ABSTRACT

Liquid metal-cooled fast breeder nuclear reactors (LMFBRs) employ sodium as the coolant and steels of different grades (austenitic and ferritic) as the structural materials. The presence of an optimum amount of interstitial carbon in these structural materials is essential for maintaining good mechanical properties during the life of the reactor. Liquid sodium, which has good solubility for carbon at high temperatures (~800 K, which is normally encountered in the reactor systems), is known to function as a medium for carbon transport. Hence carburization or decarburization of the structural materials occurs, depending on the local difference in the thermodynamic activity of carbon, and this impair their mechanical integrity. An in-depth understanding of the chemistry of carbon in sodium and steel is required in order to predict the direction and extent of this phenomenon.

The total carbon content in sodium was determined by distillation and combustion followed by estimation of the resultant carbon dioxide by a low-pressure method. The carbonate content in sodium was determined by dissolving the sodium sample in water, acidifying the solution and estimating the evolving carbon dioxide by a gas chromatograph. The results showed that chemical analysis is not an adequate procedure for evaluating the thermodynamic activity of carbon in sodium.

Several methods were employed to measure the carbon activity in sodium. The carbon activity in a sodium loop was measured using a Harwell carbon meter and by the foil equilibra-
tion method. A new electrochemical meter was developed based on electrode concentration cell for measuring the carbon activity in sodium. The meter response was shown to be in agreement with expected values, by equilibrating nickel foils in sodium and comparing the carbon activity from the measured carbon concentration in nickel with those calculated from the emf of the meter (by employing Nernst equation). The two sets of carbon activity values showed very good agreement.

Chemical analysis for carbon and the direct methods for measuring carbon activity in sodium indicated that a major part of carbon exist as undissolved suspension (inactive carbon). A gas equilibration method was employed to selectively estimate the dissolved fraction (active carbon). In this method, hydrogen was allowed to react with the active carbon and the resulting total amount of methane was estimated. There was agreement between the carbon that get converted to active form and carbonate content in purified sodium. It was found that sodium carbonate undergoes decomposition in high temperature sodium (>800 K) resulting in the release of active carbon. The carbon activity in sodium was calculated from the composition of methane and hydrogen at equilibrium.

Carbon activity-composition relationship in steels is required for calculating the carbon activities in the structural components in a reactor system. A new method was developed for the measurement of carbon activity in 18/8 austenitic steels. Commercial steel (type 304 S.S) foils were exposed to high temperature liquid sodium, contained in an alumina crucible, until carbon transfer equilibrium was attained. The equilibrium carbon
activity was measured using the carbon meter dipping into the same sodium. The experiments were conducted in the temperature range of 860-960 K. Based on the present results, a modified expression is proposed relating carbon activity with the composition of the steel. The above temperature range is closer to that encountered in a fast reactor than those employed in other measurements reported in literature.

The free energy of formation of Cr$_{23}$C$_6$ reported by different workers was found to have wide variation. This is an important data for understanding the carbide equilibrium in steel. Hence it was remeasured using the electrochemical carbon meter.

Among the constituent elements of austenitic steels, chromium is known to form the most stable carbides. Upto a carbon concentration of ~1.1 wt%, the formation of Cr$_{23}$C$_6$ is expected so that the carbon potential in commercial stainless steel (carbon content - 0.08 wt% max.) should correspond to that of Cr/Cr$_{23}$C$_6$ equilibrium. However, the measured values are much higher, which is attributed to the partial replacement of chromium by iron in Cr$_{23}$C$_6$. In the present study, the carbide phase present in steel (type 304 S.S) of known carbon activity (determined by the electrochemical method) was extracted by preferentially dissolving the austenite phase in acid medium at a potential of 1.5 V, with the specimen as the anode. The residue obtained was characterised by XRD and chemical analysis. The composition was found to be Fe$_4$Cr$_{19}$C$_6$ and the XRD patterns corresponded to those of Cr$_{23}$C$_6$. The residue was also found to contain significant amounts of CrN and Cr$_2$N. The excess free
energy of formation ($G^{\text{xs}}$) of the mixed carbide ($\text{Fe}_x\text{Cr}_{23-x}\text{C}_6$) was calculated by treating it as a regular solution of $\text{Fe}_{23}\text{C}_6$ and $\text{Cr}_{23}\text{C}_6$. From this value of $G^{\text{xs}}$ the free energy of formation of $\text{Fe}_x\text{Cr}_{23-x}\text{C}_6$ was evaluated at different values of $x$ ($x=2$ to $7$) and temperatures ($850-1000$ K). This model explains the observed composition of the most stable carbide phase that precipitates at the grain boundary and the decrease in carbon potential in the steel on increasing temperature.

The carbon transport in a sodium loop consisting of both ferritic and austenitic steels is principally governed by the temperature of various zones. From the carbon activity-concentration relationships of these alloys and sodium, it was concluded that in a typical fast breeder reactor the high temperature austenitic steel components would undergo decarburization and the low temperature region would undergo carburization. The ferritic steel of the Fe-2 1/4Cr-1Mo type will undergo only decarburization whereas the direction of carbon transport in Fe-9Cr-1Mo type is decided by the carbon activity in sodium with which this alloy is in contact.

The present studies have shed new light on carbon equilibrium in sodium. A modified relation obtained between carbon activity and composition of 18/8 steel is considered more applicable for calculating the carbon activity in reactor components than those used earlier. A detailed understanding of the chemistry of carbide equilibrium in steels is also rendered possible by this study.