It is clear that while a metal is in the molten condition additional fissionable material could be added and distributed uniformly through the metal.

Thus pyrometallurgical processing, though in its very early development stages compared with more conventional types, seems to have promise of accomplishing the goals of a processing cycle at potentially less cost. To achieve the final development of such a process will require a prolonged effort on the part of metallurgists, chemical engineers, and chemists. Effort in this laboratory is continuing with experiments on scaling up and on the development of continuous extractors to operate at this temperature.

The results with the artificial fissium mixtures are not very satisfying owing to the lack of agreement in the results. Unless some improvements are made in this agreement, it may be necessary to go back to real fuels of lower burn-up and to extrapolate to the expected burn-up or to wait until fuels of high burn-up are available and have decayed to a level of radioactivity which will permit laboratory handling. Other techniques of making fissium may be more successful and will also be tried.

Before closing, it would be well to point out that this type of processing is also uniquely adapted to use with a liquid-metal fuel reactor. If the other problems which are peculiar to the use of liquid-metal fuels are solved, it is probable that there will be a strong future for pyrometallurgical processing in the reprocessing cycle of a liquid-metal reactor.

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Use of Zirconium in Liquid-sodium Systems

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The attractive nuclear properties of zirconium make it a highly desirable core material for sodium-cooled reactors. The elevated temperature strength while low is sufficient for certain applications. Development of higher strength alloys is underway. Sodium in itself is completely compatible with zirconium; however, the nonmetallic contaminants, namely oxygen, hydrogen, and nitrogen, can effect serious damage. The primary problem in the use of zirconium in a sodium system, then, lies in controlling these impurities in the sodium.

In surveying the field of materials possessing potentialities in nuclear reactor construction, one is immediately attracted to zirconium because of its low capture cross section for thermal neutrons. The fact that during the initial period of reactor design and construction metallic zirconium was essentially a laboratory curiosity resulted in the use of aluminum as the primary metallic nonfuel core material. However, with the advent of the submarine reactor and the necessity for higher operating temperatures for feasible power production, the limitations of aluminum were exceeded. Neutron economics then demanded that the application of zirconium be completely investigated. The success of this investigation and the subsequent development program is amply demonstrated by a survey of the literature.

As the primary objective of the zirconium development program was the Submarine Thermal Reactor, or S.T.R., it was natural that water-corrosion resistance was of the utmost importance. As a consequence, until very recently essentially all processing and fabrication developments have been directed toward eliminating those impurities found to be detrimental with respect to corrosion. The fundamental objective of the alloy-development program also was the compensation for those deleterious impurities which cannot conveniently be removed.

The current interest in nuclear stationary power plants has prompted a reevaluation of power reactors primarily promoted by the economic factors imposed by nonmilitary applications. Here neutron economy is of even greater importance, as is core life. In addition power costs are directly related to the temperatures involved in the heat transfer system and hence to the reactor-core operating temperature. Because of the advantages to be gained by increasing the temperatures in the reactor an evaluation of the over-all problem at North American Aviation, Inc., has resulted in the decision that sodium-cooled reactors have advantages over water-cooled systems in that the opportunities for development in the direction of increased operating temperatures are much more broad. For this reason, efforts have been concentrated upon the sodium-cooled graphite-moderated reactor for the production of power.

In selecting the core materials for a reactor of this type there are three essential requirements, (1) low thermal neutron capture cross section, (2) satisfactory elevated-temperature properties, and (3) compatibility. Breaking down the second and third requirements into further details, the materials must possess satisfactory elevated-temperature mechanical strength; have reasonable heat transfer characteristics; be capable of fabrication into relatively complex configurations; be dimensionally stable; be resistant to attack by sodium; and be able to exist in contact, either direct or through sodium, with the inevitable dissimilar materials.

The austenitic stainless steels are the obvious choice of available material based upon a precursory survey of the problem. They satisfy the mechanical-property requirements and have been found to be capable of satisfactory operation in sodium at the temperatures under consideration. The cross section, approximately 3 barns, is however a decided disadvantage, and in the interest of neutron economy the investigation of other materials was warranted.

Here again from the nuclear standpoint zirconium appears most attractive. The neutron cross section of zirconium (0.18 barn) is slightly smaller than that of aluminum (0.22 barn) and decidedly more favorable than the cross sections of the stainless steels (about 3 barns). The ability of this material to fulfill the other requirements may be evaluated from a brief survey of its pertinent characteristics.

PHYSICAL PROPERTIES AT ELEVATED TEMPERATURES

The properties of zirconium at both room and elevated temperatures are significantly affected by the impurity level and hence by the method of production. For the purposes of this discussion, those properties resulting from the current production method, arc-melted sponge, will be considered. Figure 1 indicates the strength characteristics vs. temperature of this material, in the form of 0.035-in. sheet taken from a production run. The rather serious temperature limitations imposed by unalloyed zirconium are readily apparent. If one considers that most elevated-temperature applications must be designed on the basis of creep strength rather than yield or ultimate strength, this limitation becomes even more severe.

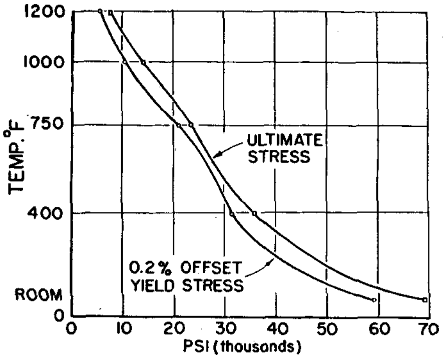

Fig. 1. Temperature dependence of strength of zirconium.

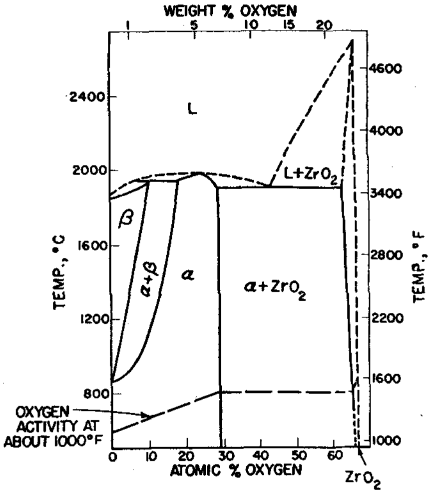

Fig. 2. Partial diagram of the zirconium-oxygen system.

For some time a program directed toward improving the elevated-temperature strength of zirconium without seriously sacrificing its nuclear advantages has been underway. To date this program has had the additional goal of providing resistance to hot-water corrosion, a fact which has restricted its value to the sodium problem to some extent. However a few values obtained by Schwope and Chubb (*1*) indicate the potentialities of further work. Table 1 contains the strength data at 500°C. of several experimental alloys reported by the authors. For comparison purposes the yield stress of type 347 stainless steel may be taken as 31,000 lb./sq. in. at 500°C. The favorable comparison of this with the listed values for the zirconium alloys indicates the possibilities in the development of zirconium alloys for elevated-temperature applications.

FABRICATION POTENTIALITIES

Zirconium and a majority of its alloys which exhibit promising elevated-temperature properties have without serious difficulty been rolled into plates and sheets, the starting material for most reactor-component fabrication. Seamless tube drawing has presented difficulties, primarily because of die seizure. However, it has been found that proper lubricants can overcome this disadvantage. In fact, 0.750-in.-diam. tubing with 0.010-in. wall thickness has been drawn in lengths up to about 14 ft.

Zirconium is probably one of the easiest of the metals to weld if the necessary precautions are taken. In the molten state and at very high temperatures in the solid state the metal is exceedingly reactive with both oxygen and nitrogen. Both of these gases form compounds which are detrimental to the ductility of the contaminated metal. As a result, it is essential that the weld be well shielded with an inert gas. Zirconium welding was developed by use of a dry-box technique, which seriously limited the operations that could be performed. Recently, however, at North American Aviation a program to develop techniques for the automatic welding of relatively large components from thin sheets of zirconium, 0.035 in., has been successfully carried out. By proper torch design and suitable welding fixtures butt welds up to 10 ft. long have been made by modified heliarc methods. Standing lip welds in various configurations have also been successfully accomplished by hand welding. Tensile tests of welded coupons indicate that the welds are superior in strength to the parent metal. Ductility, as measured by bend tests, is superior in the weld metal as compared with the parent material. Care must be taken, however, to avoid an embrittled heat-affected zone. This can largely be taken care of by proper surface preparation prior to welding. The production of large-diameter thin-walled tubing is apparently no problem as this has been and is being done essentially on a commercial scale. In most cases zirconium can be formed cold; however, some of the higher strength alloys require heat to facilitate the operation. These materials can be worked in air for short times at temperatures up to about 600°C. without seriously impairing the properties. It has been noted, however, that working at from

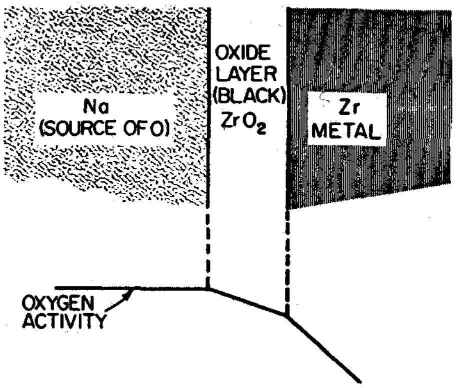

Fig. 3. Schematic diagram of zirconium-sodium interface during rapid transfer of oxygen. Lower curve shows relative oxygen activities.

100° to 200°C. will appreciably reduce the work-hardening rate and thus permit a greater amount of essentially "cold" work.

Zirconium has the serious disadvantage of forming brittle intermetallic compounds with practically all the conventional structural materials. This complicates its use in applications which require the metallurgical bonding of zirconium to these other materials as part of the structure. It has been found, however, that flash welding produces a joint, with considerable strength and some ductility, between zirconium and the stainless steels, both ferritic and austenitic. Such joints are essential in many designs calling for a closed cooling system, as zirconium is much too expensive to permit its use external to the reactor core, where the nuclear advantages are unimportant.

COMPATIBILITY

With regard to the behavior of zirconium and its alloys in dynamic sodium it would perhaps be well to consider briefly liquid-metal corrosion in general. Miller (*2*) lists the following mechanisms by which liquid metals can react with certain materials:

1. Solution attack
2. Direct alloying
3. Intergranular penetration
4. Corrosion by contaminants
5. Corrosion erosion
6. Facilitation of self-welding
7. Mass transfer

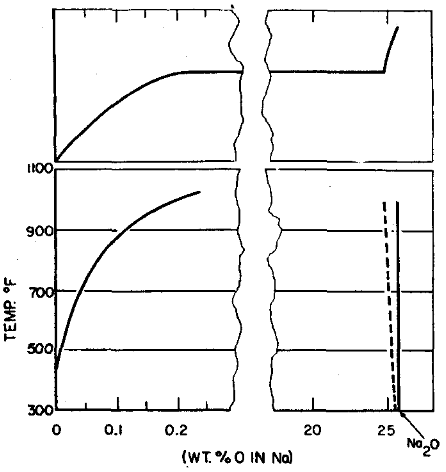

Fig. 4. Schematic representation of oxygen activity in sodium at 1,000°F. (upper curve) compared with solubility curve.

At temperatures up to 600°C. sodium apparently has no significant solubility for zirconium. The reverse of this is also true, and so the first two methods of possible attack can be eliminated. Sufficient stress-rupture work with zirconium and its alloys has been carried out to indicate that intergranular penetration is not a problem. Such tests are more conclusive for this type of corrosion as grain boundary attack is usually accelerated by the application of stress.

Corrosion by contaminants is the principal means by which sodium affects zirconium as well as many other materials.

Zirconium is a very reactive metal at high temperatures. It readily takes nonmetals (oxygen, nitrogen, hydrogen, carbon) away from other metals and for that reason has often been used as a getter. In the structural applications of zirconium these nonmetals are harmful and act as corroding agents.

In the sodium-cooled graphite-moderated reactor system under study at North American Aviation, the zirconium cans of the moderator are in contact with molten sodium at high temperatures. The zirconium is thus susceptible to corrosion by any nonmetals that get into the sodium-coolant stream, and so the effect of such corrosion and the means of controlling it are being studied.

THE ZIRCONIUM-OXYGEN SYSTEM

Because quite a lot is known about the effects of oxygen on zirconium, it is used as a typical nonmetal for this discussion. Oxygen is very soluble in alpha zirconium to form a solid solution. Domagala and McPherson (*3*) have reported the phase diagram shown in Figure 2. Under equilibrium conditions at 1,000°F. the solubility of oxygen in alpha zirconium is about 29 atom %. When more oxygen is added, it reacts to form the new phase, zirconium dioxide. An estimate of the activity of the oxygen in zirconium-oxygen mixtures is given by the dotted line. However if oxygen is added too rapidly for equilibrium to be attained, then the situation will probably be as shown in Figure 3. There the oxygen has not been able to diffuse into the metal rapidly and a layer of zirconium dioxide had formed before the entire metal phase became saturated with oxygen. Therefore in practice the relative rates of diffusion of oxygen in the metal and diffusion of oxygen from the sodium to the zirconium are important because they determine whether or not a layer of zirconium dioxide will form on the metal. These properties are currently being studied.

TABLE 1. TENSILE PROPERTIES OF SOME ZR ALLOYS AT 500°C.

Composition	0.2% Offset yield stress, lb./sq. in.	Ultimate stress, lb./sq. in.	Elongation, %
Zr	16,000	24,000	30
2 wt. % Al	32,000	46,000	25
1.2 wt. % Mo	35,800	48,010	44
2.2 wt. % Nb	35,000	43,000	9
10.4 wt. % Ti	41,200	58,300	33
3.9% Ti + 1.9% Mo	37,600	52,500	30
4.6% Ti + 0.8% Al	32,000	46,800	23

THE SODIUM-OXYGEN SYSTEM

The solubility of oxygen in liquid sodium is small, the limits being shown in Figure 4 (*4*). As oxygen is added to sodium, it dissolves until the solubility limit is reached and then sodium monoxide begins to precipitate. The activity of oxygen dissolved in sodium at 1,000°F. is given in a general way by the curve at the bottom of the figure.

The state of the oxygen dissolved in the sodium is not as Na_2O but probably as $O^=$. In zirconium metal the dissolved oxygen is also $O^=$. Therefore the transfer of oxygen from sodium to zirconium probably does not involve any change of the state of the oxygen.

When liquid sodium and zirconium are put in contact, the oxygen will transfer from one metal to the other until the oxygen activity is equalized in the two metals. In Figure 5 a schematic comparison of the oxygen pressure in equilibrium with sodium-oxygen and zirconium-oxygen mixtures is given. As the oxygen pressure over a mixture of sodium and zirconium at 1,000°F. is increased, oxygen dissolves in both metals, but to a greater extent in zirconium. At a certain pressure (roughly 10^{-30} atm.) zirconium dioxide begins to form, and at slightly higher pressures all the zirconium is in the form of zirconium dioxide, while only a fraction of a per cent of oxygen is in the sodium. Further increases in oxygen pressure eventually convert the sodium to sodium monoxide (complete at about 10^{-20} atm.).

The significant feature of this diagram is that the zirconium system is far below the sodium system. To maintain the oxygen concentration in zirconium at

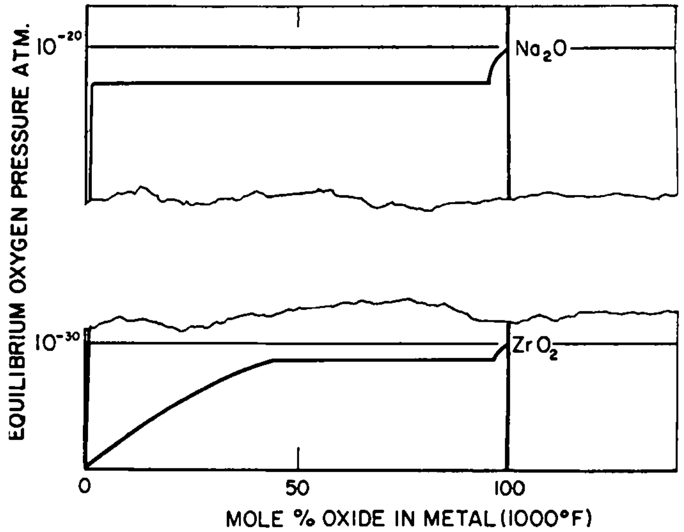

Fig. 5. Comparison of oxygen pressure in equilibrium with sodium-oxygen and zirconium-oxygen mixtures.

an arbitrary low value, it is necessary to hold the oxygen in the sodium to an extremely low value; for example, to hold the oxygen in zirconium to 0.5 wt. %, the oxygen in sodium must be kept below 10^{-10} wt. % or so. These estimates are open to a great deal of uncertainty, but the over-all principle is apparent.

It must be remembered, however, that thermodynamic considerations forecast equilibrium conditions. The rate at which these conditions are realized must be determined by other means. It is obvious that oxygen contents of the order of 10^{-10} % in sodium cannot be attained. The life, then, of zirconium in a sodium system is necessarily determined by (1) maximum tolerable concentration of the nonmetallic in zirconium based on its effect on physical properties and (2) the rate at which this concentration level is reached. This rate is determined by one of two diffusion processes: the diffusion of $O^{=}$ in zirconium or in ZrO_2. Fundamentally it would be interesting to know the conditions under which each process becomes dominant but practically it is the end effect that is of utmost importance.

The experimental effort, therefore, has been directed primarily toward obtaining strictly engineering data. It has been found that with oxygen levels in sodium above about 0.005 wt. % the rate of weight gain with zirconium is essentially independent of the level. This amounts to approximately 0.50 mg./(sq. cm. of surface area) (month). The data appear to follow a parabolic rate law. In addition to the weight gains noted, evidence of diffusion of oxygen into the metal is given by a definite increase in surface hardness as determined by microhardness measurements. The depth of penetration as measured by this technique appears to proceed at about 0.0015 in./month at 1,000°F. There are, as yet, insufficient data to establish the actual oxygen concentration gradient represented by this hardness change. A serious loss in room-temperature ductility in this hardened layer is, however, indicated. Such embrittlement results in a serious loss in fatigue strength in a notch-sensitive material such as zirconium. Fortunately this hardening and embrittling effect disappears for oxygen contents encountered this far at the elevated temperatures contemplated for the applications. However, in view of the relatively high solubility of oxygen in zirconium it is apparent that with time the oxygen level could reach the point when the effect of temperature is no longer so pronounced and serious trouble could be anticipated.

It is, then, obvious that in reactor systems, in which the occasional introduction of contaminants such as oxygen is an inherent possibility, provision must be made for maximum protection for the zirconium. In order to provide such protection two possible approaches are available. The concentration of oxygen (and other nonmetals) in the sodium must be reduced to and maintained at a minimum. A nonreactive and impenetrable barrier may be applied to the zirconium.

The concentration of oxygen in sodium can be reduced by (*a*) cold trapping and (*b*) gettering. Cold trapping works on the principle that cooling the sodium will precipitate out sodium oxide. In Figure 3 one sees that the solubility of oxygen in sodium decreases rapidly as the temperature is lowered. The lowest temperature that can be used is the melting point of sodium, and there the solubility is 0.003 wt. % oxygen. However, as we have seen, to protect zirconium a much lower oxygen concentration is required. An alternate method is to introduce a more reactive metal than zirconium to getter the oxygen. A number of getters in small-scale capsule tests have been investigated. The results with these are given in Table 2. Zirconium-titanium alloy seems most promising at present. In the future it is planned to run a sodium loop with a hot section containing this alloy to test its effectiveness.

TABLE 2. GETTERS FOR PROTECTING ZIRCONIUM FROM OXYGEN IN SODIUM

(All tests made at 1,200°F. in stainless capsules for 1 month)

Getter	Effect
Al	Alloyed with Zr and attacked it badly
Mg	Alloyed—some attack
Ca	Alloyed—seemed to protect Zr slightly
Th	Seemed to protect—no apparent effect on Zr
Zr-Ti	Seemed to protect—no apparent effect on Zr

The other method mentioned for protecting the zirconium is to provide a barrier that will prevent the oxygen from contacting the zirconium. Such a barrier might be a metal plating or a nonmetal layer of some sort. A useful plate would have to be insoluble in the zirconium as well as in the sodium so as to remain on the surface. A metal plating would therefore have to be of a nonalloying metal. Alternately, a nonmetal coating would have to be nonreactive. For instance, zirconium dioxide would not do, as the oxygen would diffuse into the zirconium. Very little has been done in this area.

To summarize briefly, it appears that the nuclear advantages of zirconium can be utilized in sodium-cooled reactors if proper provisions are made to accommodate for the nonmetallic impurities. Oxygen and hydrogen in particular are readily introduced into sodium and are readily removed by solution in any contacting zirconium at elevated temperature. A serious loss in physical properties is possible if such a reaction is permitted to proceed to any extent. Contaminant removal from the sodium by proved trapping methods and the possibility of barrier coatings on the zirconium promise to guarantee a satisfactory life for zirconium components of systems now contemplated.

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