Metals for Reactor-Core Construction[1]

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WITH THE ADVENT of the atomic energy program, the materials engineer was faced with many new and trying problems. A new criterion, that of nuclear properties, was added to the usual consideration of physical and chemical properties. Frequently the materials engineer found that nuclear properties overruled all other considerations, even cost. This new concept plagued him even in unexpected cases. He found that items such as steel which were normally considered stock items sometimes contained traces of boron and other high-cross-section elements. No material could be accepted at face value.

As the program developed, it was found that most of the materials which could be used in atomic energy applications were either extremely rare or had to be in a highly purified state. To grasp the problem that faced the materials engineer, let us consider the state of development in 1940. Uranium was a laboratory curiosity. Some of its ores had been mined primarily to obtain the radium that occurred with it. Very small quantities of metal of questionable purity were being produced by either the reduction of the oxide or fused-salt electrolysis. The situation on thorium was a little better as considerable quantities of oxide had been produced for gas mantles and small quantities of metal had been produced. The processes in use, however, were far from adequate for large-scale production of high-purity material. Beryllium and zirconium had been produced in various degrees of purity but in very limited quantities.

It is obvious that remarkable developments have been made in the field of reactor materials during the past ten years. In discussing the status of various reactor materials, it is desirable that they be broken down into classes. For this presentation, I would choose to divide them by their function in a reactor. The classifications are fuels, cladding and structural materials, moderators, and control materials.

The fuel or fissionable material is essential to the operation of a reactor. For our purposes, we will consider uranium, thorium, and plutonium as fuels. In the strict sense, thorium is not a fuel, per se, but is included since it can be converted to a fissionable material.

Uranium is the basic fuel material for reactors. Any reactor must contain either one of the fissionable isotopes of uranium, or plutonium, which is itself made from uranium. Although uranium has been considered extremely rare, it does make up 0.0004 percent of the earth's crust. This is more than such metals as cadmium, bismuth, mercury, and silver, which are not considered rare. Uranium is found in various types of rock as a great variety of minerals. The highest concentrations occur in igneous rocks; sedimentary rocks (sandstones) contain about half as much. Uranium has been found in sea water, river water, and in living organisms. Pitchblende is the richest uranium mineral, whereas the major production comes from carnotite or roscoelite. The uranium content of these latter minerals is usually quite low.

Through a variety of chemical treatments, the uranium-bearing minerals are extracted and purified to produce a high-purity uranium trioxide. Uranium metal has been prepared by several methods. In 1789, Klaproth reduced UO_3 with carbon, obtaining what was then considered to be uranium metal. Peligot showed in 1840 that Klaproth's product was UO_2 and succeeded in preparing the metal by the reduction of UCl_4 with potassium. A number of investigators produced small quantities of uranium metal powder on a laboratory scale by four methods: (1) reduction of uranium oxide with carbon; (2) reduction of uranium oxides with aluminum, calcium, or magnesium; (3) reduction of uranium halides with alkali metals or alkaline earth metals; and (4) electrolysis of uranium halides.

More recently, efforts have been concentrated on the reduction of oxide or halides with the alkali metals, or the electrolysis of uranium halides. Uranium powder of a high degree of purity is produced rather easily by treating uranium metal with hydrogen at about 450° F to form the hydride. This hydride is then decomposed by heating in vacuum at around 900° F.

Since the uranium produced by any of the methods is not in the proper massive shape for fabrication, it was necessary to develop methods for melting and casting into conventional ingots. This problem was made more difficult by the high chemical reactivity of uranium with the atmosphere and with most ceramic crucibles. Considerable effort was expended in the development of furnaces which would permit the melting and casting of uranium without its being in contact with the atmosphere. The solution of the crucible problem also required much work.

In general, uranium is a reasonably well-behaved metal. It can be forged, rolled, swaged, or drawn into any number of shapes including plates, rods, tubes, wire, and thin foils. The only problem in its fabrication is caused by its chemical activity with the atmosphere. This makes it necessary to heat the metal in a protective atmosphere. The chemical activity of

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uranium makes joining of uranium by welding or brazing troublesome but not impossible. Here again the use of vacuum or protective atmospheres during heating is helpful. Uranium is only moderately difficult to machine. The chief problem lies in its chemical activity. Proper lubricants and coolants are needed to prevent excessive burning of the metal. As might be expected, the corrosion resistance of uranium in most media including air and water is very poor. This has led to considerable interest in protective coating by electroplating or other techniques. A large number of metals can be plated on uranium from conventional plating baths.

Considerable work has been done on the physical and chemical properties of uranium. Some of the important data are shown in Table 1. Frequently, the physical and chemical properties of a metal can be improved by alloying. In the case of an enriched reactor fuel, it is also advantageous to make use of an alloy to dilute the concentration of the fuel. For these reasons, a large number of uranium-alloy systems have been investigated. As one might expect, a number of types of constitutional diagrams are encountered. In Fig. 1 is shown the uranium-aluminum system. It is quite complicated and has several compounds. Similar systems are developed with beryllium, bismuth, carbon, cobalt, copper, iron, lead, manganese, mercury, nickel, oxygen, silicon, and tin. In Fig. 2, the uranium-vanadium system, we have the other extreme, a simple eutectic system with little solid solubility. Chromium forms a similar system. Molybdenum, niobium, titanium, and zirconium show extensive solid solubility at elevated temperatures and contain no true compounds. Tantalum and tungsten form a peritectic-type system, whereas thorium forms a monotectic.

TABLE 1. Properties of uranium.

Density near 20° C, g/cm^3	19.1		
Melting point, °C	1133		
Boiling point, °C	3900		
Specific heat near 20° C, cal/g °C	0.028		
Coefficient of linear thermal expansion, 10^{-6} per °C			
Direction parallel to axis	25°–125° C	25°–325° C	25°–650° C
a	21.7	26.5	36.7
b	− 1.5	− 2.4	− 9.3
c	23.2	23.9	34.2
Volume coefficient	45.8	48.6	61.5
Thermal conductivity near 20° C, cal/sec cm °C			0.060
Electrical resistivity, microhm-cm—25–50 (25° C)			
Allotropic transformations, °C			
Heating	α–β	663	
	β–γ	764	
Cooling	γ–β	762	
	β–α	660	
Crystal structure			
alpha, orthorhombic			
beta, tetragonal			
gamma, body-centered cubic			

Average Tensile Properties of Alpha-Rolled, Alpha-Annealed Material

Test temp., °F	Yield strength (0.2% offset), psi	Ultimate strength, psi	Elongation, %
Room	25,000	90,000	13.5
570	18,000	32,000	43.0
930	6000	10,000	57.0

Young's modulus, psi 30×10^{-6}

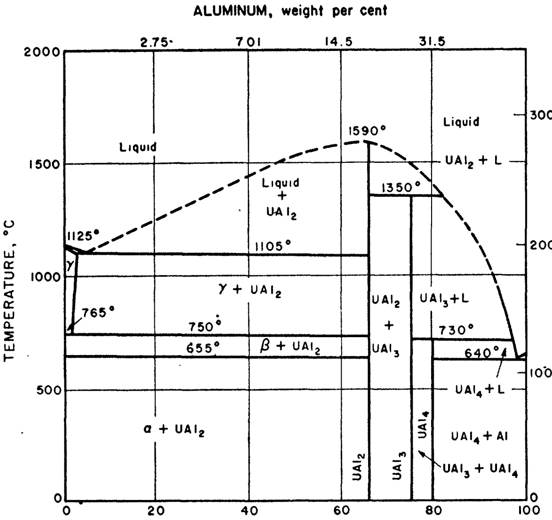

FIG. 1. Uranium-aluminum constitutional diagram.

Thorium is considered as a secondary reactor fuel since it will, during irradiation, absorb a neutron and become U^{233} which is in itself fissionable. By this mechanism known as breeding, we might be able to increase our supply of nuclear fuel. Thorium is found principally as the oxide in monazite sand. Chemical methods similar to those employed for uranium are used to prepare high-purity oxides or halides of thorium. These compounds are reduced to metal by the techniques previously described for uranium. For some special purposes requiring high-purity metal, the deBoer iodide process has been used. In this process, thorium tetraiodide is thermally decomposed on a heated filament. The process is carried out inside a sealed tube. The product is a loosely knit crystalline product which is then arc melted. The melting of thorium, like uranium, has offered considerable difficulty. The higher melting point of thorium has made the crucible problem even more difficult.

Thorium fabricates very well. It can be worked by a variety of methods either hot or cold. It is very ductile and permits large reductions before requiring annealing. Thorium has been forged, rolled, swaged, extruded, and drawn to produce rods, sheet, thin-walled tubes, fine wire, and thin foils. Again the chemical activity of the metal dictates heating in a protective atmosphere or salt bath. Welding of thorium has been only partly successful. In addition to the atmosphere problem, the metal seems to be sensitive to small

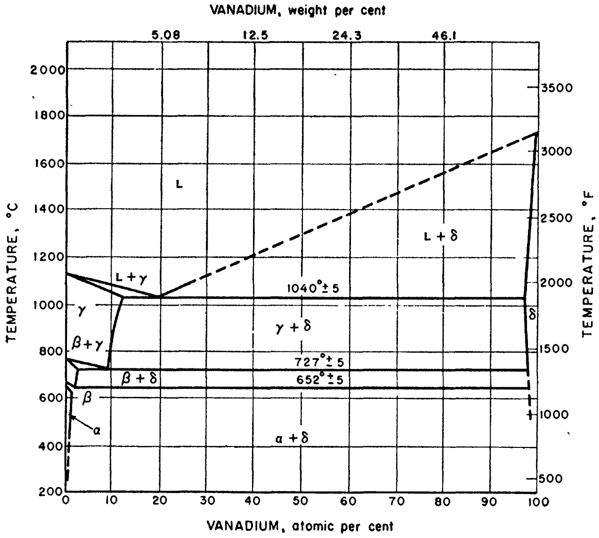

FIG. 2. Uranium-vanadium constitutional diagram.

amounts of impurities. Furnace brazes, when they have been produced, are brittle and unreliable. The machining characteristics of thorium are similar to those for mild steel. Coolants are desirable but not essential. Thorium, like uranium, has poor corrosion resistance. In general, it is somewhat better than uranium. Protective coatings are desirable and can be obtained easily by electroplating. Data on the physical and chemical properties of thorium are given in Table 2.

Because uranium and thorium are neither corrosion resistant nor very strong, it is necessary that another metal be used either for cladding or support. The same metal is likely to be used as the principal structural material for the reactor core. In addition to the usual requirements of structural materials, such as adequate strength, fabricability, thermal stability, and satisfactory corrosion resistance, we must add nuclear properties.

The number of metals suitable for structural use in thermal reactors is severely limited since only aluminum, beryllium, magnesium, and zirconium have thermal-neutron-capture cross sections of less than 0.5 barn/atom. Of these metals, aluminum and magnesium are certainly well-known commercial metals, and their production and fabrication warrants no further discussion. Beryllium and zirconium, both considered rare and exotic, deserve some consideration of their production techniques.

Beryllium is a very light white metal which has become well known for its toxicity and unexplained poor ductility. Its high melting point, low capture cross section, and good moderating qualities make it a promising reactor material. These are offset by poor ductility, erratic corrosion resistance, and considerations of health. Although beryllium exists in approximately thirty minerals, only one is of commercial importance. This is beryl, a beryllium aluminum silicate which usually contains from 8 to 14 percent of beryllia. The beryl ore is treated chemically to produce beryllium fluoride. This is then reduced to metal by either calcium or magnesium.

The product of the reduction process is a pebble or lump which must be reprocessed for further fabrication. It can be vacuum melted to form massive ingots or treated to form powder. The melting and casting of beryllium have not been completely satisfactory. The ingots produced are likely to contain nonmetallic impurities and do not produce good finished shapes. Powder metallurgy has been developed to such a point that most of the billets for further fabrication are produced by this method.

Beryllium does not fabricate easily. It has been extruded to form various shapes. Hot forging and rolling are usually done in a steel jacket. Cold working is difficult. In spite of its poor fabricability, a rather large number of shapes have been produced. Beryllium can be joined by either welding or brazing. The techniques are complicated by the rapid oxidation of the metal in the atmosphere. The machining of beryllium is made difficult by its tendency to surface damage. Cracking can occur below the surface unless great care is exercised. The corrosion resistance of beryllium in air and water is poor. It is not as bad as uranium or thorium, however. Considerable effort has been placed on electroplating. Once the surface has been chemically cleaned, plating with copper, nickel, zinc, tin, iron, or silver is quite feasible.

At the present time, zirconium with its low thermal cross section, excellent corrosion resistance, good mechanical properties, and good fabricating qualities is the leading cladding and structural material for thermal reactors. It is interesting to note that zirconium has not always been regarded so favorably. All zirconium ores contain small amounts (0.5–3%) of hafnium which is not removed during ordinary production of the metal. The high cross section of hafnium caused the values for zirconium to appear high also. It was only after a sample of pure zirconium was prepared that its low cross section was demonstrated and a great

TABLE 2. Properties of thorium.

Density near 20° C, g/cm^3	11.71
Melting point, °C	1690
Boiling point, °C	> 3000
Specific heat near 20° C, cal/g °C	0.028
Coefficient of linear thermal expansion near 20° C, 10^{-6} per °C	11.15
Thermal conductivity near 20° C, cal/sec cm °C	0.09
Electrical resistivity, microhm-cm	18
Crystal structure, face-centered cubic	

Average Tensile Properties of Alpha-Rolled, Alpha-Annealed Stock

Test temp., °F	Yield strength (0.2% offset), psi	Ultimate strength, psi	Elongation, %	Young's modulus, 10^6 psi
Room	27,000	37,500	40	10
570	12,000	22,000	38	8
930	9500	17,000	50	7

TABLE 3. Physical and chemical constants of aluminum, beryllium, magnesium, and zirconium.

Property	Aluminum	Beryllium	Magnesium	Zirconium
Thermal-neutron-absorption cross section, barns/atom	0.215	0.009	0.059	0.18
Density near 20° C, g/cm^3	2.699	1.85	1.74	6.5
Melting point, °C	600	1315	650	1845
Boiling point, °C	2327	2970	1120	
Specific heat, cal/g °C	0.215	0.43	0.25	0.069
Coefficient of linear thermal expansion, 10^{-6} per °C	23.8	11.6	26	5
Thermal conductivity, cal/sec cm °C	0.50	0.38	0.38	0.057
Electrical resistivity, microhm-cm	2.655	5.9	4.46	41
Crystal structure	FCC	CPH	CPH	CPH

boom in popularity was started for this once rare metal.

Zirconium occurs in a number of minerals which are widespread over the earth. The principal commercial sources of zirconium are zircon ($ZrSiO_4$), zircite (ZrO_2), and baddeleyite (ZrO_2). All ores contain hafnium, generally in amounts from ½ to 3 weight percent, but some contain as much as 20 weight percent. The principal problem in the production of zirconium metal is the hafnium removal. After much effort, several methods have been developed that produce a high-purity low-hafnium oxide. To produce metal, the oxide is chlorinated either with CCl_4 or by mixing with carbon, pelletizing, and treating with chlorine at elevated temperatures. The chloride is purified by distillation and reduced by magnesium. The product is a slightly porous sponge.

Sponge zirconium can be further refined, using the deBoer iodide process. In this process the sponge is converted to zirconium tetraiodide, which is then thermally decomposed on a heated zirconium filament. This operation removes oxygen, nitrogen, and magnesium. As the quality of zirconium sponge has improved, more emphasis has been placed on direct melting and casting. A high degree of chemical activity again rules out conventional melting methods. Two methods, vacuum-induction melting in a graphite crucible and arc melting in a water-cooled copper crucible are used successfully. For some time, induction melting was preferred. The high carbon content of such metal has led to development of better arc melting techniques. Arc melting is now the leading method. For arc melting, the sponge is pressed to form square bars which serve as the consumable electrode. The metal is melted in a direct-current arc which is maintained between the electrode and the molten bath. The molten bath is contained in a water-cooled copper crucible.

Zirconium is very ductile and can be fabricated easily. All conventional fabrication methods are used to produce a wide variety of shapes. Some precautions are necessary because of the moderately rapid oxidation. For shapes which are to be machined to final size, there is no problem. Material which is to be fabricated to close tolerances should be protected by an inert atmosphere or by jacketing. The same precautions are required during annealing. Zirconium welds easily in a good protective atmosphere. A heliarc torch operated in a helium-filled chamber works well. Brazing is made difficult by the fact that brittle compounds are formed between zirconium and the common brazing metals. Machining characteristics of zirconium resemble those of aluminum. Zirconium is very soft and ductile and galls readily with materials rubbed against it. For some applications it would be desirable to coat zirconium with thin layers of another metal. Electroplating with either nickel or iron is possible. In either case, the electroplate must be diffusion annealed to promote adherence. Properties of the four leading structural materials for thermal reactors are given in Tables 3 and 4.

A great many more structural or cladding materials become available if a higher cross section can be tolerated. Pure metals include niobium, iron, molybdenum, chromium, copper, nickel, vanadium, and titanium. A number of alloys such as stainless steel or Inconel are available in the intermediate cross section range. Moderating materials for thermal reactors should be capable of reducing neutron energy rapidly. This requires a low atomic weight. Good moderators have a high scattering cross section and a low absorption cross section for thermal neutrons. The only good solid moderators are beryllium, beryllia, and graphite. Beryllium has been discussed in detail as a structural material. In spite of many shortcomings, beryllium and beryllia have been used as moderators. Graphite has found widespread use as a moderator because it is cheap, abundant, easy to work, and has good physical properties.

Materials for control must possess high cross section for the absorption of neutrons. They should also have some strength, be fabricable, and have reasonable corrosion resistance in the reactor coolant. Of the material elements, boron and cadmium meet most of these requirements and have been used extensively. Hafnium, with its high cross section and metallurgical properties similar to zirconium, should make an excellent control material. Some of the rare earths have very high cross sections but have not been available in sufficient quantities. As they become available, they will no doubt be used either alone or in alloys.

It might be well to consider reactor materials of the future. For fuel, we will still have uranium and thorium with more emphasis on plutonium. In the field of structural materials we are bound to see a number of changes. As power levels increase, operating temperatures also increase. We are fast reaching the point where aluminum is losing out because of lack of strength and corrosion resistance at elevated temperatures. Zirconium can, of course, compete to much

Table 4. Tensile properties of aluminum, beryllium, magnesium, and zirconium.

Property	Test temp., °F	Aluminum	Beryllium	Magnesium (Alloy AZ92)*	Zirconium
Yield strength (0.2% offset), psi	Room	5,000	33,000	16,000	18,000
	400	3,000	20,000	13,000	10,000
	600	1,500	15,000	7,000	8,000
Ultimate strength, psi	Room	13,000	80,000	24,000	32,000
	400	6,000	50,000	19,000	20,000
	600	2,500	40,000	9,000	16,000
Elongation, %	Room	45	2	1	25
	400	70	8	9.5	50
	600	90	17	22.5	60
Young's modulus, 10^6 psi	Room	10	40	6.5	13.8
	400	9			11.5
	600	6.5			10.5

* Alloy AZ92 (Mg 9.5A1—2Zn) was selected as typical of the magnesium-rich alloys suitable for reactor application.

higher temperatures. Eventually, for water-cooled reactors, we may have to go to titanium and stainless steel. For gas-cooled reactors, the operating temperatures must be much higher. Stainless steel only begins to meet these requirements both from the viewpoint of strength and oxidation resistance. Molybdenum has adequate strength but low oxidation resistance. Alloys such as iron-chromium-aluminum have adequate oxidation resistance but little strength. For very high temperatures, probably only ceramics have a chance. They do have serious shortcomings in lack of tensile strength and poor thermal-shock resistance. Apparently, the materials engineer will have his problems for many years in the future.

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