of the Indian practice with regard to the recovery of nuclear grade zirconium from zircon is shown in Table V.

Unalloyed zirconium cannot be used as a thermal reactor structural material because it does not possess satisfactory corrosion resistance or strength under the service conditions obtained in a power reactor. However, suitable alloying can improve these properties in a marked manner. The zirconium base alloys that are being widely used today in nuclear technology are the zircaloys (containing 1.5 per cent tin and small quantities of iron and chromium, with or without nickel) and the zirconium–2.5 per cent niobium alloy. These alloys possess good strength and corrosion resistance, together with satisfactory stability against radiation induced effects. In the Indian thermal power reactors, the alloy zircaloy–2 (Analysis in Table VI) has been extensively used. However, it is likely that in our future reactors of this type, the zirconium–2.5 per cent niobium alloy may replace zircaloy–2 as the pressure tube material, in view of the higher strength of the former. The use of a stronger alloy permits a reduction in the wall thickness and thus leads to a better neutron economy.

TABLE VI

Analysis of reactor grade zircaloy–2 (substitutional additions and some important interstitial impurities shown)

Tin	:	1.20–1.70 wt%	
Iron	:	0.07–0.20 wt%	0.18–0.38 wt%
Chromium	:	0.05–0.15 wt%	
Nickel	:	0.03–0.08 wt%	
Oxygen	:	1000–1400 wt. ppm	
Carbon	:	<500 wt. ppm	
Nitrogen	:	< 80 wt. ppm	
Hydrogen		< 25 wt. ppm	
Hafnium	:	<100 wt. ppm	

Mention can be made here of two special problems that have been faced while using zircaloys as reactor structural materials and of the manner in which these problems have been resolved. The first is essentially a hydrogen embrittlement problem. In the reactor core, hydrogen can be picked up by the structural components from the metal-water/steam reaction and also from the radiolytic decomposition of water. The solubility of hydrogen in alpha zirconium, the lower temperature allotrope, decreases with decreasing temperature rapidly so that hydrogen dissolved at higher temperatures precipitates as hydrides at the lower temperatures. These precipitates, depending on their orientation with respect to the direction of application of stress, can bring about a very significant reduction in the ductility of the material. In the case of fuel cladding or pressure tubing, the principal stress in service is a hoop stress. It has been found that for these components, radially oriented hydrides cause severe embrittlement while those circumferentially oriented do not show this deleterious effect. The fabrication process for these tubes has, therefore, been so devised that the resultant texture is conducive for the hydride particles to form in the circumferential direction. The second problem, which is associated with the use of zircaloys in fuel clads, pertains to stress corrosion cracking caused by the interaction between the fuel and the clad. In pressurised water reactors, the high coolant pressure causes the thin wall cladding to come in contact with the fuel. There may be localised rise in the fuel temperature immediately after refuelling or during control rod movements or due to power ramps. Such a situation may lead to the release of fission gases like iodine and a simultaneous stressing of the clad, owing to the differences in the thermal expansion behaviour of the fuel and the clad. When the fission gas concentration and the stress exceed some threshold values, stress corrosion cracking of the clad may occur. The incidence of such cracking can be minimised by inhibiting fuel-clad interaction. This can be achieved by graphite lubrication of the inner surface of the cladding tube.

Table VII shows a flowsheet, with special reference to the Indian practice, for the fabrication of cladding, pressure tubes and calandria tubes.

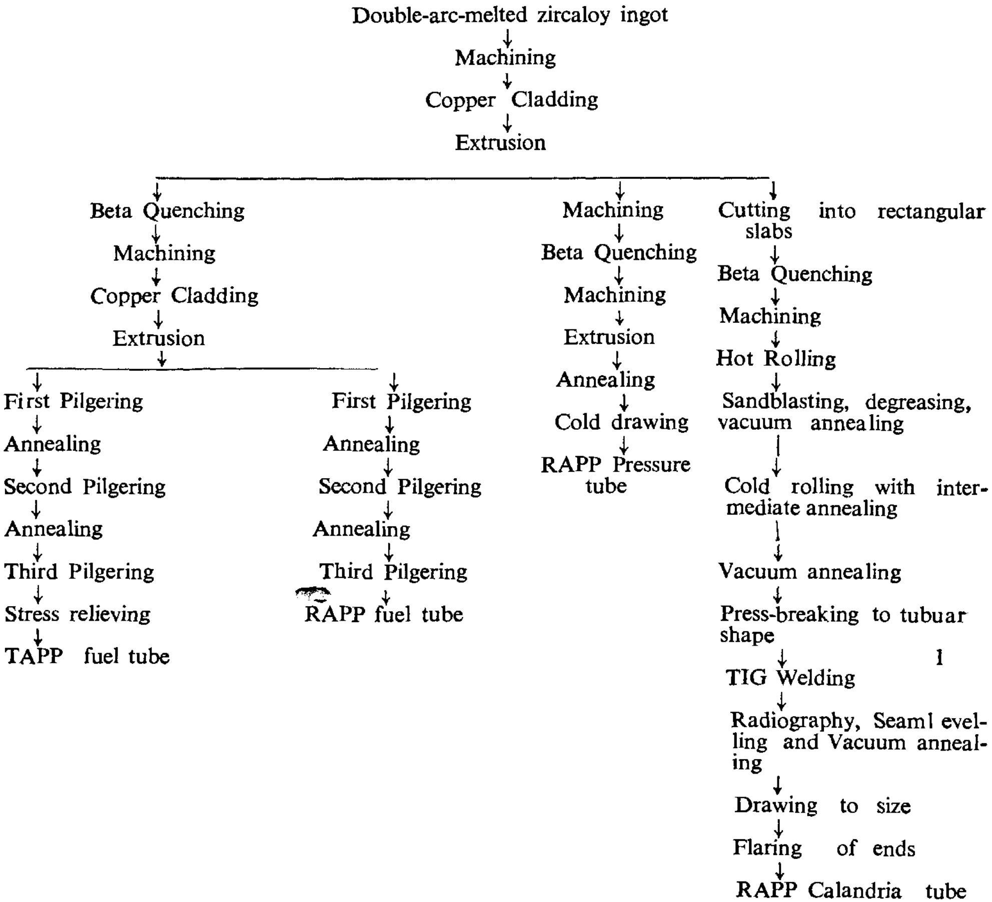
The likelihood of the increasing use of the zirconium–2.5 per cent niobium alloy in our nuclear power programme has already been mentioned. There is another niobium bearing alloy—zirconium—2.5 per cent niobium–0.5 per cent copper—which is used for making the garter springs which are used as spacers between the calandria and the pressure tubes. Since niobium is used in these alloys, a brief mention would be made of the indigenous niobium technology.

In India, the principal niobium bearing mineral is columbite-tantalite where niobium occurs in association with tantalum, which has a high neutron absorption cross section. As in the case of zirconium and hafnium, it is necessary that niobium meant for application inside the reactor core has to be totally separated from tantalum. In the Indian practice, the columbite-tantalite ore concentrate is treated with acids to yield water soluble acids of niobium and tantalum. The separation of the metal values from the leach liquor is effected by solvent extraction. Starting from niobium pentoxide obtained from the solvent extraction-precipitation stages, the metal is produced either by carbothermic or by alumino-thermic reduction. The as-reduced niobium metal is impure and refinement is achieved by electron beam melting under high vacuum.

Fast Reactor Structural Materials: There are two major differences in the property requirements of the in-reactor structural materials for thermal and for fast reactors. The first is that materials with fairly large neutron absorption cross sections can be used in the fast reactor core because their effect on the overall neutron economy is not very significant. The second point of difference arises because of the fact that the coolants used in the two types of reactor are entirely different. In a fast reactor, where liquid sodium (or sodium-potassium) is used as the coolant, it is important to ascertain that the structural materials are compatible with flowing molten sodium and are not susceptible to mass transfer *via* this coolant. In view of their high melting points, satisfactory physical and mechanical properties at elevated temperatures and good compatibility with molten sodium, austenitic stainless steels containing 18 per cent chromium and 8 per cent nickel (types 304, 316, 347 and 348) have

TABLE VII

Flowsheet for the fabrication of zircaloy fuel tubes, pressure tubes and calandria tubes at the Nuclear Fuel Complex, Hyderabad



Double-arc-melted zircaloy ingot
↓
Machining
↓
Copper Cladding
↓
Extrusion

Beta Quenching ↓ Machining ↓ Copper Cladding ↓ Extrusion ↓ First Pilgering ↓ Annealing ↓ Second Pilgering ↓ Annealing ↓ Third Pilgering ↓ Stress relieving ↓ TAPP fuel tube	Beta Quenching ↓ Machining ↓ Copper Cladding ↓ Extrusion ↓ First Pilgering ↓ Annealing ↓ Second Pilgering ↓ Annealing ↓ Third Pilgering ↓ RAPP fuel tube	Machining ↓ Beta Quenching ↓ Machining ↓ Extrusion ↓ Annealing ↓ Cold drawing ↓ RAPP Pressure tube	Cutting into rectangular slabs ↓ Beta Quenching ↓ Machining ↓ Hot Rolling ↓ Sandblasting, degreasing, vacuum annealing ↓ Cold rolling with intermediate annealing ↓ Vacuum annealing ↓ Press-breaking to tubuar shape ↓ TIG Welding ↓ Radiography, Seam levelling and Vacuum annealing ↓ Drawing to size ↓ Flaring of ends ↓ RAPP Calandria tube

(Dimensions in inches)

Length 152.7 ± 0.02;	Length 19.126 ± 0.002;	Length 214±1/16;	Length 201 + 0.0 —1/16;
Wall thickness 0.032± 0.003;	Wall thickness 0.016 + 0.003	Wall thickness 0.158 to 0.174;	Wall thickness 0.049 +0.002 —0.0
		ID 3.25 + 0.018 —0.0;	
ID 0.499 ± 0.0015	OD 0.601 ± 0.0015	Maximum OD 3.607	Minimum ID 4.240 Maximum mean OD 4.360

found application in these reactors, where the environmental conditions for many of the components are much more hostile than in thermal reactors.

The fuel assembly in a fast reactor has to reckon with irradiation induced swelling and creep associated with high fluences of fast neutrons. Extensive displacement damage is caused in the structural materials and this process leads to an increased concentration of non-equilibrium vacancies. These defects agglomerate, at suitable temperatures, to form a very large number of microscopic voids. As a result, volume changes occur in the cladding and in the coolant channel. This irradiation induced swelling becomes rampant at temperatures pertinent to fast reactor operation. The excess non-equilibrium vacancies also lead to enhanced creep. It has however been found that the use of cold worked stainless steels minimises these deleterious effects. Certain minor composition modifications as well as the incorporation of fine dispersions of coherent precipitates in the austenite matrix also look promising in this regard.

Though cold worked austenitic stainless steels, in particular the type 316, have been found reasonably satisfactory, there is a strong incentive for developing structural materials which would be better suited for fast reactor core structural applications. A fairly large number of austenitic and ferritic alloys and precipitation strengthened nickel base alloys are being considered in this context.

NUCLEAR FUEL COMPLEX

Due to paucity of time, it will not be possible to give a detailed account of the activities of all the various units which play very important roles in the attainment of self-sufficiency in reactor materials. However, the range of activities of one of these units—Nuclear Fuel Complex at Hyderabad—will be briefly described.

The experience gained in Trombay in the matter of making and shaping reactor materials had led to the establishment of Nuclear Fuel Complex with a view to meeting the materials requirements of the chain of power reactors to be built up during the first stage of the Indian nuclear power programmes. This integrated complex consists of several production plants including the following:

(*i*) a uranium dioxide plant for producing ceramic quality, nuclear grade uranium dioxide from indigenous uranium concentrates obtained from Uranium Corporation of India Ltd., Jaduguda;

(*ii*) an enriched uranium dioxide plant for producing uranium dioxide powder from enriched uranium hexafluoride (imported), to meet the fuel requirements of the reactors at Tarapur;

(*iii*) an integrated zirconium plant for producing the following hafnium free, nuclear grade products: zirconium oxide, zirconium sponge, finished zircaloy tubes and other shapes required for fuel cladding and core structurals; and

(*iv*) a ceramic fuel fabrication plant for producing zircaloy clad natural and enriched uranium dioxide fuel bundles for the power reactors in operation.

All the facilities have been operational and the fuel produced at this unit is being used by the reactors at Tarapur and at Kota. In addition, the fabrication of zircaloy core components like calandria tubes, coolant tubes and calandria manifolds for the reactors at Kalpakkam has also been completed.

Starting from the early days of the awareness that the development of nuclear power would be desirable in this country, we have come a long way, crossing many a hurdle and bridging many a gap. A modern technology has been built up in its totality, starting from scratch. The process has had beneficial fall outs not only with regard to the energy scene but also in relation to the indigenous growth of several other technologies.

METALS AND MATERIALS FOR SPACE PROGRAMME

Like nuclear technology, space technology is also a hybrid technology requiring interaction of various disciplines such as aeronautics, avionics, propulsion, materials as well as other technologies. The similarity extends further in as much as there is no infrastructure in the country in many areas and there are often difficulties in importing high technologies involved. In most cases, it is almost impossible to have any collaboration with other countries for development of these technologies because of their strategic applications. This is inspite of the declared objectives and open pursuit of the Indian Space Programmes which are geared for only peaceful purposes, the three primary objectives being the use of space for meteorology, communication and resources management. This demands successful development of spacecraft and satellite launch vehicles. Indigenous development of rocket technology depends to a great extent on successful development of various materials and special chemicals.

Polymers are used in all the major sub-systems of a rocket. The sub-systems in a vehicle can be identified as relating to the propellant, the inhibition, the insulation, the ignition, the motor casing and the nozzle. In each one of them, the part played by polymers is discussed in brief in the following:

Solid Propellant Systems : Solid propellant is composed of an oxidiser, which is generally ammonium perchlorate, aluminium powder—a metallic fuel—to raise the combustion temperature to around 2500 °K and a polymeric binder which acts as an organic fuel and also as a binding matrix Propellant, a rubber-like material, exhibits visco-elastic properties and these are the direct consequence of the polymer being used as a binder system. Liquid polymers in the molecular weight range of 4000 or so are used in the propellant processings; this on being subjected to an elevated temperature for the required durations, develop three dimensional polymeric net-work systems. Propellants are classified into different categories based upon the polymer used as binder, e.g., polyester propellant, polysulphide propellant, polyurethane propellant, polybutadiene propellant, etc. Whatever the binder system, the aim is to first synthesise a good polymeric binder which can accommodate ammonium perchlorate and aluminium powder to the extent of 85–90 per cent by weight. While accommodating such a high solid loading, one must ensure that the solid-liquid slurry has a sufficiently low viscosity so that it is processable. Also the slurry, on being cured at an elevated temperature must give good mechanical properties to the propellant. On ignition, the propellant must burn completely and give low molecular weight gaseous products which, in turn, produce high exhaust velocities. Synthesis of various polyurethane and polybutadiene binder systems have been successfully carried out and used in ISRO (Table VIII).

Among the various propellants, those formulated on polybutadiene liquid polymers give very high specific impulse which is a measure of the energy content and hence the capability of imparting thrust to the rocket. The polybutadienes with thermal shocks and vibrations. Solid propellants developed have achieved the performance as good as those developed elsewhere. Pilot plants have been set up which are now being operated both at Trivandrum and Sriharikota.

Inhibition System: The design of some propellant grains requires that certain portions of the propellant grains are not exposed for combustion. This necessitates protection of certain propellant surfaces by non-combustible or inhibiting materials. Such inhibition systems are again based on polymers. However, when two polymer systems come into contact, compatibility problems can arise. The inhibitor should adhere to the propellant surface throughout the combustion phase and should not itself burn. When inhibited propellant grains are stored, migration of certain inert materials such as plasticizers to the interface occurs resulting in separation. This, to a great extent, is prevented by the use of the same type of polymer as inhibitor as is used in the propellant system. Inert fillers such as asbestos are also used in inhibitors.

Insulation System : During propellant grain curing phase or under flight conditions, rocket motor cases with propellants cast inside are subjected to heating due to different co-efficients of expansion and consequently to differential thermal stresses which get developed in the propellant matrix. The magnitude of these stresses should be limited so as not to exceed the strain capability of the propellants, or otherwise cracks will develop in the propellant grains rendering them useless. To protect the rocket motor chamber from the intense heat of a burning propellant, insulators are introduced between the rocket motor casing and the propellant grains. The insulators are made out of polymers that are either by themselves compatible with the propellants or lined by a thin polymeric layer which is compatible with the propellant. The insulators are firmly bound on one side to visco-elastic propellant and on the other to the motor case. The function of the insulator is to avoid heat transmittance from the motor case to the propellant or vice-versa. Insulators for various propellant formulations and adhesives for proper bonding have been developed at the Vikram Sarabhai Space Centre. These insulators are based on polymers like nitrile rubber or ethylene propylene co-polymer. Bonding them firmly to the propellant poses problems and they have been overcome by adopting a suitable adhesive lining.

Ignition System : An ignitor initiates the combustion of the propellant in a rocket motor, by sprinkling hot burning particles on the propellant. Electric spark through a squib initiates the pyrotechnique charge, which in turn ignites a fast burning propellant Fast burning propellant throws out hot particles on the rocket propellant. The fast burning propellant is again based on a polymer binder system. The entire ignition duration is generally from a few milliseconds to a second. High temperature performance adhesive sealants developed to seal the ignitor lead to avoid any leakage of hot gases.

Use of polymers in motor casing and nozzle systems: Fibre reinforced composite motor casings have been developed for the use of upper stages of multi-stage Satellite Launch Vehicles. Motor cases have been fabricated using glass fibre composite with epoxy resin matrix. The motor cases for the third and fourth stages use this fibre reinforced plastic in SLV-3. A pilot plant based on the technology developed by the Centre has been set up at Trivandrum. For higher specific strength, the development of upper stage motor cases using Kevlar–49, an organic fibre, polyamides has commenced.

In the nozzle systems, where ablative materials are required, polymeric composites are used. The back-up structures for the nozzle are also made from phenolic composites. For a high strength-low weight nozzle construction for rocket motors, work with carbon-carbon composites is being taken up at the Centre.

It is evident that polymers play a vital role in most sub-systems of a rocket and satellite launch vehicles. The various sub-systems using the polymers have been integrated and the rocket systems have been qualified and flight tested. Polymers also find various miscellaneous uses such as the paints, potting and sealing compounds for electronic components, structural adhesives, etc. Paints based on polymers protect the rocket casings from aerodynamic heating during flight. Polymeric sealing compounds offer protection from vibrational loads and short-circuiting in the electronic packages. Special care is taken in the formulation of sealants to avoid high exotherms while curing. All the above products have been used in the rockets and their payloads.

Structural Materials: Most of the materials used in the structure of the satellites and rockets need to have high strength to weight ratio. This is in order to maintain the structural factor which is the ratio of the weight of mechanical hardware to the weight of charged rocket motor, to a minimum so that the useful payload capability is maximised. Any extra weight in a satellite or in the upper stages of a multi-stage launch vehicle would need higher requirements of propellants in the upper stages which again would call for additional requirements of propellant in the lower stages. The energy or the propellant requirements follow an exponential law and as such any marginal improvement in the structural factor would lead to large saving in the energy requirement and correspondingly the cost of the system.

The flight environment also rapidly changes and the materials have to exhibit a high degree of stability in respect of their properties. In addition, the materials are subjected to severe thermal and mechanical loads during flight. As the materials satisfying these requirements are easily not in general industrial use and because the quantities that are required are rather small, it often becomes necessary to develop the materials in-house. For use in spacecraft structure in Indian built satellites, the 7000 series of aluminium alloys and AZ series magnesium alloys have been formulated and the fabrication and process parameters have been established. Components like adopters, mounting blocks, payload decks for *Aryabhata* and Satellite Earth Observation 1 (SEO–1), satellites have been fabricated in these alloys. Seven thousand series of aluminium alloys will be required in the fabrication of liquid engine sub-assemblies like injector, propellant tanks, etc.

For correcting the attitude of the satellite, thrusters are necessary. This is an essential element in most of the satellites because of the perturbations due to drag or changes in geopotential are always present. There is also the demand for a pointing system such as orienting the solar array towards the sun or a camera directed towards the earth. One method of achieving the attitude control of the satellite is through cold gas thrusters, operated with nitrogen gas stored under high pressure.

Gas bottles store such high pressure gas. These gas bottles are fabricated in Ti-alloy as it would keep the weight to the minimum. Ti-alloy gas bottles are used in *Aryabhata* and SEO-1 satellites for station keeping purposes. Such gas bottles would also be required in liquid engines. The technology required for the fabrication of these gas bottles in Ti-alloy (Ti-6 Al-4 V) has been developed.

The consideration of minimum structural factor applies to motor cases of rockets which form the upper stages of a satellite launch vehicle. Composite materials are usually chosen for the fabrication of these motor cases. These composites are made with fibres as reinforcement and polymeric substances as matrix material. With bought out glass fibres and polymer matrices, the Centre has successfully developed the technology for fabrication of motor cases and gas bottles. This development was made possible by the design and fabrication of machines for polar and helical filament winding. In addition to machinery development, the technology of filament winding, in terms of selection of proper fibres and matrices, winding angles, etc., to achieve the desired mechanical and physical properties, is in itself an important development for successful fabrication of rocket motor cases. This achievement is adequately demonstrated in the use of filament wound rocket motor cases for the third and fourth stages of SLV-3 vehicle.

Technology for carbon fibre composites has also been developed. Carbon fibre reinforced plastics are used in the fabrication of the reflector for the onboard antenna of Ariane Passenger Payload Experiment (APPLE) Spacecraft. This spacecraft which has been designed and fabricated in India will be launched in 1980 by the European Space Agency (ESA).

In the booster rockets, which form the lower stages of launch vehicles, weight penalty of the structures are not as severe as in upper stages. The motor cases are made of maraging steel 250 grade or low carbon alloy steel. The one used in Indian Space Programme is 15 CDV6, a low carbon alloy steel. The technology for roll bending, forging, welding, machining and heat treatment has been established and the motor cases and other hardware of most of the sounding rockets and the lower stages of the Satellite Launch Vehicle are fabricated in this material.

The nozzles of rocket motors demand materials which not only have good structural properties but also are characterised by good thermal and ablative properties. The materials used for nozzle construction are expected to withstand instantaneously developed severe temperature conditions, ranging between 3000 to 4000 °K and exhaust gas velocities of the order of 3 km per second. Composite material systems like S-glass-phenolic, carbon fibre-phenolic, asbestos-phenolic have been developed and successfully used in the nozzle where erosion is severe. The technology, at laboratory level, has also been developed for deposition of pyrolitic graphite as coating on graphite and as thin slabs. Pyrolytic graphite as coating on graphite or as nozzle throat insert withstands very high temperature and minimises erosion at the nozzle throat.

Ablative materials are also required in fabrication of heat-shields for the launch vehicle. This is primarily to protect the apogee motor and the spacecraft from excessive heat. Heat-shield has been developed as a sandwich structure using honeycomb cores, sandwiched between two ablative terminated skins on either side. The bonding between the skin and the core is achieved by film adhesives.

Materials with good thermal properties are also required in the space programme. For instance, there would be extreme gradient in temperature in the spacecraft. The side facing the sun attains temperatures as high as 250 °C while the opposite side as low as — 50 °C. Thermal coatings with specific absorptivity and emmissivity values are used for passive thermal control of satellites. Acrylic and silicone based paints have been developed and used in ISRO for spacecraft. Both *Aryabhata* and SEO (I) have used thermal paints for passive thermal control.

A number of materials for various specific requirements have been developed. Mention should be made of special catalysts The catalyst specially has been developed in VSSC, for spontaneous decomposition of hydrazine fuel used in control rockets of thrust of 1 kg, 5 kg and 25 kg used in the third stage motor of SLV-3. Micro-thrusters using hydrazine and catalysts are under development at the Centre for their application in spacecraft.

Another exotic material which has been developed is dry solid lubricant. In extreme vacuum conditions of space, to have moving parts operate successfully over years, use of dry lubricant becomes obligatory. Molybdenum disulphide is used as dry lubricant and techniques have been developed for coating this material on the cage in ball bearings used in spin up mechanisms of launch vehicle and spacecraft sub-systems like momentum wheel and solar array drive for spacecrafts.

It can be said that no space research programme can ever be successful without there being a significant effort in the development of basic materials, the processes and technologies to utilise the materials for component and system realization. It has been demonstrated that successful realization of space programmes has also yielded phenomenal benefit to the world in terms of technological fall-out.

To sum it up, the development of materials for atomic energy and space applications is an area of many challenges as well as opportunities to meet them. The progress made so far and the experience gained has generated confidence for the indigenous development of numerous materials for the present and future programmes required for specialised applications for specific needs of atomic energy and space. In a field which is rapidly changing and has a high growth potential, there is a constant need to have the plans reviewed and up-dated, and even the strategy changed as the programmes advance.