Electroless Nickel Coatings on Copper Electrodes For Wear - and Corrosion - Resistance

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THE paper reports the use of electroless nickel coatings on copper electrodes used in MHD power generation programme for protection against erosive wear and corrosion due to fused alkalies. The electrodes were coated from an acidic bath (pH 4.5) operating at temperatures around 75°C using sodium hypophosphite as a reducing agent. These Ni-P alloy coatings were bright, pore-free and non-magnetic having uniform thickness (deposition rate 7–8 microns/hr) The adhesion of the coatings to copper substrate was excellent, bond strengths being as high as 1050 Kg/cm^2 in as-plated condition and over 1400 Kg/cm^2 for coatings vaccum baked at 240°C for 4 hrs. The microhardness of the coatings was seen to increase on vacuum annealing at elevated temperatures ; the value being 800-850 Kg/cm^2 for coating vacuum annealed at 400°C for half-an-hour as compared to 500–550 Kg/cm^2 for as-plated coating. This increase in microhardness is because of precipitation hardening of nickel due to precipitated phosphides, Ni_3P.

THE electrode module of the test channel for Magneto Hydro Dynamic (M.H.D.) power generation programme uses copper electrodes, for both anode and cathode. These copper electrodes will have to be in direct contact with high speed plasma (velocity 0.5 to 0.8 Mach number) containing seed materials, alkali carbonate. Though these copper electrodes are water-cooled the temperature at the tip of the electrode in contact with plasma is expected to be around 250°C, and the plasma to be used is a natural gas type having oxygen enrichment of over 50%. It is thus very essential to give a suitable coating to these electrodes, which should have high resistance to erosive wear as well as to high temperature oxidation. In addition, the coating should be corrosion-resistant to fused alkalies. This requirement certainly warrants the use of nickel coatings. But electrode geometry is very complex and it will be preferable if the coating is non-magnetic. Electroless nickel coatings from a hypophosphite bath would be ideally suited for the purpose. It is well known that electroless plating process gives uniform, pore-free coating irrespective of any shape or size of the object. The coatings from hypophosphite baths are essentially Ni-P coatings, phosphorous being present as super-saturated solid solution in nickel[1-3]. The very fine poly crystalline solid solution bordering as amorphous or liquid (glass) like metastable structure of these coatings provides the structure required for non-magnetic behaviour[4-6]. The present work deals with the electroless deposition of Ni-P coatings on the copper electrodes using a hypophosphite bath.

EXPERIMENTAL

The Bath : It has been reported in literature[5-6] that deposits from ammoniacal baths tend to be less protective than those produced from acidic baths. The low temperature acidic hypophosphite bath developed in our laboratory as a metallisation technique for direct bonding of electroless nickel to sintered alumina blocks[7], has thus been used. The essential feature of the bath are given below :

Source of nickel ions	Nickel chloride
Complexing and buffering agent	Tri-sodium citrate
Reducing agent	Sodium hypophosphite
pH	4.5
Temperature	70–80°C

The bath has good stability and long operating life and gives bright deposits over the entire operating life.

The Deposition : The copper electrodes, after a thorough cleaning cycle were etched in mild etching solution, $FeCl_3$ 5 gms, Ethylalcohol 95 ml, water 96 ml, 2 ml HNO_3 operating at room temperature. The use of strong etchant solution was avoided to protect the brazing joints. Since copper cannot directly receive the reduction of nickel ions on its surface, "galvanic initiation" technique was used to get an initial layer of Ni-P coating. This

coating being autocatalytic allows thicker deposits to be formed. The plating was carried out in a two litre glass beaker heated in an isomantle having a temperature control. The plating solution was periodically made up to maintain more or less constant concentration of nickel ions and reducing agent, which get used up in the process. Copper electrodes were continuously rotated by mechanical means to avoid hydrogen adherance to the electrodes during plating. This also helped in avoiding the concentration gradients in the bath.

Properties evaluation : The properties of the electroless nickel coatings were evaluated by plating test samples, 2.5 mm dia 10 mm thick, fabricated from the same material that has been used for the fabrication of copper electrodes.

Phosphorous content of the coatings was analysed by the "weight difference" method i.e., by analysing the nickel content and computing phosphorous by the difference between total deposit and gravimetrically determined nickel.

Coating thickness was measured by magnetic thickness gage, attractive force type, using mild steel as substrate.

Adhesion of the coatings to the substrate was determined as tensile bond strength by Instron testing machine.

Microhardness of the deposits was measured by Leitz Mini-Load hardness tester, operated at 50 gms load. A minimum of eight indentations were made on the sample, the values reported are the average values.

RESULTS AND DISCUSSIONS

Rate of deposition : The following reactions have been proposed[5,8-10] to account for the electroless deposition of nickel from hypophosphite baths

$$H_2PO_2^- + H_2O \xrightarrow[\text{surface}]{\text{catalytic}} H_2PO_3^- + 2H^+ + H^- \quad \ldots 1$$

$$Ni^{++} + 2H^- \longrightarrow Ni + H_2\uparrow \quad \ldots 2$$

Hydride ions may also react with hydrogen ions, thereby reducing the effiency of hypophosphite utilisation.

$$H^- + H^+ \longrightarrow H_2\uparrow \quad \ldots 3$$

Reactions suggested for codeposition of phosphorous are[5,8-10]

$$3H_2PO_2 \longrightarrow H_2PO_3^- + 2P + H_2O + 2OH^- \quad \ldots 4$$

or

$$H + H_2PO_2^- \longrightarrow P + OH^- + H_2O \quad 5$$

Reactions (4) & (5) clearly suggest that phosphorous content of the deposit will decrease with increase of bath pH, but the rate of deposition would increase as per reaction (1). Since the aim was to get a deposit high in phosphorous content, from both non-magnetic behaviour and high hardness view point, low bath pH was used. It was observed that rate is extremely low, 1-2 microns per hour, at pH's less than 3.5. Above pH 6, sparingly soluble salts are likely to be precipitated. The most suitable pH was observed to be 4.2 to 5.0, the optimum value being at 4.5. A 10% NaOH solution was periodically added to the bath, with agitation, to maintain bath pH at 4.5. At this pH, no nickel phosphite precipitation was observed. The rate of deposition at this pH and at an operating temperature of ~ 75°C, was seen to be 7–8 microns per hour.

As stated earlier, 'galvanic initiation' technique has been used to get an initial layer of Ni-P alloy. In the normal mode of operation, the work piece was touched by a clean aluminium rod for less than 30 seconds for the purpose. It was observed that this time of contacting the work piece with aluminium rod affects the deposition rate, the rate increasing with increase of time of contact. A rate of 12 microns per hour when time of touch was 2 minutes and around 25 microns per hour when time of contact was 10 minutes, was observed. Even at this high rate of deposition, the bath was seen to be quite stable. Touching the work piece by aluminium in the plating bath is a case of 'galvanic couple' in which the work piece i.e. copper electrode is the cathode and aluminium the anode. This operation of making the work piece cathodic is responsible in getting an initial layer of Ni-P alloy coating, which is autocatalytic and so the deposition continues. This also accelerates the deposition rate.

Bath temperature is also one of the most important factors affecting the rate of deposition. The deposition rate increases almost exponentially

with temperature. This also increases the phosphorous content of the deposit ; phosphorous content of the deposits obtained at 80°C being 10.9% and that obtained at 70°C being 9.3%.

Agitation was seen to be very desirable in order to dislodge gas bubbles, replish solution in corners and holes and decrease the concentration gradient of the reactive components.

The deposits were seen to be free from any porosity, as seen under optical microscope using a magnification o 400-600.

Adhesion of the deposits : The adhesion of the electroless Ni-P coating on copper was observed to be quite good ; tensile bond strengths being around 1050 Kg/cm^2 for as-plated coatings. Vacuum baking at 240°C for 4 hours improves adhesion ; the tensile bond strengths being over 1400 Kg/cm^2. Baking is also beneficial in the release of codeposited hydrogen.

Hardness and Wear resistance : Electroless nickel-phosphorous coatings are considerably harder and more wear-resistant than conventional electroplated nickel. In addition, these have excellent galling resistance[6]. It has been reported that wear of electroless coatings is minimum at maximum hardness[3],[6]. Heat treatment has a marked effect on the hardness and wear resistance of electroless nickel coatings. Microhardness of the electroless nickel coatings in the as-deposited condition was seen to be around 500-550 Kg/mm^2. which increased to a value of 600-650 Kg/mm^2 for heat treated coatings at 240°C for 4 hours. After heat-treatment at 400°C for $\frac{1}{2}$ hour, the value was seen to be 800-850 Kg/mm^2. This increase in hardness has been attributed to precipitation hardening ; nickel phosphide, Ni_3P, precipitates causing general hardening of the alloy[1],[6].

The electroless nickel coated copper electrodes were baked in vacuum at 240-400°C for $\frac{1}{2}$ to 4 hours prior to their use in M.H.D. channel. These copper electrodes, after the plating cycle and vacuum baking were subjected to hydrostatic testing to test the brazing joints, the rejection being none.

The performance of these plated copper electrodes has been found to be excellent on actual testing at U.S.S.R., from corrosion, oxidation and erosive wear view point.

CONCLUSION

1. Uniform, pore-free and adherent electroless nickel coating were obtained on copper electrodes from an acidic (pH ~ 4.5) hypophosphite bath operating at temperature (70-80°C).

2. Heat-treatment of the coatings at temperatures 240-400°C for 0.5 to 1.0 hour increases microhardness and tensile bonding. Heat-treated deposits exhibit superior corrosion, oxidation and wear-resistance.

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