ABSTRACT

Literature survey indicated that when metals are in contact with aqueous solution three types of behavior are known (i) immunity when the metal is thermodynamically stable against oxidation (ii) corrosion when the metal continuously undergoes oxidation because the oxidation product is soluble in the solution and (iii) passivation when the oxide or hydroxide is insoluble and thus forms a more or less protecting layer. The behavior of the elements depends on the potential of the metal in solution and the pH of the solution. The stability at potentials in the range where hydrogen is evolved and oxidized in alkaline solutions is also important. Except palladium, metals that have strong affinity for hydrogen also have stronger affinity for oxygen. These metals when in contact with aqueous solution form very stable oxides and hydroxides that may be soluble or insoluble in alkaline solution. The transition metals manganese and nickel form such couples. The transition metal manganese forms oxides that are soluble in alkaline solutions as manganite ions, thus leading to continuous corrosion of the alloy. Nickel on the other hand is immune to alkaline corrosion. It was hence, proposed to study the effect of alloying this couple with other elements.

Hydrogen reacts with elements from most groups of the periodic system to form hydrides. The metallic hydrides formed by transition and rare earth or lanthanide groups of metals are capable of hydrogen storage. Research and development on intermetallic compounds of the type AB$_2$ and AB$_3$ that absorb and release large quantities of hydrogen is gaining momentum. These compounds may be used as negative electrodes to replace cadmium electrodes in the nickel-cadmium batteries. Recently titanium alloy based metal hydrides have been of
great interest because of their high storage capacity. Research is devoted to the
design of TiMn₂ based alloys that can yield high hydrogen storage capacity.

Literature survey indicated that all the alloys studied for
electrochemical hydrogen storage in intermetallic alloys have the element nickel
as an important constituent in the alloy due to its resistance towards oxidation and
its catalytic property to oxidize hydrogen despite its inability to store hydrogen. In
order to achieve high capacity it was proposed to select an alloy with high
hydrogen storage capacity and impart the desired characteristic such as catalytic
properties and corrosion resistance by suitable substitution on its constituent
elements. According to Brewer-Engel Valence bond theory synergistic effects
might be expected when transition metal having internally paired d-electrons are
alloyed with transition metal having vacant ‘d’ orbitals.

Thus, TiMn₂ alloy was selected and it was proposed to study the effect
of various elements by substitution of titanium and manganese with other
elements. The objective of the study is to achieve high hydrogen storage capacity
for the alloy with high stability in alkaline solution.

The objectives of the present research work are:

i) To study the effect of nickel substitution on high storage capacity
TiMn₂ alloy in KOH solutions. The series of alloys TiMn₂,
TiMn₁₋₀.₂Ni₀.₂, TiMn₁₋₀.₄Ni₀.₄ and TiMn₁₋₀.₅Ni₀.₅ were prepared to
study their electrochemical properties.
ii) Based on the literature survey of available methods to protect the alloy from corrosion, it was proposed to study the effect of copper encapsulation on the electrochemical properties of TiMn$_2$ alloy.

iii) To study the effect of carbon black (Vulcan XC72) as an additive for TiMn$_2$ alloy.

iv) Based on the literature methods to activate the alloys to achieve high capacity, activation of the alloy powder in H$_2$O$_2$, HF solutions was carried out and its effect on the electrochemical properties of TiMn$_{1.6}$Ni$_{0.4}$ were studied.

v) Zirconium is an element that was reported to provide good hydrogen storage and is known to form passive oxide. It was, hence, proposed to study the effect zirconium in a high hydrogen storage capacity TiMn$_2$ alloy. The alloys studied include Ti$_{0.9}$Zr$_{0.1}$Mn$_{1.6}$Ni$_{0.4}$ and Ti$_{0.8}$Zr$_{0.2}$Mn$_{1.6}$Ni$_{0.4}$.

vi) It was proposed to study the effect of another element, which forms soluble oxide with zirconium (that forms passive oxide), Viz., vanadium instead of nickel. Thus the alloy Ti$_{0.9}$Zr$_{0.1}$Mn$_{1.6}$V$_{0.4}$ was studied for its electrochemical properties.

Electrochemical studies such as charge-discharge capability, high current discharge capability, cycling ability, cyclic voltammetric studies, controlled potential discharge studies, dc polarization studies and ac impedance studies were carried out on all these alloy electrodes. The study provided a better understanding of the effect of the alloying element such as nickel, zirconium and vanadium on TiMn$_2$ alloys. It was found that nickel improved the electrochemical properties of the alloy. It was found to play an important role in improving the
corrosion characteristics of the alloy and overall performance of the alloy electrode. It was found that zirconium and vanadium addition did not improve the electrochemical behavior of TiMn$_2$ alloys. Copper encapsulation of the alloy was found to improve the electrochemical characteristics of the alloy. It was also found that activation of the alloy leads to better electrochemical properties. However, as produced alloy electrode was found to have better durability than the activated alloy electrode.

These studies on TiMn$_2$ alloys indicated that the performance of the electrode could be improved by proper choice of the alloying element and by identification of suitable composition. The results of this investigation are of value in providing a better understanding on (i) the influence of alloying elements such as zirconium, nickel and vanadium (ii) on the effect of encapsulation on the properties of the alloy and (iii) effects of activation of the alloy on durability of the electrode.