RECENT DEVELOPMENTS IN THE TECHNOLOGY
OF SODIUM-GRAPHITE REACTOR MATERIALS

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I. INTRODUCTION

The basic technology of the sodium-cooled graphite-moderated power reactor has been discussed previously ¹. This system employs liquid sodium as the coolant to remove heat from the fuel elements at high temperature. Graphite, separated from the sodium by a suitable cladding medium, provides neutron moderation. Zirconium, or a zirconium based alloy is the preferred cladding medium for the core region; austenitic stainless steel provides satisfactory cladding in the reflector regions.

Fuel elements are in the form of solid metal rods, thermally bonded with NaK alloy to their thin-walled stainless steel jackets. Operational experience gained with a twenty-megawatt experimental reactor of this type forms the subject of another paper being given at this conference ². Experiments conducted with this reactor and in other liquid sodium facilities have given insight into the behavior of reactor materials immersed in sodium under conditions reflecting normal and off-design operation.

II. SGR CORE STRUCTURAL MATERIALS DEVELOPMENT

Pure sodium is relatively unreactive toward materials of construction. Metals of interest in SGR systems, such as stainless steel, zirconium, molybdenum and niobium, enter into no direct reaction with sodium itself. They do, however, have measurable solubility which increases with increasing temperature. The solubility of stainless steel components is not unequivocally known, but is much less than one part per million in the SGR temperature range ³. What added solubility

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is caused by oxidation is also not specifically known for low oxygen levels. In any event, the role of true solubility in "pure" sodium below 650°C is minor, and is important only in relation to radioactive material transport.

Impurities are always present in sodium, however, and it is because of the inescapable presence in sodium of the non-metallic elements oxygen, hydrogen, and carbon, that reactions between structural materials and sodium become important. The rate and extent of reaction is dependent on temperature, and of course differs among materials.

A. Transfer of Oxygen and Carbon

Oxygen is present in liquid sodium as oxide anions. Therefore combination of dissolved oxygen with metals does not involve any change in state of the oxygen. In sodium containing more than 50 parts per million oxygen, stainless steel will oxidize appreciably at temperatures above 550°C. If the combination of temperature and oxygen level is present at a thin membrane, such as is found in a bellows, failure can occur. Below 650°C this oxidation is too slow to cause serious concern for massive structural members. Stainless steel will also react with carbon present in a sodium stream to give a brittle carburized case which reduces the ductility of the metal. The temperature threshold for this reaction in 18-8 stainless steel saturated with carbon is at about 560°C. The form in which carbon is present in sodium is not known.

Metallic zirconium is much more reactive toward oxygen at high temperatures than is stainless steel. If oxygen is present in liquid sodium in amounts greater than about 5 parts per million, it will react with zirconium to form an adherent layer of zirconium oxide. The oxide then diffuses inward from the oxide-metal interface, driven by the concentration gradient. The rates for both oxidation and diffusion of oxide are strongly temperature dependent.

Experiments in dynamic sodium systems at various temperatures have shown that the oxidative weight gain for zirconium may be described by the equation $w = kt^{1/2}$, in which w is the weight gain per unit surface area in time t , and k is a constant for a given temperature. This equation holds well for the 350°C to 550°C temperature range, with some decrease in the exponent of t above 550°C. Data for the rate constant k , derived from isothermal weight gain observations, fall in a line in an Arrhenius plot against reciprocal absolute temperature. From this plot, shown in Figure 1, the activation energy for oxidation of zirconium in sodium was found to be 29.2 kilocalories per mole, with an estimated uncertainty of about 1 kilocalorie. Dependence of the oxidation rate on the concentration of oxygen in the sodium is small for oxygen levels above 20 parts per million. Below this concentration, the oxidation rate falls off with decreasing oxygen level to levels where no oxidation is detectable.

B. Hydrogen Transfer

Hydrogen is present in sodium as dissolved NaH, and is thus able to react with any elements whose hydrides are more stable than NaH. With stainless steel under SGR pressure and temperature conditions no effect attributable to hydrogen has been observed. Zirconium, however, reacts readily to form zirconium hydride, ZrH_x , which has appreciable solubility in metallic zirconium, especially at high temperatures. The rate of reaction with hydrogen increases with increasing temperature. On the other hand, the equilibrium concentration of hydrogen in the zirconium decreases with increasing temperature. Therefore the situation existing at any given time in a non-equilibrium system is difficult to predict. It is influenced further by variables such as oxide film present on the metal and hydrogen pressure over the sodium.

Hydrogen dissolved in zirconium has little effect on its mechanical properties ⁴. As solubility is exceeded at any temperature, zirconium hydride precipitates along grain boundaries. Slow cooling from higher temperature will cause grain boundary hydride to appear at 150°C when the hydrogen concentration is as little as 10 ppm. The presence of the hydride phase imparts impact sensitivity and brittleness to zirconium, as will be discussed later.

If a thermal gradient is imposed along a zirconium part, (e.g., a moderator can shell), migration of hydrogen will take place through the metal and through the surrounding sodium. A theoretical study ⁵ has shown that at steady state conditions with a linear temperature gradient from 250°C to 500°C, complete conversion to delta phase hydride might occur in the lowest temperature regions. Thermal diffusion against a concentration gradient in the long zirconium part is negligibly slow. However, transfer of hydrogen from zirconium into sodium at high temperature and in the reverse reaction at lower temperature can take place in principle. Because an appreciable oxide film is inescapable on zirconium under operating conditions, the migration of hydrogen between sodium and zirconium is greatly impeded. The problem of delta phase formation is not judged to be serious in the light of present knowledge.

C. Nucleative Grain Growth in Zirconium

An important phenomenon which can occur in zirconium in a sodium reactor environment is strain-nucleated grain growth ⁶. In a thermal environment above 500°C recrystallization occurs if nuclei are present on which new grains can form. Very coarse grained structures are developed where the metal has been locally plastically strained by a critical amount during some manufacturing process, and this strain subsequently anneals slowly in the reactor. The grain size obtained on such recrystallization is determined by the rate of nucleation of new grains and the rate at which they grow. Low nucleation rate and high growth rate lead to a coarse grained structure. This is the

situation that exists in zirconium which has been strained just the critical amount and annealed at a temperature above 500°C. Figure 2 shows the critical strain for germinative grain growth as a function of temperature for zirconium strained at different temperatures. The formation of these exaggerated grains lowers the fatigue life of the metal, as will be discussed later.

Zirconium alloys enter into reactions with dissolved impurities in sodium in a manner similar to unalloyed zirconium. The rate of reaction differs with the alloy composition, however. Zircaloy-2, a two phase alloy containing approximately 1.5% tin, 0.15% iron, 0.1% chromium, and 0.05% nickel, has a rate constant k in the parabolic expression $w = kt^{1/2}$ only about one-quarter as large as that for unalloyed zirconium at a given temperature. Other alloys, both commercial and experimental, are under preliminary study in AI laboratories.

Alloying also affects the grain growth phenomenon in zirconium. For example, zircaloy-2 exhibits no germinative grain growth up to at least 650°C, due apparently to a stabilizing effect of the second phase present.

D. Effect on Mechanical Properties

These phenomena--oxidation, carburization, hydriding, and grain growth--can have a deleterious effect on the physical properties of reactor materials if not controlled.

Excessive amounts of oxygen can be troublesome because of danger of precipitation of sodium oxide in cool portions of the system. The differential solubility of corrosion products from steel can also cause obstruction of sodium flow in low temperature parts of the system. Failure of thin steel members is possible if large amounts of material are dissolved in hot regions and deposited in cool zones. If the temperature is below 650°C and the oxygen level under 50 parts per million, as in present SGR system designs, this problem is minor.

Carburization in sodium of stainless steel has the effect of decreasing ductility of the metal, as shown by low elongation in tensile tests. Results obtained on 0.037" sheet of 304 stainless carburized to a depth of 0.004" showed that neither the tensile nor stress-rupture properties are seriously affected, however.

With zirconium, the effects of oxidation are more severe than with steel in a given temperature range. Oxide layers in excess of 0.1 milligram per square centimeter markedly reduce fatigue life, as shown in a study conducted at temperatures up to 530°C⁴. Thicker layers cause continuing decrease in fatigue life up to thickness corresponding to 0.5 milligrams per square centimeter. The surface oxide acts as a crack initiator in a fatigue situation. Because of the extremely adherent nature of the oxide film, cracks which form in it propagate into the metal substrate and result in failure.

With 0.5 milligrams per square centimeter of oxide, the fatigue life of 0.035 inch zirconium sheet was found to be one-quarter that of the unoxidized material, as shown in Figure 3.

Grain boundary hydride precipitation also lowers zirconium fatigue life, particularly at temperatures below about 260°C. Above this temperature the hydride phase passes into solid solution, and the failure phenomenon becomes less marked. The presence of hydride enhances the effect of grain size resulting from germinative grain growth at all temperatures investigated, (up to 530°C) however. The data are scattered, but a reduction in fatigue life by a factor of two to six is found whenever any germinative grain growth occurs.

Prolonged exposure to sodium at 590° C has produced no detectable changes in weight or structure in molybdenum, either in a system containing 10 parts per million oxygen or in an "oxygen free" system. Niobium reacts with dissolved oxygen in sodium to form a non-adherent oxide. Weight loss from this reaction amounts to approximately one milligram per square centimeter per day at 590°C in a 10 part per million oxygen system.

E. Control and Measurement of Sodium Impurities

1. Control Measures

To combat the previously discussed detrimental effect of impurities in sodium on structural materials, it is important to control and measure impurity concentration. Oxygen is universally present in commercial sodium, and without effective control measures its presence would prevent satisfactory operation of a sodium reactor system. The solubility of oxygen in sodium is strongly temperature dependent, so large amounts of Na_2O may be removed by means of a "cold trap" maintained at a temperature somewhat above the melting point of sodium. Such a device is limited in its capability to reduce oxygen content of a system, however, because oxygen is soluble to nearly 10 parts per million in sodium at the lowest practical operating temperature for a cold trap. The design of a cold trap to remove large amounts of oxygen is rather critical because of problems with excessive precipitation and plugging.

To accomplish intensive oxygen removal, the hot gettering principle is useful, using zirconium or an alloy such as ZrTi in the form of thin foil. A "hot trap" filled with this material and heated to 650°C will reduce the oxygen level of a sodium system to an unmeasurable value, well below 10 parts per million. A configuration like that shown in Figure 4 has proved satisfactory. To prolong the effective life of the hot gettering material, cold-trapping to an oxygen concentration below 20 parts per million is advantageous. Subsequent removal of the cold trap from the system is necessary to prevent it from becoming an oxygen source after hot trapping is started.

Cold-trapping for oxygen will remove some hydrogen contamination from sodium also, since the solubility of NaH is temperature dependent. Hot-trapping with zirconium and its alloys will permit removal of a small quantity of hydrogen with the hot trap filler, since the rate of reaction at hot trap temperatures is very rapid compared with that in other parts of the system. As previously mentioned, equilibrium thermodynamics favor the ultimate concentration of hydrogen in lower temperature areas of the zirconium, however.

Control of carbon impurity in sodium is best accomplished by preventing contact of the sodium with carbonaceous material. In a system using a hot trap, the steel walls of the hot trap will act as a sink for carbon.

2. Analytical Methods

In order to determine the effectiveness of impurity control measures, and to monitor sodium system purity, analytical methods for oxygen, hydrogen, and carbon in sodium are required. Oxygen determination methods may be classed in two groups--laboratory determinations and field determinations. In the laboratory, a reaction involving the solution of sodium in a 50% mixture of butyl bromide and hexane, with subsequent aqueous extraction of the unreacted Na_2O , has proved to be reliable ⁷. The aqueous extract is titrated with standard acid. Similar good results are reported for a method involving mercury amalgamation of the sodium before adding water and titrating the oxide ⁸. Both of these laboratory methods suffer the major disadvantage of requiring a sample to be removed from the sodium system and transported to the laboratory. Sampling and handling technique, therefore, becomes of utmost importance if meaningful results are to be obtained. These methods are applicable to a lower limit of about 20 parts per million of oxygen in sodium.

A volatilization-titration method, which involves collection of the sample in a nickel cup in equipment integral with the system being sampled, also requires titration of the sodium oxide present ⁹. In this method, the separation of the oxide from the sodium is accomplished by distilling the sodium out of the sample cup, leaving the oxide behind. The sample cup must be removed from the system for titration. This method has, so far, failed to give reproducible results.

The most useful field method involves making use of the oxide solubility vs. temperature curve. A stream of sodium is cooled slowly while being pumped through one or more orifices. The temperature at which precipitation of Na_2O begins is found by plotting pressure drop across the orifice plate against temperature. The oxide concentration corresponding to this temperature is then found from the solubility curve. This "plugging meter" method gives reproducible results. Present knowledge of factors influencing sodium oxide precipitation, and the effects of other impurities such as NaH on plugging meter determinations, are not sufficiently well known to make the method

more than an empirical one.

None of the above methods can be used for oxygen levels below 10 to 20 parts per million of oxygen. They are, however, the best currently available for this determination.

Analysis of sodium for hydrogen encounters the same problem in sampling and standardization discussed for oxygen analysis. The actual determination on a separated sodium sample consists in thermally decomposing the NaH present in a vacuum-tight system ¹⁰. The pressure developed by the liberated hydrogen is measured and related to sample size to give the original hydrogen concentration.

Analysis for total carbon is accomplished by use of the conventional Van Slyke reagent, a chromic acid oxidant ¹¹. The carbon present is oxidized to carbon dioxide and measured volumetrically. Carbon present in the form of carbides is conveniently determined by dissolution of the sodium sample in water, followed by separation and measurement of the acetylene formed. Sampling and handling of samples intended for carbon analysis is less critical than for the other determinations, since contamination is less probable.

III. MODERATOR STUDIES

A. Radiation Effects on Graphite

1. General

A completely satisfactory theory of irradiation damage in graphite remains to be formulated. However, graphite has been studied more thoroughly in this respect than any other substance, and the general features of the damage mechanism are known ^{12,13}. At low temperatures where interlamellar diffusion between hexagonal layers in the graphite crystals is retarded, stable lamellar vacancies and interlamellar displaced atoms are produced by fast neutron irradiation. At a higher temperature the displaced atoms become labile and form interlamellar complexes, although there is the competing possibility of recombination with nearby lamellar vacancies at this temperature.

At temperatures of 150°C and above the phenomenon of irradiation annealing (variously termed "nuclear annealing," "pile annealing," "neutronic annealing") is observed in graphite ¹³. This phenomenon manifests itself as an alleviation of radiation damage beyond that attributable to thermal annealing alone. The probable mechanism is radiation-induced breakup of the interlamellar complexes at a temperature high enough to promote recombination of splinter atoms with lattice vacancies.

2. Temperature of Irradiation

The surface of moderator graphite in a sodium cooled reactor is essentially at the temperature of the coolant stream. The stream of

sodium rises in temperature as it rises through the reactor, imposing a vertical distribution of graphite surface temperature. In the Sodium Reactor Experiment coolant entrant temperature of about 250°C establishes the minimum graphite temperature at the surface of the moderator at the bottom of the reactor core. Graphite surface temperatures at the top of the core normally will be 500°C or higher.

The distribution of temperature of the graphite moderator as a function of distance below the cooled surface depends upon the density of energy dissipation by penetrating radiation and upon the thermal conductivity of the graphite. The latter is, in turn, a function of the graphite temperature and of the extent to which radiation induced changes have affected the graphite structure. To arrive at a general theory of the distribution of temperature in a moderator body, it is assumed that all radiation induced imperfections affect the temperature independent scattering of phonons similarly.

3. Thermal Conductivity of Irradiated Graphite

The lattice thermal conductivity of solid matter is approximately described by the Debye relation:

$$K \propto C_p \lambda v,$$

where C_p is the lattice specific heat, λ is the total scattering, and v is the effective phonon velocity. In the temperature range 0°C to 2000°C the thermal conductivity of graphite is characterized by dominance of the temperature dependent portion of the scattering factor, defined by the equation:

$$\frac{1}{\lambda} = \frac{1}{\lambda_i} + \frac{1}{\lambda_e},$$

where λ_i is the temperature independent boundary and imperfection scattering, and λ_e is the temperature dependent scattering. The temperature dependent scattering may be taken to be approximately $\lambda_e = b/e$, where b is a constant.

Multiplication of C_p (e) by λ yields a quantity proportional to the thermal conductivity. A set of derived curves shown in Figure 5 have been normalized by a choice of $v \lambda_i$ to yield approximately the peak transverse thermal conductivity observed in unirradiated CSF graphite. Curves are plotted for various values of the ratio λ_i/λ_e at 300°K. The lower values of this ratio correspond to the smaller values of λ_i attributable to incomplete graphitization or to irradiation damage. It is notable that there is little variation of curve shape for λ_i/λ_e values above 60.

The existence of the unique set of (density normalized) thermal conductivity curves for graphite is proposed. The acceptable manner in which the experimental curves of Mrozowski¹⁴ and Deegan¹⁵ shown

in Figure 6, match the theoretical curves of Figure 5 lends credence to the assumption for graphitization and irradiation damage, respectively. Such a set permits the complete description of the thermal conductivity profile from a measurement of thermal conductivity at any temperature. Of course, the thermal conductivity profile for irradiated graphite cannot be considered to extend above temperatures at which irreversible changes due to thermal annealing take place. However, it is proposed that the interrupted thermal conductivity curve for such graphite lies on the complete curve for a higher temperature annealing graphite having identical thermal conductivity at low temperatures.

Thermal conductivity of samples of graphite irradiated at 500°C has been measured in the range 150°C to 650°C and compared with that for virgin graphite of the same type. The data agree well with theoretical predictions, as is seen from comparison of Figures 5 and 6.

4. Surface Radiation Damage Concentration, Planar Case

Data relating thermal conductivity changes sustained upon controlled temperature irradiation up to 400°C as reported by Fletcher¹⁶ and Synder¹⁷, are given in Figure 7. Here thermal conductivities are those measured at 25°C after irradiation at the indicated temperature. (Fast dosage is approximate. No thoroughly adequate means for defining damaging dosage in terms of nvt exists). Replotting of these data for selected radiation levels is carried out in Figure 8, with an extension of the curves to higher irradiation temperature indicated. We have now assembled graphical relationships on the basis of which it is possible to calculate the steady state temperature distribution at the cooled boundary of a moderator element. For planar heat flow, the temperature gradient at any normal surface is:

$$\frac{de}{dx} = W(x)/K(e, x),$$

where W is the rate of heat flow per unit area at a depth x from the cooled surface, and K is the thermal conductivity of the radiation damaged graphite existing at depth x from the cooled surface, measured at temperature, e , which exists there.

Integration of this equation yields:

$$e - e_0 = \sum_0^x \left\{ \left[W_0 - \int_0^x \varphi(x) dx \right] \Delta x / K(e, x) \right\},$$

where e_0 and W_0 , respectively, are the temperature and the heat flux at the cooled surface. $\varphi(x)$ is the radiative heat dissipation density in the graphite.

Near the graphite surface the integral $\int_0^x \varphi(x) dx$ is small compared to W_0 , and the equation reduces to:

$$e = e_0 + W_0 \sum_0^x \left\{ \Delta x/K(e, x) \right\}.$$

Curves of e versus xW_0 have been obtained by iteration. By using plots of published data on K_{25} (thermal conductivity measured at 25°C) versus temperature of irradiation (Figure 8), a member of the family of thermal conductivity curves (Figure 5) is selected. This curve is then used to determine the value of $K(e, x)$. Results of these iterations from $e_0 = 30^\circ\text{C}$ are shown in Figure 9, for the case where the variation in $\int \varphi(x)dx$ due to volume heat generation has been neglected. The corresponding curves for thermal conductivity variation with depth are given in Figure 10.

It is to be noted that, in the planar case, the curves may be applied to various rates of volume heat dissipation by selection of the appropriate value of W_0 . Choice of boundary temperatures different from 30°C is effected by making appropriate linear transformation of the abscissa origin.

5. Radiation Damage Inhomogeneity, Reactor Geometry

The actual geometry of the cooled reactor graphite surface differs substantially from a plane. Heat flow is to cooled fuel channels which occupy cylindrical holes in the moderator graphite. For the case of radial heat flow, the equation becomes:

$$e = e_0 + \sum_{r_0}^r \left\{ \left[\int_{r_0}^r r \varphi(r) dr \right] \Delta r / r K(e, r) \right\},$$

where r is the radius to a point in the graphite measured from the axis of the fuel channel, r_0 is the radius of the channel, and $2r_0$ is the reactor lattice spacing. It is assumed that heat is removed from the graphite only through the fuel channel.

Calculations of power dissipation in moderator graphite of SRE geometry have been made¹⁸ yielding φ as shown in Figure 11. The integral $\int_{r_0}^r r \varphi(r) dr$ is also plotted. The radial temperature distribution¹⁸ is determined by an iterative process similar to that used for the planar case. However, in this case account is taken of both volume heat generation and the convergent heat flow. The results for a moderator section cooled by low temperature coolant ($e = 200^\circ\text{C}$) and for a moderator section cooled by high temperature coolant ($e_0 = 550^\circ\text{C}$) are shown in Figure 12. It is seen that temperature gradients increase with increasing radiation dosage, but there appears to be a convergence as dosage and temperature increase. The corresponding calculated values for the graphite thermal conductivity, $K(e)$ and for the graphite irradiation damage as indicated by K_{25} are shown in Figure 13. Lack of high temperature irradiation damage data limits the calculations to temperatures below 700°C .

6. Surface Stress Gradient

At a cooled moderator graphite surface the low temperature surface graphite tends to expand due to accumulation of irradiation

damage. The resultant stress gradient is:

$$\left(\frac{dS}{dx}\right)_\varphi = E \frac{d}{dx} \left[\frac{\Delta L}{L}(x) \right],$$

where E is Young's modulus, and $\frac{\Delta L}{L}(x)$ is the irradiation induced expansion extant at depth x . This irradiation-induced stress gradient tends to be ameliorated by an opposing gradient in thermal stress. The stress gradient due to the temperature gradient is:

$$\left(\frac{dS}{dx}\right)_\theta = -E \left(\frac{d\theta}{dx}\right) \alpha(\theta),$$

where $\frac{d\theta}{dx}$ is the temperature gradient away from the cooled surface and $\alpha(\theta)$ is the coefficient of thermal expansion at temperature θ . Residual stress gradients may be determined by combination of the two contributions. Calculation of the residual surface stress for any particular case may be made by using an empirical relationship between thermal conductivity change and physical expansion. At any given level of irradiation, the curves of property versus irradiation temperature for thermal resistivity and for physical expansion are very nearly proportional to one another, as can be seen by comparing curves of Figure 14 with those of Figure 8.

At reactor shut-down the ameliorative effect of thermal stress is lost, and irradiation induced stresses remain. In the case of the concave surface of a coolant channel, the irradiation damaged graphite layer is confined in compression by the bulk of unaffected graphite, and stability against fracture is likely. On the other hand, cooled surfaces of planar and convex geometry experience normal tensile stresses, and are subject to spallation. Such conditions may occur at moderate integrated irradiation in a water cooled reactor, but will appear only after more extensive irradiation history at liquid sodium coolant temperatures.

B. Evolution of Gas from Moderator Graphite

As has been mentioned above, zirconium and zirconium based alloys offer marked nuclear advantages for use as a moderator sheathing material, but are subject to attack by gases exuded from graphite. The extent to which mechanical deterioration of such sheathing can occur depends upon the influence of radiation upon mobility of sorbed impurities in graphite. Operations to date have shown no detectable sign of radiation-induced outgassing from SRE moderator graphite. About 5% nitrogen has appeared in the monitored graphite element atmosphere, presumably due to thermal outgassing.

C. Sodium-Graphite Compatibility

1. Sodium-Graphite Reactions

While under normal design conditions graphite is separated from

the sodium in the SGR, a component failure can result in contact between the two materials, and it is important to understand their behavior under such circumstances. It has been established that any possible interaction is not exothermic, and there are indications that the two substances are intrinsically inert with respect to one another. There is no doubt, however, that the presence of certain impurities in either medium can lead to substantial reactions.

A sessile drop of liquid sodium, when placed in vacuum on a piece of graphite at 300°C gradually becomes wetting and after 5 minutes soaks completely into the graphite. If the sodium soaked graphite is maintained in vacuum at this temperature, the sodium slowly distills from the graphite onto colder objects in the vacuum system. After 2 hours pumping thus, a graphite sample weighing 12 grams which had absorbed approximately 0.3 gram of sodium from its surface, was found to exhibit substantially its initial weight. However, this process is accompanied by the 1% linear expansion of the graphite and by failure of inter-particulate material, giving rise to fine cracks in the bulk graphite. No change in the crystalline lattice parameter was detected upon subsequent x-ray examination of the material through which the sodium had passed.

It is possible to observe marked crystalline effects attributable to interaction with sodium under certain circumstances. For example, the presence of as little as 0.1% potassium in the sodium led to thorough disintegration of the graphite, and a readily observable crystalline effect. The potassium atom is one of several which can act as a "spacer" to permit entry of sodium atoms forming characteristic lamellar graphite compounds.

2. Protective Adherent Surface Coatings for Graphite

Thin layers of metallic materials compatible with sodium have been applied to graphite bodies and their impermeability tested by immersion in molten sodium. In all tests failure of the protective layer occurred. Failure seems to be initiated by microscopic penetration through intergranular imperfections or "pin-holes." Once penetration of the graphite substrate has been accomplished, a gross failure of the protection material is promoted by dilation of the underlying graphite and by escape of displaced impurity gases from the graphite.

IV. FUEL MATERIALS

A detailed discussion of development work on fuel for use in reactors at liquid sodium temperatures is being given in a written paper by Hayward 19. Since conditions of SGR fuel usage are somewhat different than those met in most other power reactor concepts, these investigation programs are of a new type. The desired coolant exit temperatures of 600°C requires a fuel surface temperature of 620°C. The high specific rate of heat removal from the fuel surface imposes high normal temperature gradients leading to

peak fuel element core temperatures of 770°C and above. A brief discussion here will serve to illustrate the current state of the technology.

1. Fuel Element Experience

Large volumes of experience have set statistically significant limits to the burnup which may be sustained at low fuel surface temperatures. Data obtained at Westinghouse Atomic Power Division ²⁰, at Argonne National Laboratories ²¹ and at Harwell ²² have indicated that severe swelling accompanies burnup in the tenth of one per cent region, when the fuel surface temperature rises above about 550°C. Their work shows that judicious use of such alloying ingredients as zirconium and molybdenum increases the threshold temperature for swelling by 100° to 150°C.

A screening program for experimental elements has been underway in the Materials Testing Reactor. The samples being subjected to screening tests are incapsulated with a thermal bond of sodium-potassium alloy in stainless steel. Provisions are included for continuous monitoring of fuel element central temperatures. The experimental elements are heavily enriched in U²³⁵ so as to provide fission heating to the required temperatures. In the process of irradiation at the Materials Testing Reactor, they suffer irradiation damage at an accelerated rate. Materials already subjected to such test include uranium, uranium base 2 w/o zirconium alloy, uranium base 1.2 w/o molybdenum alloy, and thorium base 10 per cent uranium ²³⁵ alloy. Measurements are made on changes of diameter and density of the 3/8 inch diameter x 1½ inch long fuel samples. The extent of burnup, and the metallographic changes experienced by the fuel material are determined by destructive testing of the samples. Tentative conclusions based on post-irradiation measurements of changes in density and diameter are consistent with data reported in the literature ^{20,21,22}.

All experimental fuel samples irradiated at less than 500°C to approximately 0.05 atom per cent burnup exhibited only very small dimensional changes. Gross swelling was observed for all uranium-base specimens with burn-up of 0.2 to 0.4 atom per cent at central temperatures greater than 550°C. Under these conditions none of the unalloyed, rolled and heat treated specimens could be removed from their thermal shield capsules for measurement. Several of the alloy specimens could not be removed. The alloyed specimens that were removed were found to have increased in diameter by from 8 to 12 per cent. A set of five Th-10 w/o U specimens irradiated to 0.3 to 0.4 atom per cent burnup at a measured center temperature of approximately 650° C showed volume increases of from 2.4 to 4.8 per cent.

In Figure 13 a selected example of the change which is experienced by a fuel element under irradiation is shown. In many tests complicating effects due to temperature and flux gradients in the test samples were observed. A change in density was invariably experienced by the

specimens tested, and it was found that the selected alloy specimens show smaller changes than uranium metal under identical high temperature irradiation circumstances. As shown in the table, use of

TYPICAL FUEL BEHAVIOR

<u>Specimen</u>	<u>Burnup MWD/T</u>	<u>Temp °C</u>	<u>Volume Change %</u>
U-1.2 w/o Mo	2000	675	+ 22
Th-10.0 w/o U ²³⁵	3500	665	+ 4.5

thorium base uranium alloy appears yet more favorable than experience with uranium base alloys. This conclusion must be considered tentative until statistically significant comparative data are collected. Such data, at temperatures over 550°C and for burnups from 200 MD/ton up will be available following operation of the SRE with a thorium-uranium loading beginning in the summer of 1958.

2. Reactor Fuel Performance

During initial operation of the SRE alpha-rolled, beta-heat-treated uranium containing about 2.7% U²³⁵ has served as fuel. At the time of writing of this paper insufficient data are available to permit significant conclusions as to performance. Subsequent tests will be directed toward obtaining statistically significant information on the behavior of alloys of uranium with thorium, with zirconium and with molybdenum when used as fuel materials at 600°-700°C.

V. SUMMARY

The inherent inertness of sodium with respect to core structural materials may be negated by sodium-borne impurities. Oxygen transported by sodium can form a fatigue-sensitive surface layer of Zr O₂ on zirconium core components. This diffusion controlled process is slowed by reduction of oxygen content in sodium to levels well below 10 ppm. Stainless steel is unaffected by oxygen content below 50 ppm. sodium. Hydrogen released from the moderator graphite at high temperature diffuses slowly through the surface oxide on zirconium to form a solid solution. Rapid cooling of hydrogen-containing metal can cause delta-phase zirconium hydride to precipitate at zirconium grain boundaries, but this will dissolve again upon slow heating. Carbon in sodium can result in appreciable carburization of austenitic stainless steels at temperatures above 550°C, with consequent deterioration of high temperature fatigue properties. Chemical and physical methods have been developed for analyses for these impurities in sodium. The control of oxygen content to the level of 10 ppm. required for satisfactory operation in a system containing Zr can be achieved by hot-trapping a side stream of sodium with thin Zr or Zr-Ti alloy sheet maintained at around 650°C.

The most formidable inherent shortcomings of zirconium as a core material have been the rapid decrease in mechanical strength at

elevated temperature, and the increase in rate of grain growth above 500°C. Zircaloy II, and Zr-Al alloys exhibit substantial improvement over pure Zr in these properties. Austenitic steels of the 18-8 series have acceptable properties, but are costly of neutrons. Ferritic alloys, typically containing 2½% Cr, 1% Mo, are satisfactory for sodium service to 560°C; above that temperature rapid oxidation and decrease in strength occurs.

Continued investigation of the sodium-graphite reaction confirms a volume expansion of the order of 5%, but reveals no clear indication of the formation of lamellar compounds, in the absence of impurities in the sodium.

An application of the solid state theory of thermal conductivity of graphite permits deduction of the irradiation damage gradients in reactor moderator structures. The surface layers of heavily damaged graphite insure radiation annealing of deeper lying graphite.

Metallic fuels have exhibited early significant volume expansions on irradiation at temperatures above 480°C. Alloys of Th-U examined appear at least a factor of six less sensitive in this regard than the uranium base low alloys of molybdenum and zirconium.

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FIG. 1

FIG. 2

FIG. 3

ZIRCONIUM HOT TRAP FILLER PROTOTYPE

FIG. 4

FIG. 5

FIG. 6

FIG. 7

FIG. 8

FIG. 9

FIG. 10

FIG. 11

FIG. 12

FIG. 13

FIG. 14

BEFORE

AFTER

TYPICAL FUEL ELEMENT

FIG. 15

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Recent Developments in the Technology of Sodium-Graphite Reactor Materials

Prepared By
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Chemical corrosion, as such, does not usually occur in sodium coolant systems, but the presence of small amounts of impurities, particularly oxygen, hydrogen, and carbon, can adversely affect the properties of zirconium and steel. Oxygen in sodium results in the solution of ZrO_2 in zirconium and the formation of a brittle adherent layer of zirconium oxide; at thicknesses greater than 0.2 mg/cm^2 , cracks propagate from this layer in the base metal and reduce its fatigue strength. The weight gain due to oxidation varies with time as $w = Kt^{1/2}$; the rate constant K has an activation energy of 30 kilocalories/mole in the range 700° to 1000°F , with little dependence on oxygen content above 20 ppm. Stainless steel is unaffected by oxygen below 50 ppm. Hydrogen in sodium in contact with zirconium results in the formation of ZrH_x in the metal. At normal reactor operating temperature the hydride is soluble in Zr and does not adversely affect its properties. However, rapid cooling can cause the hydride to precipitate at grain boundaries and embrittle the metal. Hydrogen may be present in the system as impurity in the as-received sodium, or by release from the graphite during high temperature operation. Carbon in sodium can result in carburization of stainless steel at appreciable rates above 1050°F , with consequent deterioration in fatigue and stress-rupture properties. Chemical and physical methods have been developed for the analysis of these impurities in sodium. Oxygen can be determined by butyl-bromide and mercury reactions with sodium, by vacuum distillation, or from the solubility vs. temperature behavior. Carbon may be detected by reactions producing acetylene. The control of oxygen content required for satisfactory operation in a system containing Zr, less than 10 ppm, can be achieved by hot-trapping a side stream of sodium with thin Zr, Ti, or Zr-Ti alloy sheet maintained above 1200°F .

The rapid decrease in mechanical strength at elevated temperature, and the increase in rate of grain growth above 950°F , with consequent deterioration in fatigue strength, results in marginal utility of pure Zr above 950°F . Zircaloy-II, and Zr-Al alloys exhibit substantial improvement over pure Zr, in these properties. Austenitic steels of the 18-8 series have acceptable properties, but are relatively costly. Ferritic alloys, typically containing 2-1/4% Cr, 1% Mo, are satisfactory for sodium service to 1050°F ; above that temperature rapid oxidation and decrease in strength occurs.

Continued investigation of the sodium-graphite reaction confirms earlier data on volume expansion of the order 5%, but reveals no clear indication of the formation of interlamellar compounds. This phenomenon appears to depend sensitively on impurities in sodium.

Metallic fuels have exhibited significant volume expansions on irradiation above 900°F . U-Mo(2%) and U-Zr(2%) alloys expand 100% for irradiation to 1 atom burn up, at 1200°F . Alloys of Th-U(10%) are substantially better, by a factor of at least six. UO_2 samples appear to be the best solution for use above 900°F .

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