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Corrosion by the Alkali Metals *

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ABSTRACT

This paper reviews the state of the art of corrosion testing of materials by the alkali metals, the models proposed to explain the observed corrosion results, and the status of materials selection for application in alkali metal-cooled systems. Corrosion of structural and fuel cladding materials by liquid Na and NaK has been studied intensively, but intermittently for the last eighteen years. These studies and the liquid metal cooled reactors in operation demonstrate that stainless steels can be considered for structural and cladding applications below 650°C. Above this temperature increased corrosion and radiation induced embrittlement make them unsatisfactory.

Corrosion models are reviewed and their inability to explain all the experimental observations discussed. An alternate model is proposed which qualitatively is in agreement with experimental observations. In this model, the rate controlling step is either the surface reaction of Fe with "available oxygen" (dissolved Na_2O) to form an Fe-O-Na complex or the rate at which "available oxygen" can reach the surface to form the complex; which process is rate controlling depends on the temperature, Na velocity, and oxygen concentration in the Na.

The solution chemistry of oxygen, carbon, and alkali metal-oxygen-transition metal complexes dissolved in the alkali metals is reviewed. "Molecular" complexes appear unlikely to exist in solution in the alkali metals, although the thermodynamic tendencies for them to form suggest that stable bonds exist in solution between oxygen, the transition, and the alkali metals. The insolubility of carbon in "oxygen-free" sodium indicates that carbon transfer may be associated with oxygen in sodium down to very low oxygen levels, although experimental data do not generally confirm this postulate.

Corrosion of refractory metals by boiling alkali metals at temperatures above 1000°C is markedly affected by impurities in either the liquid or refractory metal; the addition of Ti, Zr, or Hf as "getters" to the refractory alloys and proper heat treatment to react the "getter" addition with oxygen, nitrogen, carbon, and hydrogen in the alloys are required to prevent their corrosion by the alkali metals at these temperatures.

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INTRODUCTION

The corrosion of materials by the alkali metals has been the subject of intermittent but intensive work for the past eighteen years in support of reactor and space power programs. This review paper* attempts to assess the present status of the development work in this broad field. Special emphasis will be given to the studies of the corrosion of structural and cladding materials by sodium (Na) because of their importance to the liquid metal fast breeder programs. The authors will also discuss the current theories or models which have been proposed to explain the corrosion data, present yet another corrosion model, and suggest a direction for future materials development.

Na CORROSION OF IRON, NICKEL, AND COBALT-BASE ALLOYS

Corrosion studies in the early 50's showed that reasonably pure (~20 ppm oxygen) Na could be contained in stainless steels almost indefinitely at 538°C. More recent studies in the U.K. and the U.S. have established corrosion rates of various steels at temperatures up to 725°C. The effects on the corrosion rate of variables such as temperature, temperature differential, velocity and oxygen concentration in Na have also been evaluated.[7-8]

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*Other recent reviews are listed in references 1-6.

Type 316 stainless steel* (SS), 2 1/4Cr-1Mo steel, and 5Cr-1/2Mo-1/2Ti steel have been tested in the U.S. in forced convection circuits at temperatures up to 705°C, oxygen levels of 10 and 50 ppm, and velocities of 2 and 6 m/s.[7] The corrosion rate of all these steels was essentially the same. It varied with velocity, was proportional to oxygen level in the Na, was unaffected by temperature differential, and increased threefold with an increase of 55°C in the maximum temperature. Typical rates at 650°C for these steels fall between 0.013-0.038 mm/yr in Na containing 10-15 ppm oxygen flowing at 6 m/s. This is apparently the rate at which Fe is dissolving in the solution, since Ni and Cr are leached from the stainless steels leaving a ferritic surface exposed to the Na. A statistical analysis of the data has been used to develop an empirical corrosion equation[7] in which the rate is a function of velocity to the 0.88 power and oxygen to the 1.16 power.

Results on similar tests recently reported in the U.K. are in general agreement with the observations presented above.[8] In this work, however, a velocity effect on the corrosion rate was found below 3 m/s, but above this velocity (up to 8 m/s) there was no effect in a system containing 10 ppm oxygen operated at 650°C. There may not actually be a difference in the results since the U.S. data (at 2 and 6 m/s) straddle the transition velocity (3 m/s) reported in the U.K. work. The significance of these findings is discussed in the mechanisms section of this paper.

The corrosion rate of stainless steels in 650°C Na containing 10 ppm oxygen should be acceptable for reactor systems. However, the reported two to threefold increase in the corrosion rate for every 55°C temperature increase and the effect of oxygen excursions[9] limits the use of the stainless steels to 650°C. Nettley's results[8] with <5 ppm oxygen in the sodium suggest that the maximum temperature limit could possibly be raised at extremely low oxygen levels if strength is not limiting. Maintaining a large reactor system at the required low oxygen concentrations may be difficult, unless new methods of control are used.

Nickel-base alloys tested in Na and NaK at 816°C and higher show the corrosion rates to be several times greater than for stainless steels tested under similar conditions.[10] Corrosion of these alloys is characterized by leaching of Ni and to a lesser degree, Cr. A nickel alloy, Nimonic 80A[+] was tested at 650°C at various velocities and oxygen levels in Na.[8] Its corrosion rate was dependent on velocity and independent of oxygen concentration. At temperatures and flow rates of interest in reactors, unacceptable corrosion rates were obtained.

Cobalt-base alloys have not been evaluated in Na or NaK in the 650-760°C temperature range. Tests at higher temperatures (900-980°C) show the corrosion rate of Co-base alloys to be approximately equivalent to

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*Type 316 SS: 17%Cr, 12%Ni, 3%Mo, 0.08% maximum carbon, bal. Fe.
+Nimonic 80A: 19.4Cr, 1.2Al, 2.3Ti, bal. Ni.

those of Ni-base alloys.[10-11] These tests however, were conducted with high (50-100 ppm) concentrations of oxygen in the Na, (~50-100 ppm). Since corrosion of Co is probably sensitive to oxygen these results are not definitive.[12]

Refractory metals and their alloys have been used and are still being considered for core components, primarily because of their compatibility with various fuels. The affinity of most refractory metals for oxygen, nitrogen, carbon, and hydrogen, which are frequently present in Na, results in an increased corrosion rate or a reduction in mechanical properties. Unless the Na is purified to low oxygen levels with "getters", excessive weight losses are experienced with all the refractory metals with the exception of Mo. Excellent resistance of Mo to Na containing up to 110 ppm oxygen has been reported at 900°C and velocities of 2 m/sec. Under similar test conditions Nb samples are completely destroyed.[4] Vanadium and niobium have been used in the DFR; however, the operating temperature had to be limited to 480°C due to the oxygen level in the NaK.[13] Recently there has been some success in developing V alloys which have improved corrosion resistance in well cold-trapped Na. The promising alloys contain Ti and Cr.[14]

CARBON TRANSFER

Carbon transfer has been observed in liquid metal-cooled systems and is of concern because of possible effects on the mechanical properties of structural and cladding materials. Carbon transport occurs in an alkali metal-cooled system in which carbon activity differences exist between alloys in the same system, or if carbon is accidentally introduced into the system. Many studies are now in progress to evaluate the effect of carburization and decarburization on mechanical properties of stainless steels and low alloy steels.[7,15,16] Significant decreases in room temperature ductility, impact strength, fatigue life, and increased notch sensitivity could reduce the useful life of type 316 SS exposed for extended times in Na containing C.[15]* No effects of velocity or oxygen concentration below 50 ppm on the rate of carburization have been reported.

The significance of carbon transfer on the mechanical properties of stainless and low alloy steels is unresolved. Generally the carbon source is the low alloy steel used in the low temperature portions of many systems. Several investigators have demonstrated that carbon in these alloys can be stabilized to prevent carbon transfer to stainless steel located in hot portions of the system, by adding niobium, vanadium, and titanium to low alloy steels.[7,8,17] Transfer of carbon to refractory metals has been controlled by using a Nb- or Ti- stabilized stainless steel.[18,19]

CHEMICAL ANALYSIS

The above sections have discussed the important role that impurities (O, C, N, and H) play in the corrosion of materials by the alkali metals. The analysis and control of these elements is necessary to insure acceptable performance of structural and cladding materials.

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*However, carburization has little effect on its mechanical properties at 650°C.

Methods of analysis of these elements have been reviewed.[20] For oxygen in Na, the Hg amalgamation and the distillation methods have gained the greatest acceptance. Precision of ±1 ppm in the 5 ppm level is reported for the amalgamation procedure.[21] Recent results obtained by the distillation procedure indicate excellent precision in the 1-10 ppm range.[22,23] Although both procedures yield results with good precision at apparently low oxygen levels, they still suffer from the lack of a "standard" with which to determine the absolute quantity of oxygen. At least two techniques currently under development, neutron activation at General Atomic[24] and ORNL[25] and isotopic dilution at the authors' laboratory,* measure the oxygen concentration directly rather than the Na with which it was combined. The available oxygen analytical procedures, however, are adequate for monitoring Na in stainless steel systems.

The wet combustion method for elemental carbon and the dry oxidation method for total carbon are the currently accepted techniques for C determination in Na. "Round robin" analyses for C in Na (14 laboratories participated) produced mean values which varied from 20 to 200 ppm for total carbon and 10 to 50 ppm for elemental carbon.[26] There was no apparent difference in either the total or elemental carbon detected in the prepared "high", "low" and "medium" samples. These results clearly point to the need for further work on the development of techniques to measure carbon in Na, and to a lack of an understanding of the chemical state of the carbon in Na.

HIGH TEMPERATURE LIQUID METAL CORROSION

Interest in the development of high performance space power systems has stimulated extensive corrosion testing of materials in liquid and boiling alkali metals at temperatures up to 1350°C. The extensive data generated in this area are reported in a recent survey.[1] The results of recent work at BNL are described in another session of this meeting.[27]

At these high temperatures only the refractory metals and their alloys have been tested because of their strength and apparent low solubility in the alkali metals. Corrosion of Nb and Ta by the alkali metals is markedly affected by impurities in either the liquid metal or the refractory metal. Oxygen in Na in high concentration accelerates corrosion of these alloys. Oxygen as an interstitial impurity in pure Nb and Ta causes rapid penetration by high purity** Li,[28,29] Na,[30] and K.**[31] The penetration by Li occurs along grain boundaries and {110} crystallographic planes. A threshold concentration of oxygen of 200-500 ppm in solid solution in the alloy is required to initiate corrosion by Li with the depth

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*In the isotopic dilution method a known amount of O^{18} is introduced into a sample of Na in which O^{16} is to be determined. The Na is distilled off. The Na_2O^{16}, Na_2O^{18} mixture is reacted with C to form CO^{16}, CO^{18}. The CO^{16}/CO^{18} ratio is determined mass spectrographically.

**High purity alkali metal is here defined as that which has been contacted with Zr above 650°C.

of attack increasing with increasing oxygen. Similar results are obtained with Na and K but the threshold oxygen levels in the alloy have not been determined. Addition of elements, such as Zr, Ti, or Hf, which form very stable oxides, to the refractory metal essentially eliminates this penetration. Enough of these "getter" elements must be added to react stoichiometrically with all the oxygen present. Also in order to insure complete protection against this penetration it is necessary to heat treat the alloys to insure precipitation of the "getter oxide". Analysis of data obtained from experiments with K and Na in refractory metals in which a limited amount of oxygen is available suggests corrosion occurs by the formation of complex refractory metal alkali metal oxides,[32,33] which have, in some instances been identified.[31,34]

Recently several large forced-convection boiling liquid metal loops fabricated completely of refractory metals have been operated to assess the resistance of refractory metal alloys to high velocity vapor impingement. No detectable erosive effect was detected on molybdenum alloy TZM* exposed to K vapor up to 1100°C and velocities up to 405 m/s.[35] Molybdenum alloys were also resistant to Cs vapor at 840°C and 245 m/s. However, in the latter tests deposits of loop container material were found adhering to the impingement samples.[27]

PRESENT STATUS

Available corrosion data indicate that stainless steels can be used for structural and cladding applications in a reactor cooled by Na if the maximum metal temperature does not exceed 650°C. There remain however, two problems which must be solved before stainless steel can be used with confidence; radiation embrittlement, which becomes pronounced at 650°C and above,[36] and the reduction in mechanical properties due to carburization. It has been shown that carbon transfer can be minimized practically by controlling the carbon source. Study of radiation embrittlement of stainless steel suggests it can be controlled by modifying the composition and by a proper heat treatment.[36] It will be necessary to determine whether these modifications affect the corrosion resistance of stainless steel.

Increasing the reactor operating temperature to improve the economics results in unacceptably higher rates of corrosion of stainless steels. Some design studies propose 650°C as the mixed mean Na outlet temperature. This mixed mean temperature requires operation of fuel cladding at 760-815°C. In this temperature range neither the stainless steels nor the nickel alloys appear to have adequate corrosion resistance to Na and the stainless steels may not have adequate strength.

Refractory metal alloys, although they may not have as favorable nuclear properties as stainless steels, do have excellent corrosion resistance to high purity Na at temperatures as high as 1300°C. However, as has been shown in the DFR, their practical use is limited by the ability to purify Na to very low levels of oxygen, carbon, and hydrogen. Whether the oxygen content of the Na coolant of a large power plant can be lowered, maintained, and monitored at such low levels is, at present, questionable. One approach, currently underway is to develop refractory metal alloys which have acceptable corrosion rates in Na containing 10 ppm oxygen.[14]

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*TZM: 0.5%Ti, 0.08%Zr, bal. Mo.

Cobalt-base alloys have not been sufficiently studied in cold-trapped Na to eliminate them as cladding materials for use at 750-815°C. At these temperatures they have a distinct strength advantage over the stainless steels. The use of Co alloys have been under investigation at the authors' laboratory. Cobalt alloy H.A. 25* is known to lose room temperature ductility upon aging in the 650-870°C temperature range. This embrittlement can be minimized by making compositional adjustments which, however, produce a loss in the high temperature strength.[37] Currently further alloy modifications are being made to develop non-embrittling, high-strength Co alloys. In this program, elements with high nuclear cross section, especially W are being kept to a minimum.[38] A possible objection to using Co as a cladding material is its cross section. Calculations made at BNL show Co alloys require a slightly greater critical mass and give a lower breeding gain compared to stainless steel. The results are shown in Table I. However, Co is comparable to or more attractive than some of the refractory metals. Perhaps the greatest objection to the use of Co alloys is the radioactivity transferred to out-of-reactor components. The activity transferred from Co-base alloys is about 15 times greater than that from stainless steel; the isotopes also have longer half-lives.

Other areas where studies are required include the following: 1) the control of the Na purity because of its marked effect on corrosion rate of stainless steels and refractory metals; 2) the design of hot and cold traps for large systems because the kinetics of impurity removal are not well understood; and 3) the effect of the addition of soluble getters to Na. The experiments in which Ba and Ca were added to Na demonstrated that they reduced mass transfer.[12] Calculations based on typical fast reactors have shown that about 25 ppm Mg will be produced from the decay of Na^{24} in one year. Since Mg will be present in the Na, its effect on corrosion and mass transfer should be studied as part of a larger program in which other getters such as Li, Ba, etc. are also being evaluated. Results obtained from capsule tests at our laboratory indicate corrosion of stainless steel by Na containing 15 at.% Li to be equivalent to that by "gettered" Na. Chemical analysis of the Na-Li alloy showed that the oxygen was associated with Li.

The effect of accidental introduction of H_2O to the Na coolant stream needs to be studied. The current state of steam generator technology is such that failures and introduction of water into the Na must be expected. The combined effect of the products of the reaction such as Na_2O, NaOH, etc. on the corrosion must be determined. Also sporadic introduction of high concentrations of oxygen in NaK produces accelerated corrosion rates.[9] It is therefore most important to evaluate the effect of accidental introduction of impurities on the corrosion rates of proposed reactor materials.

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*H.A.25: 20%Cr, 10%Ni, 15%W, bal. Co.

MECHANISM OF CORROSION OF STEELS BY LIQUID Na OR NaK

Until quite recently, very few experimental programs were specifically aimed at obtaining information on the mechanisms of corrosion by liquid Na. Consequently the corrosion models that have been proposed had to be based on corrosion data obtained in engineering tests. In this section, we present these corrosion models and propose an alternate model which is qualitatively in agreement with the corrosion data.

The corrosion of stainless steel by liquid Na is accompanied by structural and compositional changes at the steel-sodium interface, as noted previously. Nettley et al.[8] have pointed out that the steady-state corrosion rate of stainless steels, which develops after an initial preconditioning period, is linear with time. The surface of the steel becomes enriched in Fe due to selective leaching of Ni, Cr, and Mn (except in Na containing 50 ppm or more oxygen). This suggests that solid-state diffusion of the more soluble alloying elements in the steel is not the rate-controlling step. In the following, therefore, the steady-state overall corrosion rate of a stainless steel will be assumed to be controlled by the rate of dissolution of Fe into the sodium.* The solid-state diffusion phenomena which take place during corrosion have been discussed by Brush.[39]

The General Corrosion Equation

All liquid metal corrosion phenomena arise from a difference in the chemical activity, a_x, of a species x between the liquid and the solid metals. This difference can arise from several sources, the most common being 1) the temperature dependence of the solubility of species x in the liquid metal, 2) variations in the activity of species x between several solid alloys in contact with the same liquid, and 3) the temperature dependence of the activity of species x in an alloy. The rate of dissolution of species x into liquid sodium at any point i in a corroding system can therefore be written

$$R_i(x) = k_x[a_{x(s)} - a_{x(\ell)}] \qquad (1)$$

in which the subscripts (s) and (ℓ) refer to solid and liquid; and k_x is the solution rate constant of species x. If $a_{x(\ell)}$ is greater than $a_{x(s)}$ a negative corrosion (precipitation) of species x will occur.

If we substitute Fe for species x, we can rewrite (1) as

$$R_i(\mathrm{Fe}) = \frac{d(\mathrm{Fe})}{dt}(i) = k_{\mathrm{Fe}}[a_{\mathrm{Fe}(s)} - a_{\mathrm{Fe}(\ell)}] \qquad (2)$$

Further, since we have assumed that the corroding surface is Fe, $a_{\mathrm{Fe}(s)}=1$. Also, $a_{\mathrm{Fe}(\ell)} = S_i/S_o$, where S_i represents the concentration of Fe in solution at point i and S_o the solubility of Fe in the liquid at the same point. Equation (2) becomes, on substitution,

$$\frac{d(\mathrm{Fe})}{dt}(i) = k_{\mathrm{Fe}}\left(\frac{S_o - S_i}{S_o}\right) \qquad (3)$$

The term S_o in the denominator of equation (3) can be included into the overall rate constant, so that equation (3) becomes

$$\frac{d(\mathrm{Fe})}{dt}(i) = k'_{\mathrm{Fe}}(S_o - S_i) \qquad (4)$$

Applying equation (4) to an actual system requires a detailed knowledge of the factors that influence the rate constant k'_{Fe} at all points in the system as well as the solubility, S_o of Fe in Na throughout the temperature range in the circuit. The concentration, $S_i(\mathrm{Fe})$ in Na can then be estimated at each point from the sum of the corrosion that occurred at each point upstream of point i. Such an analysis however, cannot be made at present, since the factors that influence the rate constant are often interdependent and have not in all cases been unequivocally established.

The Solubility of Fe in Na

Before reviewing the corrosion models and the observations which they must explain, the available determinations of the solubility of Fe in Na will be discussed. The results of three measurements made prior to 1955 are summarized in Table II. Epstein's[40] determinations were made by dipping samples out of sodium contained in an Fe crucible located in an inert-gas-filled bell jar. Bogard[41] distilled Na into a stainless steel crucible in which a small specimen of irradiated Fe was suspended. He made the questionable assumption that during a four-hour period the Fe^{59} activity had equilibrated by exchange between the surfaces of the specimen and the steel crucible. He repeated the experiment after intentionally saturating the Na with, first, Na_2O and, then, Na_2O and NaOH, and found an order of magnitude increase in the apparent solubility after the addition of each impurity. Rodgers et al.[42] equilibrated Na with stainless steel both in a pot and in a pumped loop, and detected no difference in the apparent Fe solubility at oxygen concentrations in Na from ~30 to 150 ppm.

No results have been published since 1955. Mottley[43] and Parkman[44] have pointed out that substituting the low data of Bogard into equation (4) and a value for the rate constant similar to that obtained from most liquid metal corrosion models gives reasonable agreement with the measured corrosion rates. However, samples of Na taken from operating loops have all contained ~2-5 ppm Fe.

A recent attempt by Thorley and his co-workers[45] to measure the Fe solubility in Na was inconclusive, but suggested the solubility was close

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*The ferritic layer, however, reaches a steady-state thickness, at which migration of Ni and Cr through the ferritic layer equals the rate of corrosion.[39]

to the higher values. An earlier attempt at Harwell[46] indicated it was less than the limit of detection, 1 ppm at 500°C. Two efforts, one at Atomics International, the other at Brookhaven National Laboratory, are underway to reinvestigate this equilibrium.

Corrosion Rate Models

At present an acceptable model must explain the following observations: 1) the low corrosion rates of steels by Na, 2) the concentrations of Fe (2-5 ppm) found in samples of circuit Na, 3) the first order dependence of the corrosion rate on the oxygen concentration of the Na, 4) the known and postulated complexes of Fe with oxygen and Na, 5) the velocity dependence of the rate of corrosion of steels by Na, and 6) the downstream effect.

Early models for corrosion were required to explain only the first three observations. In 1950 Epstein and Weber[47] concluded that the dissolution of Fe into Na was more nearly approximated by a surface-controlled dissolution reaction than by liquid boundary layer diffusion. They derived equation (5) for the corrosion in an ideal circuit in which the temperature profile along its length was represented by a sine wave:

$$R = -\frac{\alpha}{2}\frac{dS}{dT}\Delta T \qquad (5)$$

in which α is the mean rate constant for dissolution of Fe into the Na, and dS/dT is the average temperature coefficient of solubility over the temperature differential, ΔT, in the circuit. Their derivation required the ΔT to be small. The rate constant α in this equation was found to be a linear function of the oxygen concentration in the Na; also, α extrapolated to zero at zero oxygen concentration.

To explain why the dissolution of Fe into Na should be controlled by a surface reaction rather than by a liquid boundary layer diffusion (as is the case in its dissolution into most other liquid metals such as Hg, Bi, and Pb) the authors[48] and, independently, Horsley[49] suggested that the rate-controlling step was the interaction of Fe with Na_2O dissolved in Na:

$$Fe_{(s)} + Na_2O_{(\ell)} \rightleftharpoons FeO_{(\ell)} + 2Na \qquad (6)$$

Horsley contacted Fe with sodium containing several percent Na_2O and identified a complex sodium ferrite, $(Na_2O)_2 \cdot FeO$. He suggested that this, or a similar complex was the state in which Fe existed in sodium. Such a mechanism satisfactorily explains how a surface-reaction could be rate-controlling, and how the solution rate could have a high activation energy, (which is required to predict the low solution rates). However, the inability of two of the three experimenters to find an effect of oxygen on the solubility of Fe in Na, and the radiochemical techniques of the third* suggest that the dissolution process is not this simple. The

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*Bogard's "oxygen-dependent solubility" could be due to the oxygen-dependent kinetics of exchange of Fe^{59} between the radioactive specimen and the crucible.

authors[50] have pointed out, however, that the oxygen-dependence of the solubility data of Bogard are in reasonable agreement with a thermodynamic calculation of reaction (6); this calculation also suggested that the free energy change of the reaction

$$2Na_2O_{(Na)} + FeO_{(Na)} \rightleftharpoons (Na_2O)_2 \cdot (FeO)_{(Na)} \qquad (7)$$

should be of the order of -9 kcal/g-atom Fe at 753°K. Subsequently, the Fulmer Research Institute measured ΔH_{298} of reaction (7) to be -24.8 kcal/gm-atom[51] Fe, and ΔF_{923} to be -3.3 kcal/gm-atom Fe.[53] From these values, assuming ΔH is independent of temperature, we calculate that $\Delta F_{753} = -7.3$ kcal/gm-atom Fe.

Present models for corrosion have to take into account the recently observed velocity and geometry effects.[7,8] A velocity-dependent corrosion process is incompatible with the dissolution-surface reaction control previously assumed. Further, the "downstream effect" suggests that whatever species is controlling the dissolution rate approaches saturation as the sodium passes through the hot zone: the term $(S_0 - S_i)$ in equation (4) approaches zero. It is difficult to reconcile these observations with the low, oxygen-dependent corrosion rates, and the 2-5 ppm concentrations of Fe in circuit Na.

Mottley[43] suggested that the rate controlling step is the migration of a dissolved complex through the boundary layer. He developed a heat-transfer analog which accounts semi-quantitatively for all of the corrosion observations in the G.E. loops.[7] He assumed that Bogard's solubility of Fe in Na saturated with oxygen represented the solubility of the Fe-Na-O complex. The G.E. loops, however, contained very much less oxygen than the Na in Bogard's tests. Mottley implied that the majority of the Fe present in Na samples taken from these loops exists as elemental Fe, which is presumed to be soluble to several parts per million. Inherent in Mottley's treatment is the implication that oxygen in small amounts in sodium is actually a corrosion inhibitor: in oxygen-free Na, Fe should corrode by simple dissolution. Since the Fe solubility is assumed to be several hundred-fold greater than Bogard's data, steels should corrode several hundred-fold faster in oxygen-free Na than in Na containing small amounts of oxygen. Such corrosion rates have not been observed either in loops containing Zr hot traps,[8] or Li,[9] or alkaline-earth additions[12] to reduce the oxygen activity. Thus we must conclude that Mottley's treatment fails to explain the high solubility and low solution rate paradox. Tyzack[52] has suggested that a ferrite may form as a stable surface layer. This model also implies either that small amounts of oxygen in sodium act as a corrosion inhibitor or that the surface ferrites are not reduced by hot-trapped Na or by Li, Ca, or Mg dissolved in Na.

The U.K. observation of a transition at 3 m/s from a velocity-dependent to a velocity-independent corrosion rate at 650°C in Na containing 10 ppm oxygen suggests an alternative model for the rate controlling step which, at least qualitatively, is consistent with all the experimental observations. The overall corrosion rate is, of course, controlled by the slowest step in the corrosion process. The evidence cited above suggests that the majority of the dissolved Fe is present in Na as an Fe-O-Na complex. There are three possible rate controlling steps in the dissolution process: 1) the migration of Na_2O through the boundary layer to the Fe (or steel) surface, 2) the chemical reaction of the Na_2O and Fe at the interface to form the complex, and 3) the migration of the complex away from the surface through the boundary layer to the flowing stream of Na. Mottley assumed step 3) control and could not satisfactorily explain all the experimental observations. However, if the rate-controlling process is considered to be a competition between steps 1) and 2), the experimental observations can be explained.

The activation energy for step 1) should be of the order of a few thousand calories per mole, whereas the activation energy for and, the temperature dependence of step 2), should be considerably greater. Of the two, only step 1) is expected to be a function of the velocity of sodium. Both steps are first order dependent on the oxygen concentration of the sodium. The lower temperatures and higher oxygen concentrations of the pre-1955 experiments lie within the region of step 2) control. The more recent G.E. and U.K. experiments, with their higher temperatures and lower oxygen content, suggest that the rate of the surface reaction 2), with its higher temperature dependence, has exceeded the rate at which oxygen can migrate to the corroding surface at low Na velocities, so that diffusion of Na_2O to the surface becomes the rate-controlling step. At higher velocities, the diffusion path (boundary layer) for the Na_2O becomes shorter, so that Na_2O can reach the surface more rapidly than it is removed by reaction 2), and the corrosion rate becomes velocity independent. Rowland et al.[7] have tabulated the rate of hot leg metal loss, corrected to zero downstream, at temperatures ranging from 538 to 705°C, 6 m/s Na flow, and oxygen levels of 10-15 ppm and 45-50 ppm. Figure 1 shows these data plotted, according to absolute reaction rate theory, as log (R/T) vs (1/T). The apparent activation energies calculated from all four sets of data are 26 ± 1 kcal per mole of Fe, suggesting that the corrosion rate is controlled by a chemical reaction.* Similar tabulation of their low-velocity data was not available from which to estimate the activation energy under conditions in which the liquid velocity is likely to be rate controlling.

The two most difficult observations to explain by the proposed model are the low corrosion rates and the downstream effects. In fact, the model suggests that, in the velocity dependent region, the corrosion rate depends only on the diffusion of Na_2O through the boundary layer. In sodium containing an Fe-O-Na complex, most of the oxygen must be tied up as the complex, leaving a low concentration of available oxygen for migration to the corroding surface. The downstream effect in the velocity-dependent region requires that the available oxygen be depleted upstream of the downstream specimens.

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*It should be noted that the calculated "activation energies" are for k'.

It should be pointed out that the reverse of the dissolution step, decomposition of the complex into metallic (solid) Fe and available oxygen, also has a high activation energy, and, since the removal of Fe occurs at an appreciably lower temperature, it has a much lower rate than the dissolution of Fe by this reaction. Thus, in a normal pumped circuit only a small percentage of the dissolved complex decomposes during passage through the cold leg. Therefore, the cold leg process governs the overall corrosion rate in the circuit, according to this model. This model suggests that the velocity dependence of the corrosion rate is complex, and not the simple $v^{0.88}$ reported by G.E.,[7] and that the apparent Fe solubility in Na is oxygen-dependent. Further the corrosion rate in the hot leg of a loop will increase as the residence time of the Na in the cold leg increases.

SODIUM SOLUTION CHEMISTRY

The above description of the corrosion of steels by Na implies that a major part of the Fe dissolved in Na exists there as a complex with sodium and oxygen. The evidence for the existence of such complexes between the alkali metals, oxygen, and the transition metals will now be discussed. The state of nonmetals (primarily oxygen and carbon) dissolved in the alkali metals will be described.

Alkali Metal-Oxygen-Transition Metal Complexes

The existence in alkali metal solutions of complexes between the solvent, oxygen, and a transition metal solute has not been substantiated by direct observation. They have been observed after precipitation from the alkali metal solution or on surfaces contacted with these solutions; also, their existence has been inferred from the effects of oxygen on the corrosion behavior of materials in the alkali metals.

The reaction to form these complexes can be written as below, for the example of Fe in Na:

$$x\,Fe_{(s)} + yNa_2O_{(\ell)} + Na \rightarrow Fe_x \cdot O_y \cdot Na_{z(\ell)} + Na_{(\ell)} \qquad (8)$$

which can be broken down into two simple equations which can be analyzed by the application of thermodynamics:

$$Fe_{(s)} + Na_2O_{(\ell)} = FeO_{(\ell)} + 2Na_{(\ell)} \qquad (8a)$$

$$x\,FeO_{(\ell)} + yNa_2O_{(\ell)} = (FeO)_x \cdot (Na_2O)_y \qquad (8b)$$

The probability that reaction (8a) will occur to a finite extent in a dilute solution is directly related to the free energy change for this reaction.

The activity of oxygen in the alkali metal at some temperature T can be approximated as follows:

$$[a_{O\ \text{in L.M.}}]_T = [(\text{ppm O in L.M.})/(\text{ppm O soluble in L.M.})]_T \qquad (9)$$

and the free energy of oxygen in solution (i.e. $Na_2O_{(\ell)}$ in equation 8) becomes

$$\Delta F[O]_T = \Delta F + RT \log (a_{O\ \text{in L.M.}}) \qquad (10)$$

where ΔF is the standard free energy of formation of the alkali metal oxide at temperature T. Thus the solubility of oxygen in the alkali metal has a considerable influence on whether a reaction such as (8a) will occur.

Table III lists the free energies of formation of the oxides of the alkali metals at 900°K (627°C), the estimated (extrapolated) solubilities of oxygen in each metal, and the free energy of oxygen in a 100 ppm solution in each alkali metal. Table IV lists free energies of formation at 900°K of the oxides of the metals frequently considered for containment of the alkali metals, in order of increasing stability.

The corrosion of Fe, Cr, Mn, Nb, and Ta by liquid Na is a function of the oxygen concentration of the Na, whereas the transfer of Ni is not. The free energies of formation of the oxides of all of these elements, except Ni, fall within 25 kcal of the free energy of oxygen in a solution of 100 ppm oxygen in Na. Nickel oxide is more than 37 kcal less stable. Thermodynamic calculations of equation (8a) and (b) have been previously discussed by the authors.[50] The lower free energy of formation of NiO indicates that its concentration in Na from equation (8a) would $\sim 10^{-3}$ times the FeO concentration, which quantity can probably be neglected. Similarly, the equilibrium Na_2O concentration in Na in the presence of solid Ti or Zr can be calculated to be vanishingly small at this temperature.

Lithium oxide is sufficiently stable in Li that it is unlikely to interact to form complexes with any of the metals listed except possibly Ti or Zr. Lithium will, however, reduce the oxides of these metals, and, in the case of Nb or Ta, penetrate into the solid metal to interact with the oxygen dissolved in these metals.[53] It is not known at present whether a double oxide of Li with Nb or Ta is formed; the existence of such oxides has been postulated but their composition has not been identified. Mixed oxides of Li with Ti or Zr have also not been identified.

Oxygen in the alkali metals heavier than Na has a strong tendency to interact with all the metals above Ti (except, possibly Ni) to form complex oxides. The failure to obtain the predicted oxygen distribution between liquid K and the refractory metals, especially Zr, has been explained to be due to the presence of stable, complex oxides which may be substantially soluble in liquid K.[31,54]

The existence of a complex in solution in molecular form in a liquid metal is difficult to rationalize with our understanding of the atomic nature of liquid metal solutions. However, the tendency for interaction between the oxygen, the alkali metal, and the transition metal atoms must still exist in solution. Iron atoms and sodium atoms, for example, should be more strongly bonded to oxygen atoms than to each other; otherwise iron should be much more soluble in sodium than it has been reported to be. Units such as Na-O-Cr or Na-O-Fe, as distinct from complexes such as $(Na_2O)_2 \cdot FeO$, should have a high probability of existing in the liquid solution; the dissolved transition metals, especially Cr, should therefore have a measurable effect on the activity of oxygen in Na.

Since oxygen is known to lower the surface tension of liquid sodium, it has a preference to adsorb at the interface between Na and its container. Thus, a bond such as Fe|-O-Na could readily form at a solid-liquid interface. The rate-controlling process in step 2 of the kinetic argument would then be the breaking away of the surface complex which dissolves in the liquid phase.

The Nature of Dissolved Nonmetals in the Alkali Metals

By far one of the least understood aspects of liquid metal solution chemistry is the nature of the dissolved nonmetals, especially oxygen and carbon.

Oxygen in Sodium

The oxygen dissolved in sodium is generally considered to be present as dissolved Na_2O, except for oxygen present in the ternary complexes noted above. Also, it is Na_2O that precipitates from supersaturated solutions of oxygen in sodium. However, Nevsorov[55] has suggested from electromigration studies on oxygen-bearing sodium that Na_2O is at least partially ionized to Na and oxygen ions; they correlated their electromigration results with a thermally-activated ionization of the Na_2O. Further development of the electrochemical meter for oxygen in Na may throw additional light on this subject.[56]

Carbon in Sodium

The mechanism by which carbon transfers through sodium becomes increasingly more difficult to explain as more information is obtained. The transfer of carbon through an alkali metal occurs according to predictable thermodynamic driving forces; consequently, carbon behaves as though it were soluble in Na. Some years ago Gratton[57] published a solubility curve of carbon in sodium, and showed an oxygen-dependence of this solubility which suggested that at least some of the carbon exists in Na as a C-O-Na complex. Corrosion tests with sodium containing >50 ppm oxygen have shown that carbon transfer is a function of the oxygen concentration of the sodium,[58,59] as have the electromigration studies of Lyashenko and Nevsorov.[60] Carbon transfer in Na with <50 ppm oxygen has generally been found to be oxygen-independent;[7,8] however, a recalculation of the data in Table IV of the paper by Nettley et al.[8] suggests, as seen in Table V, that carbon transfer may be a function of the oxygen concentration in sodium down to below 5 ppm oxygen.

Recent attempts to measure the carbon solubility in oxygen-free Na have failed to disclose any measurable solubility.[61] An attempt by the same authors to zone-refine Na to remove C also failed, suggesting that C may be present in sodium as a dispersion rather than as a true solution. It is quite possible that C present in as-received Na could be finely dispersed, having originated either from C electrodes used in the reduction of the metal, or from traces of oils that reacted with the Na during subsequent handling. However, it is difficult to imagine that carbon transfer from low to high alloy steels could occur with suspended rather than dissolved carbon as the intermediary state in the sodium. Recent studies by Sinclair et al.,[62] Addison,[63] and Pulham[64] suggest that carbon-sodium bonds without intermediate oxygen atoms are highly unlikely; and, if carbon is soluble in Na without reaction with oxygen, its solubility must be <3 ppm. Perhaps, therefore, carbon transfer <u>is</u> a function of the oxygen concentration of Na down to very low levels.

CONCLUSIONS

1. The stainless steels should be adequate container materials for liquid sodium if the maximum temperature in the circuit does not exceed 650°C and the oxygen levels in the sodium are maintained at approximately 10 ppm.

2. The importance of the irradiation embrittlement and loss of high temperature ductility of these steels has not been evaluated at the present time.

3. Stainless steels with compositions modified to reduce their embrittlement by irradiation require corrosion testing to demonstrate their adequacy for fuel cladding and structural applications.

4. The development of new alloys for fuel cladding applications at temperatures above 650°C needs to be vigorously investigated.

5. The effects of radiogenic Mg on the corrosion process need to be studied.

6. The effects of intentional additions of soluble oxygen "getters" to Na on the corrosion behavior of steels in this liquid need further study as a method of reducing corrosion and as a test of the several proposed corrosion mechanisms.

7. The effect of residence time in the heat exchanger on the corrosion process needs to be evaluated.

8. Careful studies of the mechanism of carbon transfer are needed.

9. The relationship between the Fe solubility and the oxygen content of Na requires resolution.

10. There is a need for a general corrosion equation which can be used to predict the corrosion in a large system.

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Table I

Effect of Cladding Material in Na Cooled Fast Reactor*

Cladding Material	Critical Mass in kg	Breeding Ratio
316 SS	2000	1.25
Incoloy 800 (45Fe-35Ni-20Cr)	1991	1.26
S-1 (Co-20Cr-10Ni-6Mo-2Fe)	2077-2159	1.19-1.22
Mo	2264	1.15
V-20Ti	2062	1.24

*Fuel is PuO_2-UO_2 with a density of 11.1 gm/cm^3 representing 29% of core volume. Core: Diam. = 11.7 ft., H = 2 ft., structure and clad each ≈9% of core volume.

Table II

"Solubility" of Fe in Na at 500°C

	Bogard[41]	Epstein[40]	Rodgers et al.[42]
"Pure" Na	0.008	~12	10-13
Na + Na_2O	0.033[1]	12	10-13[2]
Na+Na_2O+NaOH[3]	0.28		

[1] Saturated with Na_2O
[2] 30-150 ppm oxygen
[3] Saturated with Na_2O + NaOH

Table III

Thermodynamic Properties of the Alkali Metal Oxides and Their Dilute Solution in Liquid Alkali Metals at 900°K

Alkali Metal Oxide	ΔF°, 900°K (kcal/g-atom O)[65]	Estimated Solubility of O, 900°K (ppm)	ΔF°(O),900°K (100 ppm O dissolved in the alkali metal) (kcal/g-atom O)
Li_2O	-113.8	3390[66]	-120.0
Na_2O	- 69.0	1580[67]	- 74.5
K_2O	- 53.8	23,000[68]	- 64.0
Rb_2O	- 49.0		~ 60
Cs_2O	- 42.0	56,800*[69]	- 53.3

*56,800 ppm = 100% Cs_2O

Table IV

Free Energy of Formation at 900°K (627°C) of Oxides of Metals Commonly Studied as Containers of the Alkali Metals[65]

Oxide*	ΔF° 0 at 900°K (kcal/g-atom O)
NiO	- 37.3
CoO	- 40.6
FeO	- 49.4
1/2 WO_2	- 49.9
1/2 MoO_2	- 50.2
1/3 Cr_2O_3	- 71.7
1/4 Nb_2O_4	- 75.8
1/5 Ta_2O_5	- 78.7
VO	- 81.0
TiO	-103.2
1/2 ZrO_2	-110.2

*When more than one oxide exists, the lowest oxide state is given, unless one of the higher oxides is more stable.

Table V

Carbon Increase After Test[8]

Steel wt.%C	T_{Na}	O_2	Time (Months)	Carbon Increase After Test* Mean	Carbon Increase After Test* 0.01cm Surface Layer
321	650	<5	6	.003	.016
0.07		5	3	.013	.017
		10	4	.012	.028
		25/30	6	.010	.040
316	650	<5	6	.003	-
0.05		5	3	.010	.017
		10	4	.007	.023
		25/30	6	.007	.023

*wt.%/month.

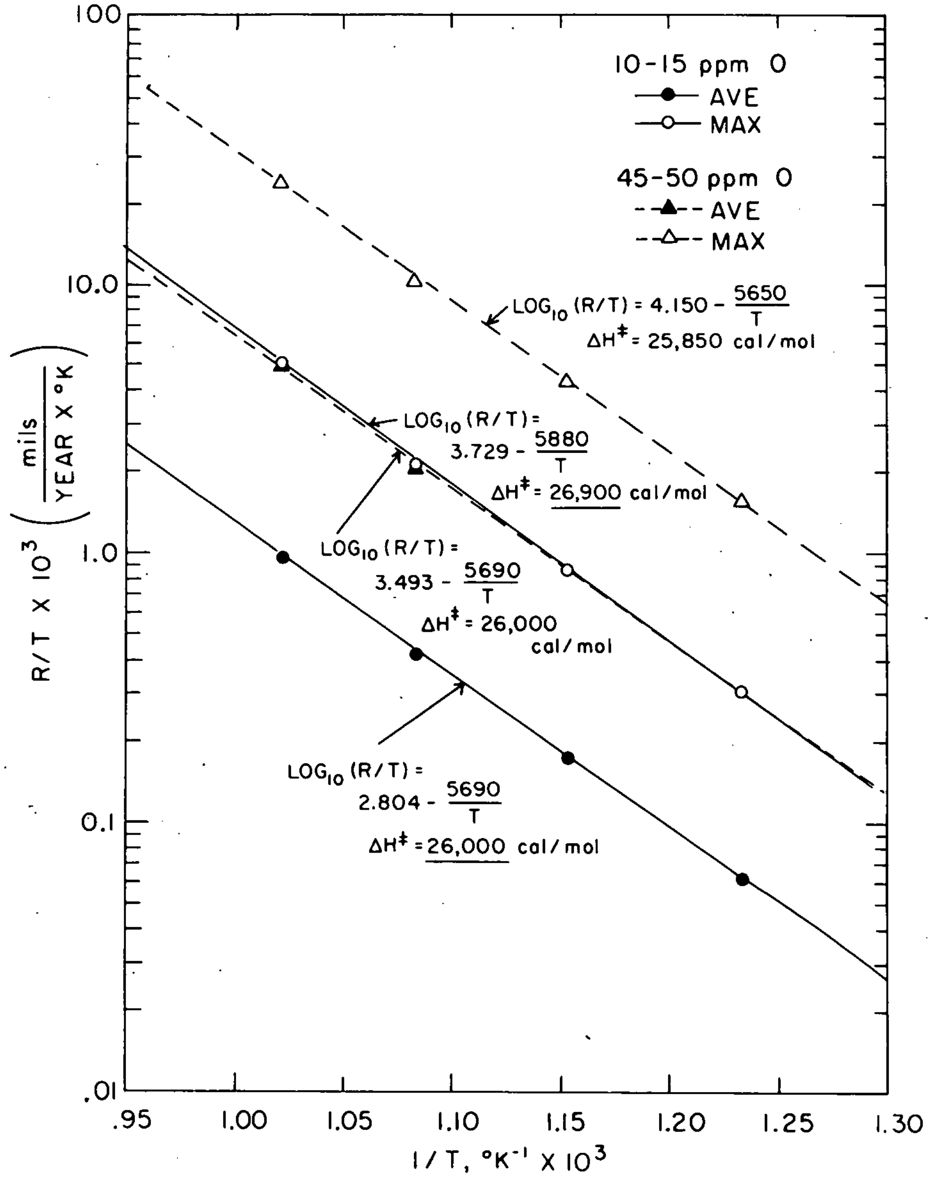

Figure 1. Temperature dependence of the corrosion of type 316 stainless steel in Na flowing at 6 m/s.[7]