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PLASMA SPRAYED RANEY NICKEL COATINGS FOR HYDROGEN EVOLUTION REACTIONS IN ALKALINE SOLUTIONS

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Raney nickel coatings of various Ni/Al ratios on stainless steel substrate were prepared by plasma spray technique. Hydrogen evolution reaction was studied on them. It was found that Raney nickel coating prepared from the composition Ni:Al = 65:35 (by wt.) exhibited a lower overvoltage of 70-80mV at $3kA.m^{-2}$ current density in 30 wt % NaOH at 353K. This composition had good stability during prolonged operations.

Key words: Plasma sparayed Raney nickel, hydrogen evolution reaction

INTRODUCTION

In view of the increased scarcity of industrial fuel supplies and phenomenal increase in energy costs, there has been a flurry of research activity to find means to reduce the electrolytic power consumption in electrochemical processes. The hydrogen evolution reaction requires very high overvoltage on most conventional electrodes such as mild steel, stainless steel, and nickel in alkaline solutions. Raney nickel catalyst is known to reduce the hydrogen overvoltage considerably [1]. Several attempts have been made to produce Raney nickel by electroplating [2-4] techniques or dipping the substrate in molten Raney nickel alloy [5,6] or sintering of alloy powder at high temperature [7]. Recently Choquette and others [8,9] prepared Raney nickel coating by uniformly agitating the electroplating solution with a special apparatus.

In the present study, Raney nickel coatings with different Ni:Al ratio have been prepared by plasma spray technique. The aluminium in the above coating was leached out in hot NaOH to obtain Raney nickel. Their behaviour for hydrogen evolution reaction in 30 wt% NaOH was studied at 353K.

EXPERIMENTAL

Preparation of electrodes

Plasma spraying

Plasma is often considered the fourth state of matter after solid, liquid and gas. This extremely hot substance consists of free electrons, positive ions, atoms and molecules. When a gas passes through an electric arc, the gas loses one of its electrons and becomes extremely hot plasma. Temperature can reach around 17000K. As the plasma leaves the spray gun, powdered material is introduced into the stream in precisely controlled amounts. The material caught up in the plasma stream becomes molten and is projected against the surface being coated when an individual particle impacts against the surface, thermal and mechanical energies are transferred to the substance producing forces which favour interatomic bonding. Under these circumstances, plastic deformation of the particle and local surface area occur. The greater the deformation of the particle upon impact, the greater the possibility of interatomic bonding.

Raney nickel electrodes

Nickel and aluminium alloy powders of (particle size 10-12μm) of nickel-aluminium weight ratios 50/50, 65/35, 72/28 and 95/5 were used. The alloy powders were plasma sprayed on sand blasted stainless steel (SS 316) sheets (of size $1 \times 8 \times 0.1$ cm) using plasma spray equipment (Plasma dyne, USA,) at a current rating of 800 A and argon pressure of 3.5 $kgf.cm^{-2}$ and powder gas pressure of 2.75 kgf. cm^{-2} at hopper setting of 4.1. Then aluminium was leached out from the above coatings by dipping in 30% NaOH solution at 353K for 5 hours to get Raney nickel electrodes. The electrodes were kept in a desiccator.

Performance tests

The electrodes were tested for hydrogen evolution reaction (HER) using PAR 273 potentiostat/galvanostat with current interruption in 30 wt% NaOH solutions at 353K. The electrode potentials were measured and reported with respect to $Hg/HgO,OH^{-}$(30 wt% NaOH) electrode. The life evaluation of coatings was carried out in 30 wt% NaOH solution, at 353K, and 3 $kA.m^{-2}$ current density.

RESULTS AND DISCUSSION

The E-log i behaviour of pure nickel and Raney nickel alloy prepared by plasma spraying of various wt. ratios of Ni and Al on stainless substrates is shown in Fig. 1. Among the studied compositions, Ni-Al alloy of 65:35 wt. ratio is having good electrocatalytic properties of having very low overvoltage of

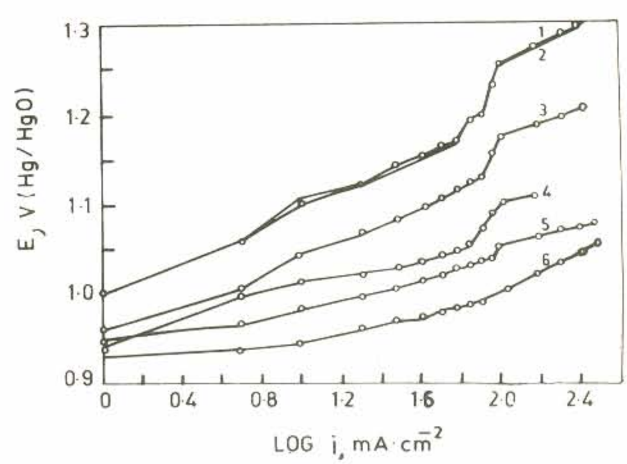

Fig. 1: i-E behaviour of various cathodes in 30 wt% NaOH solution for HER at 353K
(1) Pure nickel (2) Stainless steel (3) 95/5 Ni/Al (4) 72/28 Ni/Al (5) 50/50 Ni/Al and (6) 65/35 Ni/Al

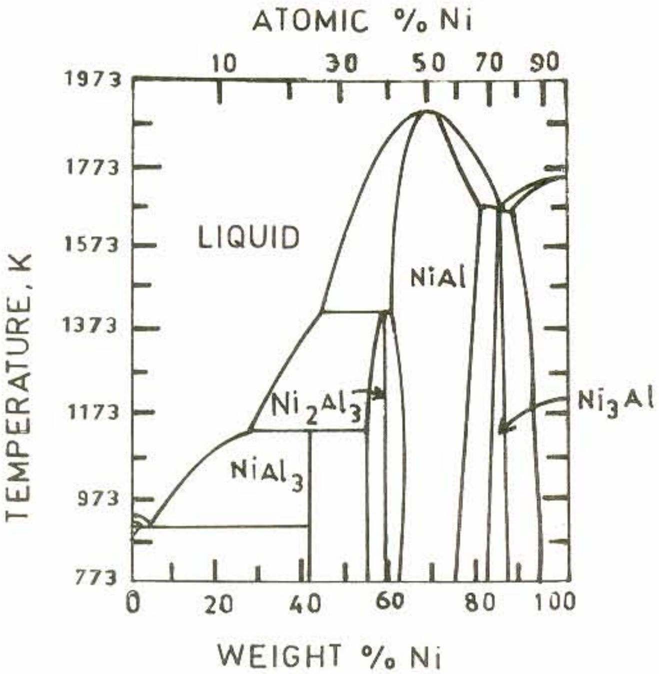

Fig. 2: Nickel-aluminium phase diagram

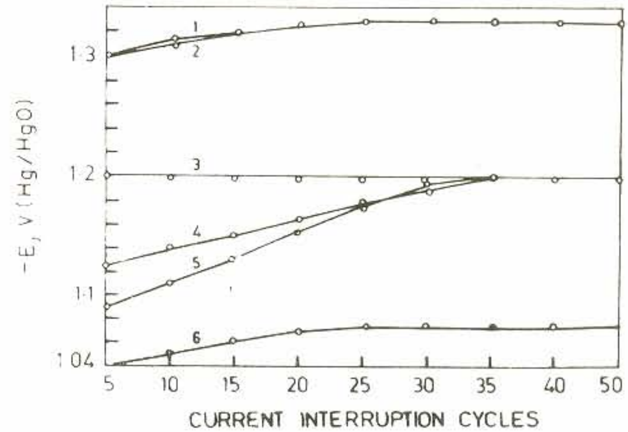

Fig. 3: Effect of current interruptions on the potential of various cathodes in 30 wt% NaOH solution for HER at 353K and current density of 3 $kA.m^{-2}$. (1) to (6) same as given in Fig. 1.

70mV at a current density of 3 $kA.m^{-2}$ and a Tafel slope of 40-50mV.decade^{-1}. The catalytic properties of all the four types of Raney nickel coatings are good compared to pure nickel. It is known that preparation of Raney nickel catalysts results in more than one crystalline structure namely β phase ($NiAl_3$) and γ phase (Ni_2Al_3) precursor alloys. The Raney nickel catalyst derived from β phase ($NiAl_3$) after leaching out Al from alloy coating is known [6] to have good catalytic properties for hydrogen evolution reactions

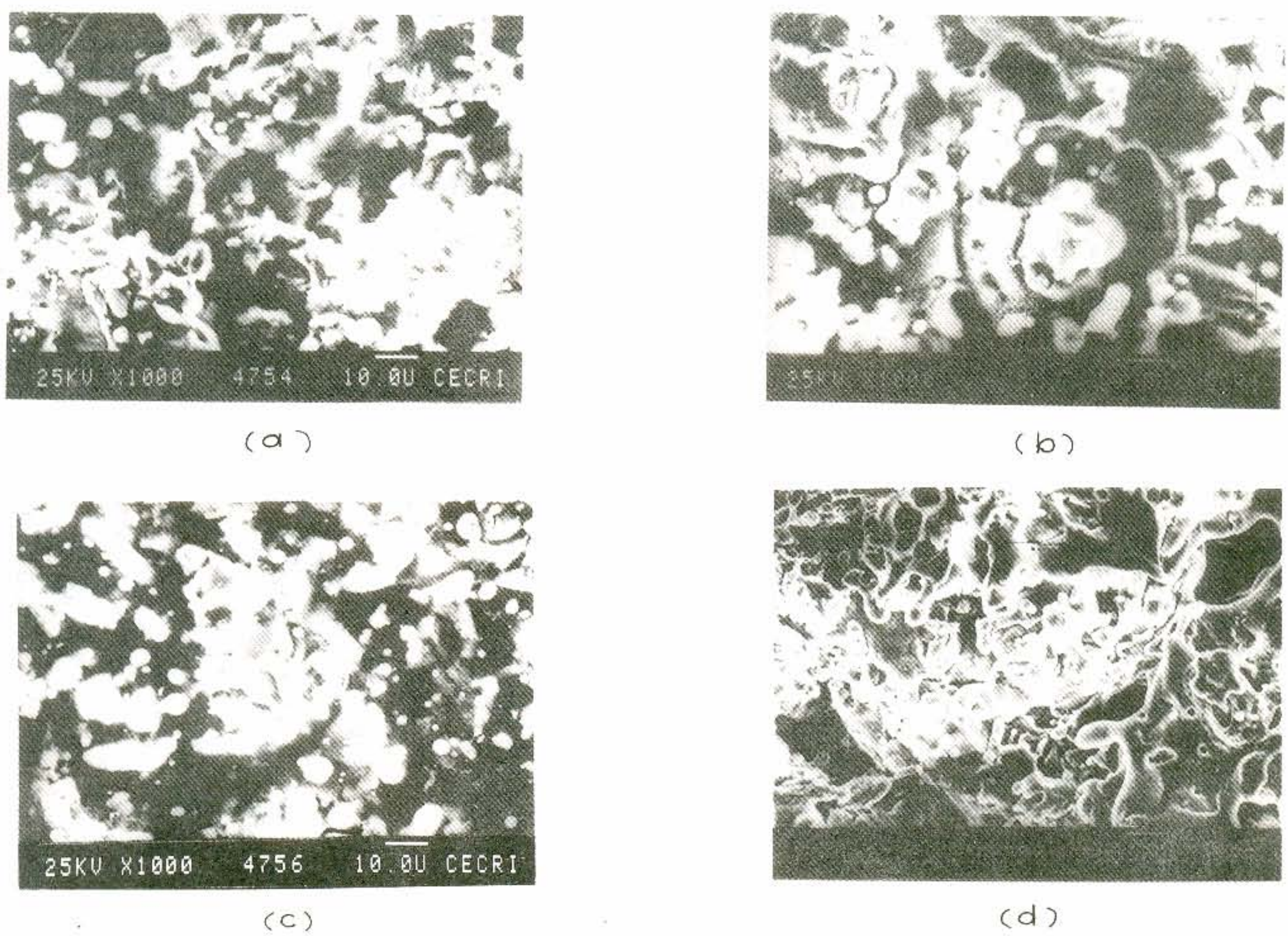

Fig. 4: Scanning electron micrographs of plasma sprayed alloy coatings (magnification 1000 X). (a) 50/50 Ni/Al (b) 65/35 Ni/Al (c) 72/28 Ni/Al (d) 95/5 Ni/Al

in alkaline solutions.

Though Ni:Al (95:5) is having higher potential of -1196mV than to that of Ni:Al (65:35) which has -1034mV at 3 $kA.m^{-2}$, yet its voltage performance is good compared to pure nickel. This may be due to increased surface area obtained by plasma spray method and subsequent leaching of the 5% Al from coating, leading to the formation of localised nickel sites derived from nickel - rich (Ni_3Al) phase precursor (Fig. 2). The nickel rich alloy 50/50 has low overvoltage performance compared to alloys of 72/28 and 95/5; but it experiences a higher overvoltage when compared to 65/35 alloy which shows very low overvoltage for HER among the alloys studied. The overvoltage performance of all the coatings at 3 $kA.m^{-2}$ current density is illustrated in Fig. 3.

Raney nickel (65/35) proved to be the best combination among the electrodes studied, as the overvoltage is very low of the order of 70mV at a current density of 3 $kA.m^{-2}$ (Fig. 1). The Ni:Al alloy electrodes of composition 65/35 and 50/50 were tested for stability evaluation with current interruption for 30 secs. for every one hour. From Fig. 3, it is seen that after every 5 interruptions, the overvoltage rises by 10mV on 65/35, 20-30mV on 50/50, 10-15mV on 72/28 and no rise on 95/5 electrodes. Except 65/35, all other alloy electrodes have reached -1200mV. The potential of the electrode 65/35 was stable at -1075mV beyond which there was no rise during interruptions. The above behaviour can be explained as follows.

The nickel-aluminium phase diagram (Fig. 2) is useful to know the type of phases that are formed at different alloy compositions and also to interpret the electrocatalytic behaviour of the plasma sprayed Raney nickel coatings. It can be observed that three intermetallic compounds form over a range of compositions, starting with nickel rich phase, they are: Ni_3Al, NiAl, and Ni_2Al_3 [10]. A fourth phase called a "line" compound is $NiAl_3$. In the present study, the alloy 50/50 has β ($NiAl_3$) and γ (Ni_2Al_3) phases, only 65/35 alloy has γ (Ni_2Al_3) and NiAl phases; 72/28 alloy has the formation of only NiAl phase and 95/5 has Ni_3Al phase alone. It is known that NiAl alloy exhibits very low solubility in hot NaOH [10]. The 65/35 electrode has both nickel and NiAl sites and fortuitously this turned out to be very beneficial. This gave rather soft, leached, very active Raney nickel a significant matrix lattice support to form a fairly solid, abrasion resistant coating. But other electrodes either have nickel or NiAl sites and hence the observed performance.

The Scanning Electron micrographs of the allloys are evident for the presence of two phases in 50:50 ; 65:35 and 72:28 alloys and are shown in Figs. 4.a, 4.b and 4.c respectively. The presence of single phase in 95:5 alloy is also confirmed by SEM (Fig. 4.d).

CONCLUSIONS

The Raney nickel alloys were prepared by plasma spraying of nickel: aluminium powders. Among the various nickel-aluminium alloys studied, 65:35 alloy is shown to have low and constant overvoltage of 70-80mV at 3 $kA.m^{-2}$ and high stability during prolonged operations with current reversals for hydrogen evolution reaction in alkaline solution.

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