Erratum BNL-14508

1) Front Cover - The word on the last line Gloucestershire

2) Page 3

Na(C) | Membrane | Electrolyte | $\begin{matrix} \text{Reference} \\ \text{Electrode} \end{matrix}$, Cell I

3) Page 5

$$c = 1/2 c_2^{-2} - e , \quad (c)$$

4) Page 15

$$\frac{\frac{dw_c}{dt} \exp(n\mathcal{E}/RT)}{w_{Na} \left(-\frac{d\mathcal{E}}{dt}\right) \left(\frac{n\mathcal{E}}{RT}\right)} , \quad (6)$$

An Electrochemical Carbon Meter for Use in Sodium*

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ABSTRACT

The feasibility of an electrochemical carbon meter which measures the chemical activity of carbon in sodium at temperatures from 600° to 700°C has been demonstrated. The meter is based on the cell

and has been shown to respond to the addition of various carbonaceous reagents which were added to the sodium, especially carburized iron. Some tests of a cell with a CaC_2 -LiCl electrolyte are also reported. The chemical activity of carbon in equilibrium with a 347 SS-sodium system has been measured. The use of the meter to indicate when carburizing or decarburizing conditions exist in the sodium is discussed. Some data on the solubility of carbon in sodium determined with the carbon meter are reported. The meter can be used to measure the concentration of carbon in sodium by making use of solubility data.

*This work was performed under the auspices of the U. S. Atomic Energy Commission, Reactor Development and Technology Division.

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INTRODUCTION

Current designs for fast breeder reactors call for the use of sodium as a coolant in systems which will contain austenitic and ferritic alloy steels. It is well known that carbon is transported via sodium from ferritic to austenitic steels and that carbon migrates through sodium from the hotter to the colder regions in an all-austenitic or all-ferritic steel system. The addition or removal of carbon from these alloys can cause significant and in some cases serious deterioration in their mechanical properties.¹ The problem is further complicated by the uncertainty in the solubility of carbon in sodium,^{2,6} lack of knowledge about the thermodynamic activity of carbon in sodium-steel systems,⁶ and only limited information on the kinetics and mechanism of carbon transport in sodium.^{3,8} Furthermore, the relation between carbon and other impurities known to exist in sodium has not been studied.⁹ The relationship between carbon and oxygen in sodium is of special interest because of the role of oxygen in the corrosion of stainless steel.

A promising approach to studying the problem of carbon in

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sodium systems is the development of a device which will continuously monitor the amount of active carbon in the sodium, the chemical activity of carbon, or some parameter related to the ability of the sodium to carburize or decarburize various austenitic or ferritic alloys - "carburization potential."

In this report we present the design details and discuss the use of an electrochemical technique which continuously measures the chemical activity of carbon in liquid sodium at temperatures from 600° to 700°C, without addition or removal of reactants from the system. The electrolyte system selected for this meter is a eutectic mixture of Na_2CO_3 and Li_2CO_3 ; an alternate electrolyte tested is a solution of CaC_2 in LiCl . The reasons for selecting the carbonate electrolyte are discussed. The final design of the meter is presented and critically compared with other devices for measuring and monitoring the activity of carbon in sodium. Preliminary data are given on the chemical activity of carbon in a sodium - type 347 stainless steel (SS) system, and on the solubility of carbon in Na in equilibrium with carburized iron (Fe_3C).

Additional applications of this electrochemical carbon meter are discussed.

PRINCIPLE OF OPERATION

The most basic approach to the development of an electrochemical technique for determining the chemical activity of carbon in

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liquid sodium is the selection of an electrolyte which can be used to construct a carbon concentration cell. The emf of such a cell, $\mathcal{E}$, is given by the expression

$$\mathcal{E} = \frac{RT}{n\mathcal{F}} \ln \frac{a_R}{a_C}, \quad (1)$$

in which R is the gas constant, T is the absolute temperature, n is the number of electrons involved in the electrode reaction, $\mathcal{F}$ is the Faraday constant, a_R is the chemical activity of carbon at the reference electrode and a_C is the corresponding value at the working electrode.¹⁰ Ideally, this electrolyte should contain a carbon bearing anionic or cationic species, have a low electronic conductivity, be easily fabricated into a solid nonporous form, and be compatible with liquid sodium. The first two requirements are achieved by carbonate electrolytes or solutions of acetylide ion (C_2^{-2}) in a fused salt. An electrolyte system which meets the last two requirements has not been found to date. In order to avoid the problem of compatibility and fabricability of the electrolyte, we have chosen to measure the chemical activity of carbon in liquid sodium via a membrane permeable to carbon.

The membrane technique can be utilized in a cell configuration of the type

where $Na(C)$ represents sodium containing dissolved carbon. If

$a_C(\text{Na})$ and $a_C(\text{M})$ represent the chemical activity of carbon in the sodium and in the membrane respectively; then, at equilibrium

$$a_C(\text{Na}) = a_C(\text{M}) \quad , \quad (a)$$

provided that the solubility of carbon in the membrane is finite. By means of this technique the problem of measuring the chemical activity of carbon in the sodium reduces to the selection of the membrane, an electrolyte system compatible with the membrane, and a suitable reference electrode. The most obvious choices for the membrane material are iron or nickel since the rate of diffusion of carbon and the solubility of carbon in these materials are sufficiently high.¹¹

We have demonstrated the feasibility of using carbonate electrolytes to construct carbon concentration cells which measure the chemical activity of carbon in iron tab samples.¹² In a series of initial exploratory measurements the authors of this paper demonstrated that a carbon concentration cell can be constructed using a Na_2CO_3 - Li_2CO_3 eutectic electrolyte.

The following results were obtained from these initial measurements of iron samples containing various concentrations of carbon in the cell configuration

in which Fe(C) and Fe'(C) corresponds to the various iron samples studied. The electrode reaction can be written as

When Fe(C) and Fe'(C) were both saturated with carbon the emf of the cell was zero at temperatures from the melting point of the electrolyte (505°C) to 725°C. When Fe(C) and Fe'(C) were below saturation and contained equal concentrations of carbon (3 ppm), the emf observed was also zero in the same temperature range. When one of the samples was pack-carburized at 950°C in vacuum and replaced in the cell an emf was observed. The emf vs temperature curve and the temperature at which the emf extrapolated to zero were in good agreement with the expected values based on the composition of the sample and the known solubility of carbon in iron, assuming ideal behavior.^{13,14}

Following the work of Hawkes and Morris,¹⁵ we have demonstrated that cells of the type

can be used to determine the chemical activity of carbon in sodium.

They showed that cell III was reversible to carbon via the acetylide ion present in the melt according to the electrode reaction

in which e corresponds to the one electron per carbon atom involved in the reaction. We present in this paper a modification of their technique, adapting it to lower temperatures by use of a lower melting point solvent i.e. LiCl , and the utilization of this technique to measure the chemical activity of carbon in sodium systems.

The polarity of cell III was found to be opposite in sign to that of a carbonate electrolyte, as would be expected from the difference in the electrode reactions b and c.

CONSTRUCTION OF THE CARBON METER

The mechanical assembly described in this section has been used to test both the carbonate and carbide electrolytes. A detailed schematic diagram of the electrochemical carbon meter is shown in Fig. (1). The sensing element of the original meter is a Ferrovac E iron cup, 5 mil wall, $1/2$ " o.d. x 2" long, machined from a piece of 1" bar stock. The upper 1" of the cup has $1/16$ " wall and is welded to a $1/2$ " type 304 SS tube.¹⁸ A 1" male "Conoseal" fitting is welded to the $1/2$ " 304 SS tube and serves to seal the meter assembly into the sodium system by means of a corresponding female fitting. The "Conoseal" fitting is positioned to allow the bottom of the cup to be immersed 6" into the sodium. A $1/2$ " "Swagelock" T is connected to the $1/2$ " 304 SS tube at a point approximately 2" above the Conoseal fitting. The "T" is connected

to a valve which is used to interconnect the gas phase over the sodium and the inside of the meter. This avoids the danger of accidentally applying a large pressure difference across the thin iron cup. Above the "T" is an electrically insulated teflon Conax fitting which serves to seal and support the reference electrode. A high purity 3/8" o.d. x 1/4" i.d. Al_2O_3 tube serves to insulate and center the reference electrode assembly. The reference electrode is a 1/8" o.d. rod fabricated from either high purity TSX graphite (National Carbon) or carburized iron and is immersed 1/2" into the salt melt which is 1" high. In order to minimize the temperature difference between the cup wall and the center electrode (due to loss of heat up the electrical lead connected to reference electrode), it is necessary to make the cross section of this wire small to reduce heat losses through this wire. The lead in the carbon meter is 1/32" o.d. Type 308 SS welding rod and is connected to the reference electrode in the hot zone and connected at the Conax fitting to 1/4" 304 SS rod which is held by the fitting. The voltage developed by the cell is measured between the 1/4" rod and the body of the meter.

Prior to assembly of the meter in a argon dry box, that portion of the meter which is inserted into the sodium and the reference electrode are each separately vacuum outgassed at 850°C. The Al_2O_3 insulator is dried by air firing to 950°C for 24 hours

and it is loaded hot (400°C) into the dry box. The final assembly of the meter i.e. the insertion of the Al_2O_3 tube, the reference electrode, and the Conax fitting is accomplished after the electrolyte in the form of 1/8" pieces are loaded into the iron cup. Initially, the reference electrode is positioned above the loose packed pieces of electrolyte. After the meter is assembled and sealed it is removed from the dry box and inserted into sodium at 120°C. The system is evacuated after the gas space over the sodium is connected with the inside of the meter. After sufficient pumping the system is back filled with pure helium and heated to 550°C. At this temperature the reference electrode is positioned in the melt by sliding the 1/4" rod through the Conax fitting with the system under positive pressure. The sodium is then heated to 650°C for a minimum of 24 hours to condition the meter before use in any experiment. A dimensioned photograph of an assembled meter is shown in Fig. 2.

Instrumentation

The emf was measured to within 0.01 mV with a high impedance electrometer (Kiethley model #602) in conjunction with a reference voltage source (General Resistance DAV 45). The output of the electrometer and the temperature were continuously recorded on a two pen recorder (Honeywell elektronik 19).

Preparation of Electrolytes

$\text{Na}_2\text{CO}_3\text{-Li}_2\text{CO}_3$

The Na_2CO_3 and Li_2CO_3 are reagent grade materials supplied by the J. T. Baker Chemical Co., Phillipsburg, New Jersey. A eutectic mixture containing equal moles of Na_2CO_3 and Li_2CO_3 is prepared from the as received powders and thoroughly mixed. This mixture is loaded into a previously vacuum outgassed mild steel crucible and placed in a quartz glass high vacuum system. The pressure in the system is reduced to 10^{-5} mm Hg at room temperature and the mixture heated by induction at a rate which maintains the system pressure below 10^{-5} mm Hg. When the mixture is molten, the heating is continued under vacuum until the temperature reaches 750°C and is held until the pressure in the system is stable (a few minutes). At this temperature, a small amount of black material deposits on the quartz envelope.

The mixture is cooled in vacuum and transferred in the quartz apparatus to an Ar glove box without exposure to the air. Inside the glove box the mild steel crucible is cut open at the bottom and down one side along previously machined seams and the charge of salt removed from the crucible with steel tools. The prepared eutectic salt is stored in a closed container in the dry box and weighed out in 7.5 gram increments as required for use in carbon meter assemblies.

$\text{CaC}_2\text{-LiCl}$

The LiCl is prepared by a technique previously described and stored to avoid contact with moisture or air.¹⁷ Prior to use, the

LiCl is vacuum melted and heated to a maximum temperature of 640°C in a previously-outgassed (950°C) high purity graphite crucible and cooled in vacuum.

The $\text{CaC}_2\text{-LiCl}$ solution is prepared in a mild steel crucible outgassed at 950°C. Reagent grade CaC_2 prepared by direct reaction of calcium and carbon at high temperature is obtained from Fischer Scientific Co. Approximately 8-10 grams of CaC_2 in the form of 1/16"-1/8" chunks is placed at the bottom of the mild steel crucible and approximately 40-50 grams of LiCl is loaded in on top. This crucible is covered but not sealed and loaded into a quartz apparatus which is removed from the dry box, placed in the induction heater and evacuated at room temperature. The mixture is heated in vacuum until molten ($>620^\circ\text{C}$) and the quartz apparatus is back filled with pure helium to approximately one atmosphere pressure. The mixture is then heated to 750°C and held (under He) for eight to 24 hours at temperature. At the end of this period the crucible is cooled under pressure until the salt is solid ($<590^\circ\text{C}$), then evacuated and cooled to room temperature. The quartz system is transferred to the glove box, avoiding contact of the salt solution with the atmosphere. Removal of the salt is accomplished by first cutting off the bottom of the mild steel crucible and removing all the excess CaC_2 which remains on the bottom. The solid salt solution is then removed from the iron crucible by cutting along a previously prepared side seam.

The color of the solid $\text{CaC}_2\text{-LiCl}$ mixture is pink. Our experi-

ence indicates that longer contact times between LiCl and CaC_2 produce darker colored mixtures which contain more CaC_2 in solution. We have not determined the CaC_2 content of these mixtures, but the solubility of CaC_2 in LiCl has been reported to be approximately 5 mole percent at 750°C . The prepared CaC_2 - LiCl mixture is stored in a closed container in the argon dry box, and weighed out in 6.4 gram increments as required for use in each meter assembly.

RESULTS

Equilibrium

Ten electrochemical meters have been built as described above, but with some minor variations. Approximately half of these contained the carbonate and the rest the carbide electrolyte. These meters were tested in 347 SS vessels approximately 2" in diameter and 10" high, which contained 1/2 lb of reactor grade sodium. Each vessel contained one meter, a thermocouple well, and an entry port for addition and removal of material from the sodium. During the course of each experiment the sodium was continuously stirred by an electromagnetic technique, which has been previously described.¹⁸

When a meter containing either type of electrolyte is immersed in the sodium, a fixed reproducible emf is developed in several hours at any given temperature in the range 600° to 700°C . The emf vs temperature behavior of each electrolyte system is shown in Fig. 3. This behavior is reproducible from meter to meter in the same vessel.

When a vessel containing a carbon meter is allowed to equilibrate at 685°C for at least 24 hours and is subsequently temperature cycled from 685°C to room temperature and back to 685°C, the equilibrium emf level is achieved in less than one hour after the vessel has reached 685°C. Figure (4) shows data obtained from a carbon meter that utilized a carbonate electrolyte and a 10 mil wall iron cup for a membrane. The emf in Fig. (4) is given by the expression

$$\mathcal{E} \text{ (mV)} = -0.194T + 127 \quad . \quad (2)$$

These data were obtained after equilibration times which ranged from 24 to 48 hours. We believe that (2) represents the carbon activity in sodium in equilibrium with type 347 SS, and therefore the carbon activity in the steel. (The sodium, in this case, acts as a C-permeable membrane.)

In an experiment described below involving additions of Na_2C_2 into sodium in a 347 SS vessel containing a carbon meter filled with carbide electrolyte, approximately 0.5 gram of carbon in the form of Na_2C_2 was added to the system in the course of three additions without significantly affecting the final equilibrium emf. These results suggest that the 347 SS-sodium system studied in these experiments buffers the activity of C in the Na, and can take up large quantities of carbon before the equilibrium chemical activity of carbon in the system is affected. However, the recovery time after the addition of Na_2C_2 did appear to depend on the amount of carbon which had been previously added. The

equilibrium values obtained before and after two successive additions of Na_2C_2 are shown in Fig. 5.¹⁹

Response to the Addition of Carburized Iron

The response of a carbon meter containing carbonate electrolyte to the insertion of carburized iron into sodium was tested in the following manner. Commercial (ungalvanized) flat steel chain 1/4" wide and weighing 0.25 grams per link was pack carburized by being immersed in a bed of natural graphite powder contained in a graphite crucible and heating in vacuum to 950°C for six hours. Approximately four grams of carburized chain were suspended in the gas phase over the sodium from a 304 SS rod which was inserted in the vessel through a sliding seal. The vessel was fabricated from 347 SS and contained approximately 1/2 lb of reactor grade sodium to which no other reagents had been previously added. When the emf was stable (indicating the buffer potential due to the steel) the carburized iron chain was immersed in the sodium. In a short period of time the emf was observed to decrease. When the emf had declined 8 to 10 mV below the starting value, the chain was pulled out of the sodium. After a short delay period, the emf began to increase. Eventually, in periods of time which ranged from a few hours to overnight, the emf returned to the original starting value. The response of the meter to the addition of carburized iron at temperatures of 600°, 650°, and 685°C is shown in Fig. (6), which is a reproduction of the original chart

recordings. The original emf levels are at the left and the pen moves from left to right on a time scale which is one minute per division for the 685° and 650°C run and ten minutes per division for the 600°C run. The scale shown is 10 mV wide and the original starting emfs were -51.3, -45.3 and -31.0 mV at 685°, 650° and 600°C respectively. The temperature traces shown were recorded on an expanded scale and are not in proportion. The 685°C run shows a second run superimposed on the original. In the experiments at 685° and 650°C the chain was immersed in the sodium for a period of 5 minutes and 3 1/4 minutes respectively. The weight changes for each of the chains before and after immersion in the sodium were 3.17 mg and 1.1 mg at 685° and 650°C respectively. In one experiment a piece of chain containing approximately 18,000 ppm carbon was immersed in the sodium for three days at 650°C; when it was removed the carbon concentration of the chain was 18 ppm by analysis, corresponding to a loss of 50 milligrams of carbon from the chain.

Solubility of Active Carbon in Sodium

Information on the magnitude of the solubility of carbon in sodium will enable the electrochemical carbon meter to be used as an analytical tool for continuous determination of the concentration and carburizing potential of carbon in Na. Conversely, the electrochemical carbon meter can be used to measure the solubility of carbon by observing

the emf changes when known additions of carbon are made to sodium. A relation can be derived which relates the solubility of carbon in sodium, the rate of change in emf with time $(\frac{d\mathcal{E}}{dt})$ and the rate of carbon loss per unit time $(\frac{dw_c}{dt})$ when a piece of carburized iron is immersed for short times in sodium containing a carbon meter.

If we assume a linear relation between the activity of carbon, a_c , and the concentration of carbon in sodium, C , then

$$a_c = \frac{C}{C_o} \quad , \quad (3)$$

where C_o is the solubility of carbon. Differentiating equation (3) with respect to time we obtain

$$\frac{da_c}{dt} = \frac{1}{C_o} \frac{dC}{dt} \quad . \quad (4)$$

If we take the derivative of a_c with respect to $\mathcal{E}$ in equation (1) when the reference electrode is at unit activity, we obtain

$$\frac{da_c}{d\mathcal{E}} = -\frac{n_f}{RT} \exp[-n_f \mathcal{E}/RT] \quad . \quad (5)$$

Substituting equation (4) into equation (5) we obtain

$$C_o = \frac{\left(\frac{dw_c}{dt}\right) (\exp[n_f \mathcal{E}/RT])}{(w_{Na}) \left(-\frac{d\mathcal{E}}{dt}\right) \left(\frac{n_f}{RT}\right)} \quad , \quad (6)$$

where w_{Na} is the weight of sodium and $\mathcal{E}$ is the average emf level before and after addition of carbon.

A carbon meter containing a carbonate electrolyte with a 5 mil iron membrane was placed in a nickel vessel. All the surfaces in the vessel exposed to sodium were either nickel or iron. This vessel was similar in most respects to the Type 347 SS vessels used in other areas of this study. The carbon and oxygen levels in the sodium in this vessel were reduced to the lowest attainable levels by repeated gettering at 650°C with Type 347 SS and uranium metal rods which were inserted into the sodium through a sampling port. The oxygen levels were reduced to <1 ppm and the emf of the carbon meter was increased by the gettering to a maximum value of 42 mV at 650°C.

A series of carbon additions were made into this nickel vessel at temperatures from 550° to 675°C and the corresponding emf changes were observed. The source of carbon was a piece of carburized iron flat chain, identical to the material used to test the response of the electrochemical carbon meter in Type 347 SS vessels. The rate of carbon addition was varied by changing the weight of the carburized chain by a factor of two and the rate of stirring was varied; neither variable was found to have a significant effect on the solubility results.

The results of these measurements are shown in Fig. (7) which is a plot of log of the solubility of carbon in sodium in ppm vs the reciprocal temperature.

In order to determine if the solubility of carbon is affected by variations in the oxygen content of the sodium, measurements of the solubility were made after additions of Na_2O to the vessel. The solubility of carbon in the sodium was studied after 100 and 240 ppm oxygen were added to the vessel. Subsequent removal of the oxygen after each addition demonstrated that 100% of the Na_2O added was recovered by uranium gettering. The results of the solubility measurements at 650°C at low oxygen (<1 ppm) and the effects of the oxygen additions are listed in Table 1.

DISCUSSION

Observations on the general response of the meter to addition of carbonaceous reagents and calcium metal as a carbon getter are presented in the appendix.

Equilibrium Emf (Buffer Potential) Measurements

The observation that electrochemical carbon meters placed in 347 SS-sodium systems give fixed and reproducible emfs at a given temperature is not unexpected. Chromium, which is a major alloying element of the steel, forms stable carbides. Since it exists at an activity in the steel of $\cong 0.2$, it is capable of reacting with any excess carbon in the system in order to satisfy the equilibrium by a reaction such as

Obviously, the presence of niobium as a carbon stabilizer in the Type 347 SS may also be influencing the chemical activity of carbon in the system.

If we assume that the chemical activity of carbon in the systems studied is controlled by an equilibria of the general type

where MC_x and MC_{x+y} represent two metal carbide phases, or if $x=0$, a metal and a metal carbide in equilibrium, it can be easily shown that the emf of the carbon meter is given by the expression

$$e = \left[\Delta S + \frac{R}{y} \ln \frac{[MC_x]}{[MC_{x+y}]} \right] \frac{T}{n\mathcal{F}} - \frac{\Delta H}{n\mathcal{F}} \quad , \quad (7)$$

where ΔH and ΔS are the heat and entropy change per mole of carbon for the above reaction, R is the gas constant, T is the absolute temperature, $\mathcal{F}$ is the Faraday constant, n is the number of electrons per mole of carbon involved in the electrode reaction and has the value four in the carbonate system and is unity for the carbide electrolyte. The terms in the square brackets are the chemical activities of the respective carbide phases. A plot of emf vs temperature will be linear if the activities of the carbide phases or the ratio of their activities are constant. Irrespective of the state of the carbide phases, the intercept at $T=0$ is a measure of the heat of reaction.

It is clear and unequivocal from the response tests involving addition of carburized Fe (and other reagents cited in Appendix A) to the sodium that these meters respond to changes in the chemical activity of carbon in the sodium. However, a significant question

remains i.e. do these electrolyte systems measure the absolute thermodynamic chemical activity of carbon in the sodium? A partial answer to this question is evident from the results in Fig. (3) which are emf vs temperature data for the two electrolytes studied in different meters in the same 347 SS vessel. If both electrolyte systems are reading the true value of the chemical activity of carbon, the data in both cases would have the same temperature intercept when the emf is zero. Furthermore, the emf value of the carbide system would be four times the value of the carbonate system at any given temperature. In actual fact, the slope of the carbonate data is one quarter that of the carbide results, but the intercepts differ by 135°C . This is not due to the use of different reference electrodes since we find it difficult to see significant differences in emf between graphite and carburized iron reference electrodes in the carbonate electrolyte at temperatures from 600° to 700°C .

Since the above cited work with carburized Fe indicates that the carbonate electrolyte gave theoretical potentials, we believe that the error in intercepts is due to the carbide electrolyte, especially because this (carbide) electrolyte is more affected by impurities such as hydrogen than is the carbonate electrolyte. These lower emf's may also be the result of significant electronic conductivity in the LiCl solution due to the relatively high activities of calcium resulting from the low stability of CaC_2 .

The results shown in Fig. (4), obtained from a carbon meter with a 10 mil iron membrane and filled with carbonate electrolyte, were taken after very long equilibration times at each temperature in a 347 SS-sodium system and best represent equilibrium thermodynamic data. Since the chemical activity of the reactant and product carbides (MC_x and MC_{x+y}) are unknown we can obtain no information about the entropy change for reaction (e), but from the intercept of Fig. (4) i.e. equation (2), we estimate the heat of reaction (ΔH) to be 12,000 cal/mole carbon. This value falls within the range of values reported for $\frac{1}{6}Cr_{23}C_6$.²⁰

The use of this carbon meter to assess the presence of carburizing or decarburizing conditions in the sodium systems studied is somewhat simplified because of the ability of 347 SS to take up large quantities of carbon without significantly affecting the equilibrium chemical activity of carbon in the system. If a carbon meter in a 347 SS-sodium system reads an emf lower than given by equation (2), a driving force for carburization exists. Similarly, emfs higher than equation (2) indicate the possibility of decarburization of the steel. This will be discussed in more detail in a later section.

Solubility of Carbon in Sodium

The solubility results obtained at temperatures from 675° to 550°C are compared in Fig. (7) to data reported by other investigators. The data of Longson and Thorley⁴ are shown in Fig. (7):

the shaded region is our interpretation of the maximum uncertainty band of their data. In the range 600° to 675°C the data of Longson and Thorley are in fair agreement with the values obtained in this study. Our data indicate that there may be a break in the solubility at 650°C, and we suggest that it be looked for in other investigations.

These results represent the first application of a new technique of measuring carbon solubility in sodium independent of chemical analysis. These measurements may be in error on the high side due to the possible presence of parasitic sinks for carbon in the system. However, we believe the greatest error results from the uncertainty in weight change measurements of the carburized iron source. These changes ranged from 0.2 to 0.7 mg in each experiment involving 200 g of sodium. Using larger vessels containing kilogram quantities of sodium would greatly decrease this error, which in the present data could be 20% at the lowest temperature. The results shown in Table 1 suggest that the effect of oxygen on the solubility of carbon is small. Also, there appears to be an anomaly in that the apparent solubility of carbon is higher at 100 ppm than at 240 ppm oxygen. These oxygen levels indicate, however, only the amount added to the sodium not analytical results. This is obviously an area for further study.

Selection of the Carbonate over the Carbide
Electrolyte for the Carbon Meter

The carbonate electrolyte is believed to give potentials that are more closely related to the thermodynamically-predicted

potentials, as cited above. Also, the carbide electrolyte appears to be sensitive to the presence of H_2 in the sodium in that we have observed the carbide electrolyte to deteriorate instantly in meters exposed to high activities of hydrogen (1 atm pressure).

Recently, we have become aware of a limitation in the application of electrochemical carbon meters based on the carbonate electrolyte. The problem is mass transport of iron from the inside wall of the iron cup to the reference electrode. Iron deposited at the reference electrode grows in the form of iron whiskers extending radially from the reference electrode, primarily at the salt gas interface. This process can eventually cause failure of the cup wall, but long before this occurs the cell is electrically shorted as a result of the whisker growth extending from the reference electrode to the cup wall. If this growth shorts a cell, the emf of the cell is easily restored by removing the reference electrode at temperature, scraping off the iron deposit and replacing the reference electrode in the meter. The driving force for this transport process may be due to a temperature difference which exists between the iron cup wall and the reference electrode and results from a heat leak up the center electrode. In meters immersed well below the sodium gas interface (4 1/2") the rate of whisker growth is slow but, it is very rapid in meters immersed at shallower depths (<2"). We believe this problem with the current meter assembly can be eliminated by appropriate design of the reference electrode, proper placement of the meter in the

sodium and restricting the operating temperature to 650°C or lower. With improvements in the engineering design and application of electrochemical carbon meters in sodium systems, we believe that the life of a meter will be extended substantially by months.

COMPARISON WITH OTHER METHODS OF MONITORING THE CARBON ACTIVITY IN SODIUM

None of the carbon methods previously proposed or currently in use directly measures the amount of carbon in the sodium which contributes to carburization, or the thermodynamic chemical activity of carbon. Simple sampling and analysis has failed to indicate carburizing conditions i.e. the presence of a graphite insert in the Na.^{21,22} The most highly developed device currently in use (the UNC meter) measures the rate of transport of carbon from sodium through an iron barrier to a highly decarburizing gas (H_2+H_2O), thus continuously removing carbon from the system, and introducing hydrogen into the sodium.²³ Also the iron membranes may pick up Cr and Ni from the sodium, as we have observed iron to do in a stainless steel system, which would likely cause the diffusion flux from a constant source to change with time. This Cr and Ni does not, however, adversely affect the operation of the BNL meter, since it requires only that the membrane equilibrate with the sodium. The electrochemical meter is believed to be less expensive to construct and operate.

Conclusions and Application

An electrochemical carbon meter has been developed to the stage where it can be used in large scale sodium systems to measure the chemical activity of carbon. The design of the meter is not fully evolved; engineering refinements are yet to be made. The electrochemical carbon meter has been used to measure the equilibrium chemical activity of carbon in a stainless steel-sodium system. Similar measurements can be made on systems containing carbide nuclear fuels in contact with sodium. The use of the meter to measure the solubility of carbon in sodium has also been demonstrated. When a solubility function for carbon in a sodium system is defined, the electrochemical carbon meter can be used to determine the concentration of carbon in addition to the thermodynamic chemical activity of carbon.

With the information gained about the equilibrium chemical activities of carbon in stainless steel sodium systems and the solubility of carbon in sodium, the meter can be used to monitor the degree of carburizing or decarburizing conditions in the system by using the type of plot shown in Fig. (8). This was developed for 650°C from the results reported above. The left ordinate of Fig. (8) shows the concentration of carbon in sodium in ppm on a log scale, whereas the right ordinate shows the corresponding activities of carbon in Na at 650° as C/C_0 . These results were calculated from equations (1), (2) and the solubility measurements at 650°C. Thus, from a measurement of the emf of

the carbon meter we know whether the sodium will carburize or decarburize the stainless steel. The buffer potential for carbon in a type 347 SS system at 650°C is 52 mV which is shown as the boundary between the shaded and unshaded regions of Fig. (8). Carbon meter emfs below 52 mV indicate the presence of a driving force for carburization, whereas values above 52 mV indicate a driving force for decarburization. The electrochemical carbon meter can be an invaluable tool in studies of the kinetics of carbon transfer in sodium systems since it measures the thermodynamic driving force for carburization/decarburization processes. The electrochemical carbon meter can also be used to determine the relation between carbon and impurities, such as oxygen in sodium and if carbon plays a role in the corrosion of stainless or other alloy systems anticipated for use in the LMFBR.

In other fields, these meters should find general use in determining the carbon activities in materials.

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TABLE I

Effect of Oxygen on the Solubility
of Carbon in Sodium
(650°C)

Oxygen concentration, ppm	Solubility of carbon, ppm	Average ppm
<1	22	20
<1	17	
<1	17	
<1	21	
<1	20	
<1	22	
100	33	32
100	31	
240	24	25
240	26	
240	26	

FIGURE CAPTIONS

1. Detailed schematic diagram of an electrochemical carbon meter.
2. A dimensioned photograph of the current version of the electrochemical carbon meter.
3. The emf vs temperature data obtained from a carbonate and carbide carbon meter in the same 347 SS vessel.
4. The emf vs temperature data obtained from a carbonate filled carbon meter with a 10 mil wall iron cup after very long equilibration times.
5. The emf vs temperature data obtained from a carbon meter filled with carbide electrolyte before and after two successive additions of Na_2C_2 to sodium contained in a 347 SS vessel.
6. Response of a carbon meter containing carbonate electrolyte upon addition of carburized iron to sodium contained in a 347 SS vessel at 600°, 650° and 685°C.
7. The solubility of carbon in sodium as determined with an electrochemical carbon meter containing carbonate electrolyte.
8. Calibration curve for a carbonate electrochemical carbon meter which can be used to determine carburizing or decarburizing conditions, the concentration of carbon and the chemical activity of carbon in sodium.

FIG. 1

FIG. 2

FIG. 3

FIG 4

FIG. 5

FIG. 6

FIG. 7

CALIBRATION CURVE FOR
ELECTROCHEMICAL CARBON METER
 $\text{Na}_2\text{CO}_3\text{-Li}_2\text{CO}_3$ ELECTROLYTE
AT LOW OXYGEN (<1 ppm)

650 °C

$C_0 = 20$ ppm *

* MEASURED IN A NICKEL VESSEL WITH A CARBON
METER HAVING A 0.005" IRON MEMBRANE,
ASSUMING IDEAL SOLUTION.

$$E (\text{mV}) = 46.5 \log \frac{20}{C}$$

FIG. 8

APPENDIX

General Response of the Meter to Carbonaceous Reagents and Calcium Metal

In order to demonstrate in a more general and unequivocal way that the carbon meter responds to changes in the chemical activity of a variety carbon species in the sodium, a series of experiments were performed in which various carbonaceous reagents, such as Na_2C_2 , CO , C_2N_2 and C_2H_2 were added to the sodium and the emf of the meter observed during and after the addition. These experiments were performed in type 347 SS vessels containing a carbon meter filled either with a carbide or a carbonate electrolyte. Additions of the above reagents were made as described below after the emf of the meter reached a stable value. The results obtained using carbide and carbonate electrolyte systems are listed separately below. All the results for a given electrolyte were obtained in the same vessel in the order listed. In general, upon addition of various amounts of the above reagents the emf decreases and in some cases could be made zero, but when the reagent was consumed the emf returns to the starting value in periods of time which ranged from a few hours to several days. Thus, the equilibrium emf can be disturbed by additions of carbonaceous reagents, but only for transient periods, after which it returns to the initial value observed prior to the addition of the reagent.

When a carbon meter was inserted into a vessel which contained a nickel liner and with no stainless steel of any kind in contact with the sodium, the emf at 650°C was within $1/2$ mV of

zero and stable. This suggests that the chemical activity of carbon in the sodium contained in this nickel vessel was close to unity. When a piece of 1/4" 347 SS rod 4" long, was introduced into the sodium at 650°C the emf increased in the expected direction and leveled off at -30 mV in 24 hours. An additional gettering with a new 347 SS rod in the same manner caused the emf to increase to -38 mV in the same time period.

Response to Specific Reagents Carbonate Electrolyte

Sodium Carbide

The equilibrium emf of the meter was established by equilibration for several days at 685°C. Temperature cycling of the vessel from 685°C to room temperature and back to 685°C established that the equilibrium emf is achieved in less than an hour after the vessel reaches temperature. Na_2C_2 was prepared in the vessel at 120°C by reaction of the sodium with C_2H_2 , using a procedure described previously which does not allow the formation of NaH .^{1*} Addition of approximately 600 ppm carbon results in transient decreases in the emf to approximately zero, followed by and increases to the original equilibrium emf in periods from several hours to several days, depending on the amount of carbon previously added to the system.

Cyanogen

C_2N_2 gas was added to the sodium by injecting it into a helium stream which passed over the surface of the sodium. Decreases in emf were observed in periods from 5-10 minutes after the C_2N_2

was added to the helium flow over the sodium. The emf recovered to the initial value several hours after the addition. The reaction between C_2N_2 and sodium at $680^\circ C$ is highly exothermic and did effect the temperature of the system during the addition. The emf of the meter could not be forced to zero by addition of a relatively large amount of C_2N_2 .

Carbon Monoxide

Addition of CO to the gas phase over the sodium caused large and rapid decreases in emf in periods from 5-10 minutes after the gas is injected into the helium flow over the sodium. In one experiment the emf was forced to zero by large additions of CO and showed no tendency to return to the starting value.

In one experiment, a sufficient quantity of CO was added until the emf of the meter was close to zero; in a 24 hour period it showed no tendency to return to the original equilibrium value observed prior to addition of the CO. Approximately 150 g of 304 SS powder were added at $120^\circ C$ and when the vessel was heated to $685^\circ C$ the emf began to increase. After three days the emf returned to the original starting value observed prior to addition of the CO.

Acetylene

Large decreases in emf (30 mV) were observed shortly after C_2H_2 was added in small amounts (10-15%) to the helium gas phase over the sodium. This result was obviously complicated by the presence of hydrogen (see below).

Hydrogen

The emf of the meter decreases when hydrogen gas at 1 atm

pressure is passed over the surface of the sodium. The nature of the hydrogen interactions is complex and it is not clear what effects are attributable to reaction between hydrogen and the sodium, or if the chemistry of the electrolyte is effected by the hydrogen. In one experiment, where both the sodium and the reference electrode were in contact with 1 atm pressure of hydrogen, the emf was zero, but recovered to the expected value when both systems were flushed with helium to remove the hydrogen.

Oxygen

Addition of oxygen to the gas phase over the sodium when the oxygen content of the sodium was probably high (close to saturation) had no effect on the emf of the meter. Subsequent addition of similar amounts of oxygen as CO resulted in a decrease in the emf of the meter.

Carbide Electrolyte

Sodium Carbide

The procedure was similar to that described above for the carbonate electrolyte and the results were the same.

Calcium

When calcium was added to the sodium we have observed increases in emf, and in one experiment observed a decrease when it was first added to the vessel. Except in this case where the emf decreased from +100 mV to +50 mV, the emf increased when the calcium was added but always returned to the initial starting value in three subsequent additions. Normally, we expect calcium to be a

getter for carbon and cause the emf to increase. We believe that the decrease in emf observed reflects the complex chemistry of these systems and the possibility of carbon interactions with impurities such as oxygen.

Hydrogen

The presence of hydrogen causes degradation of the carbide electrolyte.

We have observed carbide electrolyte to deteriorate instantly and completely in meters exposed to high activities of hydrogen (1 atm pressure) external to the iron membrane.