ABSTRACT

Liquid sodium is used as the heat transfer medium in fast breeder reactors and is a candidate working fluid in high temperature heat pipes. While austenitic stainless steels and ferritic steels are used as structural materials in fast breeder reactors, hastelloys, molybdenum alloys, austenitic stainless steels and niobium alloys are considered as structural materials for sodium filled heat pipes. In these systems, transfer of interstitial alloying elements and corrosion of substitutional alloying elements of structural materials occur. Dissolved oxygen impurity in sodium enhances the corrosion processes. This is due to the formation of ternary oxygen compounds and their participation in the rate determining steps of the corrosion reactions. A knowledge of the thermodynamics of ternary Na-M-O systems (M = alloying elements of structural materials) is essential for an understanding of the basic processes of these reactions. In this work, studies on Na-Cr-O and Na-Mo-O systems are carried out so as to delineate the conditions necessary for the formation of the ternary oxygen compounds in these ternary systems.

NaCrO$_2$(s) is the compound that is generally encountered in sodium systems when chromium containing steels are used as structural materials. Threshold oxygen concentrations for the formation of this compound in sodium loops predicted from its Gibbs energy of formation data have been found to be much lower than the values that are actually observed. In the present work,
direct measurement of oxygen potentials in sodium containing Cr(s) and NaCrO₂(s) were made using solid-oxide electrolyte galvanic cells. The equilibrium oxygen potentials can be represented as,

\[ \Delta G_{O_2} = -800847 + 147.85 T \text{ (±1.35 kJ) J/mol O}_2 \text{ (657-825K)} \]

Equilibrium sodium pressures over NaCrO₂(s)-Cr(s)-Cr₂O₃(s) phase field were measured by Knudsen cell mass spectrometric technique. The Gibbs energy of formation of NaCrO₂(s) derived from the sodium pressures can be expressed as follows:

\[ \Delta G_{f,T}^{c} <\text{NaCrO}_2> = -870773 + 193.171 T \text{ (±1.3 kJ) J/mol} \text{ (825-1025K)} \]

The threshold oxygen concentrations calculated from the oxygen potentials measured directly in sodium yield values which are higher by an order of magnitude than those derived from the Gibbs energy data. This has been experimentally proved to be due to the interaction of the carbon impurity with chromium that results in the establishment of the following equilibrium.

\[ \text{CrC}_x + 2[O]_{\text{Na}} + \text{Na}(1) \rightleftharpoons \text{NaCrO}_2(s) + x[\text{C}]_{\text{Na}} \]

In this case, CrCₓ has been found to be Cr₃C₂(s). A phase stability diagram for Na-Cr-O-C system has been constructed to explain this behaviour. The reported observations in operating sodium loops could also be explained on this basis as chromium-rich carbides have always been detected along with NaCrO₂(s).
The literature data on Na-Mo-O system is not self consistent. Observations indicating both the stability of ternary oxygen compounds of molybdenum in liquid sodium as well as indicating their instability are reported. In this work, a critical review of these reported data is made first. Experiments involving in-sodium equilibrations, pseudo-isopiestic equilibra-
tions and heating of Na₂O(s) and Mo(s) under high vacumm were conducted. These experiments clearly indicated that Na₄MoO₅(s) would be the phase that would be stable in liquid sodium at 923K. At lower temperatures, Na₂O(s) would be the stable phase in sodium containing molybdenum metal. The invariant temperature at which Na₂O(s), Mo(s) and Na₄MoO₅(s) coexist with liquid sodium has been determined as 681.1K by carrying out oxygen potential measurements in liquid sodium to which molybdenum bearing compounds were added. Solid oxide-electrolyte galvanic cells were employed for this purpose. From the oxygen potentials measured above this temperature, the Gibbs energy of formation of Na₄MoO₅(s) could be deduced as:

\[
\Delta G_f^0,T_{Na₄MoO₅} = -1907223 + 436.13 T \ (\pm 5.3 \text{ kJ/mol})
\]

(681-773K)

Equilibration of oxidised molybdenum foils in a bench-
top sodium loop with oxygen cocentration as high as 44 ppm did not yield any ternary oxygen compound, which is in accordance with the above observations. Only carbides of molybdenum were observed. A phase stability diagram of Na-Mo-O-C system has been constructed to explain this behaviour.
Polymolybdates of sodium were reduced under a flow of hydrogen gas and various coexisting phase mixtures were obtained. These phase mixtures were compacted together and heated for prolonged periods for confirming their coexistence. Based on these results isothermal sections of the phase diagram of the Na-Mo-O system are reported in the temperature range of 673 to 923 K.

In the light of the above experimental results and reported data on other ternary oxygen compounds of relevance in sodium systems, a comparison of the threshold oxygen concentrations for their appearance is made. Influences of other dissolved non-metallic impurities such as hydrogen, carbon and nitrogen on these threshold oxygen concentrations are analysed in a consolidated manner. These analyses revealed that carbon and to an extent hydrogen would influence the threshold oxygen concentrations for the formation of stable ternary oxygen compounds in LMFBR sodium circuits and heat pipes.