Pulsed electrodeposition of nano-crystalline Ni with uniform co-depostion of micron sized diamond particles on annealed copper substrate

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Abstract

Nanocrystalline nickel was deposited on annealed copper substrate of unit surface area (1 cm^2) via pulsed electrodeposition technique using potentiostat (model 263A, Princeton Applied Research, USA) from Watts bath containing nickel sulfate, nickel chloride , boric acid and sodium citrate. Diamond particles of three different dimensions, viz., 1, 3, and 6 micron were added separately (5 g/L) to the watts bath and co-deposited along with nanocrystalline nickel.The temperature was kept constant at 55 °C. The solution was sonicated for 45-60 minutes prior to deposition to disperse the diamond particles uniformly in the bath. Depositions were carried out at different current densities, viz., 50, 100 and 200 mA/ cm^2 for different durations, i.e., 7, 14 and 21 minutes and best results are optimized for 200mA/cm^2 so it is used for all process here .Scanning electron micrographs(SEM) show uniform deposition of microstructure of micron diamond on the surface of copper embedded in the nickel matrix. Elemental mapping confirmed uniform deposition of nickel and diamond with almost no cracks or pits. Mechanical properties of the sample such as, Vicker's hardness increased abruptly after the electrodeposition .Improved microstructural and mechanical properties were found in the case of electrodeposited surfaces containing followed by 3 and 6 micron diamond. The properties were also found better than those processed via stirring the solution during deposition.

Keywords: Annealed copper, Codeposition, Electrodeposition, Nanocrystalline Ni,Scanning electron micrographs

1. INTRODUCTION

In the current work, nanocrystalline Ni-Diamond films were synthesized by pulsed electrodeposition using a watts bath . Depositions were optimized on the current density range of 50-200 mA/cm^2 and 200mA/cm^{2}was best suited to achieve a uniform equiaxed coating with a target of high Ni-Diamond content owing to their superior corrosion resistance and enhanced hardness.

Nowadays, in order to fabricate nanocrystalline metallic films, many deposition techniques are available, such as sputtering, molecular beam epitaxy, vacuum evaporation, sol-gel, thermal spray, etc. But all these methods require high precision process control, which demand higher capital cost and incur huge material waste. But electrodeposition is an established and inexpensive technology among other fabricating processes which is accomplished by fabricating metallic alloys using low-temperature synthesis from aqueous solutions. This has an advantage of preparation of films over a large surface area without impairing materials purity in a relatively shorter period of time. In the electrodeposition process, the film properties mainly depend on deposition conditions, e.g, current density, deposition potential, bath type density, deposition potential, bath type density, deposition potential, bath type the electrochemical deposition conditions as well as physical parameters such as thickness, the substrate type, and orientation, it is possible to control and optimize the electrodeposited films (such as coating thickness, cluster size, etc.)

Nanosized Ni deposits require the application of much higher current densities, which normally leads to cracks in films. Pulse electro deposition provides more

uniform and crack-free deposits with required properties. The pulse electrodeposited nanocrystalline (nc) Ni-Diamond films can receive great attention due to enhanced mechanical properties, and improved corrosion resistance when the nanocrystalline films are dense and defect free.

1.1 PROBLEM STATEMENT REGARDING EXPERIMENT–Major obstacle regarding the experimental research was that we were unable to get a uniform co- deposition of the diamond particles on the annealed copper substrate (due to very early settling down of diamond particles owing to their higher density) during the pulsed electro deposition of nickel on the annealed Cu substrate using potentiostat and hence we cannot get effective simultaneous deposition of both Ni and diamond.

1.2 STRATEGY USED TO OVERCOME- We used a ultrasonicator before the pulsed deposition which sent ultrasonic waves into solution and would not allow the diamond particls to settle down very early and we can get an uniform coating with uniform deposition of diamond particles.

2. EXPERIMENTAL DETAILS

Nanocrystalline nickel was deposited on annealed copper substrate of unit surface area (1 cm^2**)** via pulsed electro deposition technique using potentiostat (model 263A, Princeton Applied Research, USA Fig. 2.1) from Watts bath containing nickel ($NiSO_4 \cdot 7H_2O$)**,** nickel chloride ($NiCl_2.6H_2O$), boric acid and citrate complexing agent sodium citrate($Na_3C_6H_5O_7.2H_2O$). Copper was used s cathode and nickel as anode. Both electrodes were subsequently grinded and then firstly polished using various emery papers and finally we went for the alumina & diamond polishing for the better finish on surface. We marked 1cm*1cm for electrodeposition and rest of electrode was insulated to avoid electrodeposition over it.

Diamond particles of three different dimensions, viz., 1, 3, and 6 μm were added separately (5 g/L) to the watts bath and co-deposited along with nanocrystalline nickel. The temperature was kept constant at 55 °C. The solution was sonicated for 45-60 minutes prior to deposition to disperse the diamond particles uniformly the bath. . Then three cycles of depositions was followed with 3 minutes of sonication for each set of diamond particles i.e 1 , 3 and 6 micron diamond particles so that it does not gives the time to the diamond particles to settle down in the bath and giving a uniform deposition of diamond particles on the nanocrystalline nickel matrix .

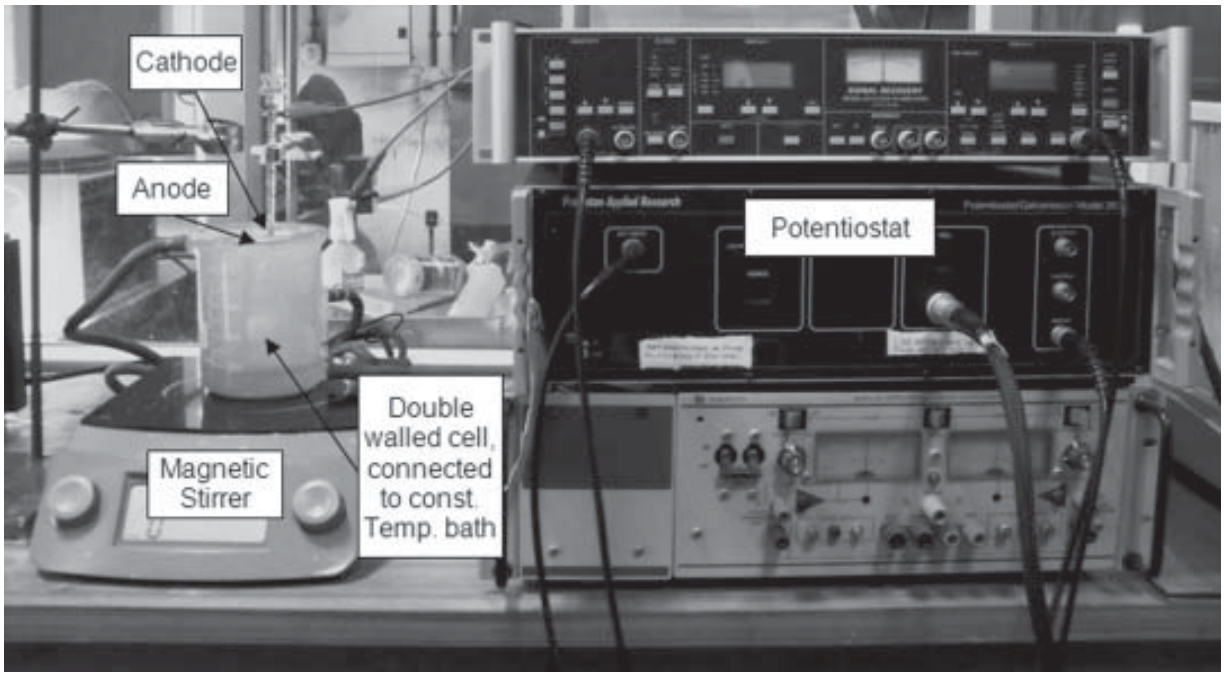
2.1 Electrolyte Bath Compositions Utilized for the Co-deposition of Ni-Diamond film

COMPOSITION	CONCENTRATION
$NiSO_4.7H_2O$, g/L	250
$NiCl_2.6H_2O$,g/L	40
H_3BO_3, g/L	40
Sodium citrate, g/L	25

Depositions were carried out at different current densities, viz., in 50, 100 and 200 mA/ cm^2 for different durations, i.e., 7, 14 and 21 minutes. One cycle of deposition corresponds to 1 minute. Here we used the results of 21 minutes i.e 21 cycles only .Scanning electron micrographs show uniform deposition (as shown by Fig 3.1, 3.2, 3.5, 3.6, 3.7, 3.8) of micron diamond embedded in the nickel matrix. Elemental mapping (Fig.3.4 &3.4) confirmed uniform deposition of nickel and diamond with almost no cracks or pits. The analysis of the electrodeposited surfaces were done using SEM and micromechanical properties such as, Vicker's hardness. Improved microstructural and mechanical properties such as hardness

(Table 4.1) were found in the case of electrodeposited surfaces containing 6 micron diamond followed by 3 and 1 μm diamond. The mechanical properties were also found better than those processed via stirring the solution during deposition.

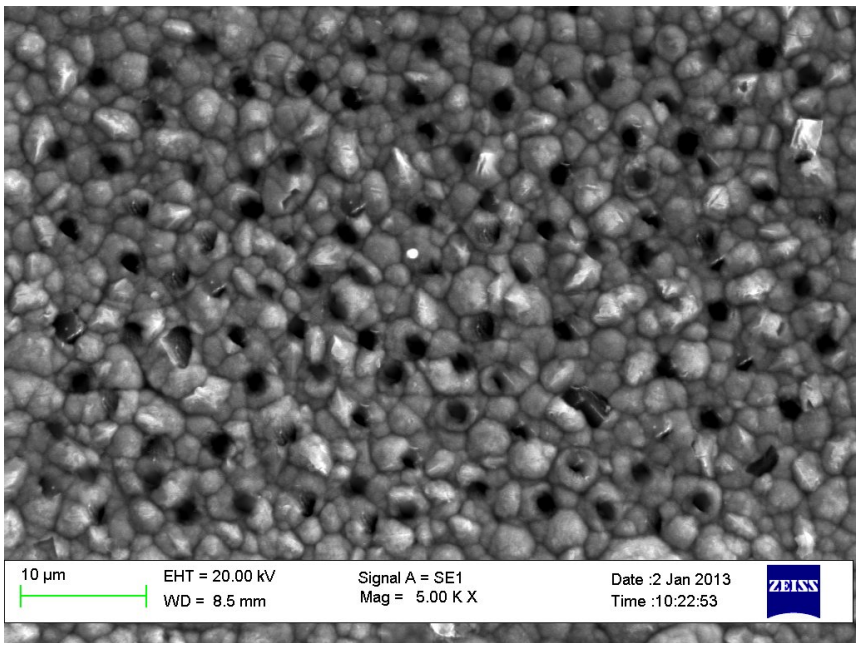
FIG. 2.1 POTENTIOSTAT USED FOR PULSED ELECTRODEPOSITION :- (MODEL 263A, PRINCETON APPLIED RESEARCH, USA)

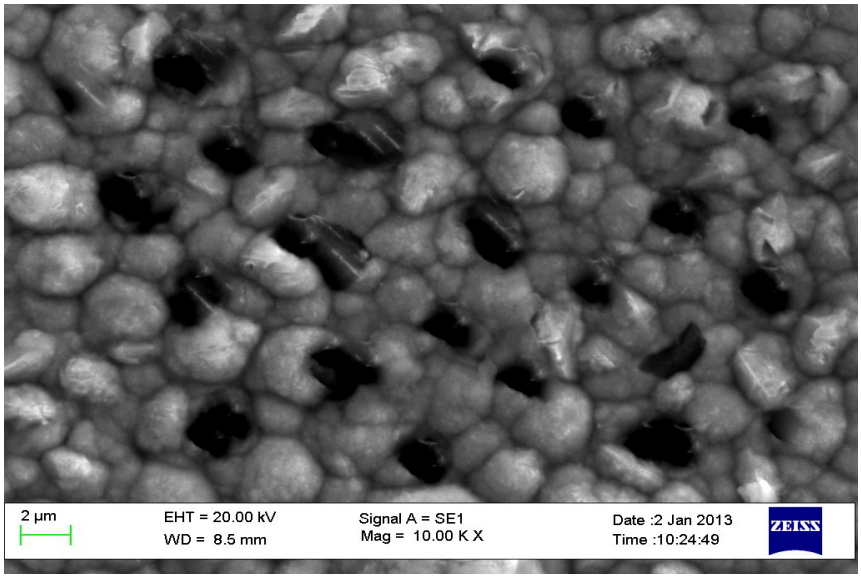


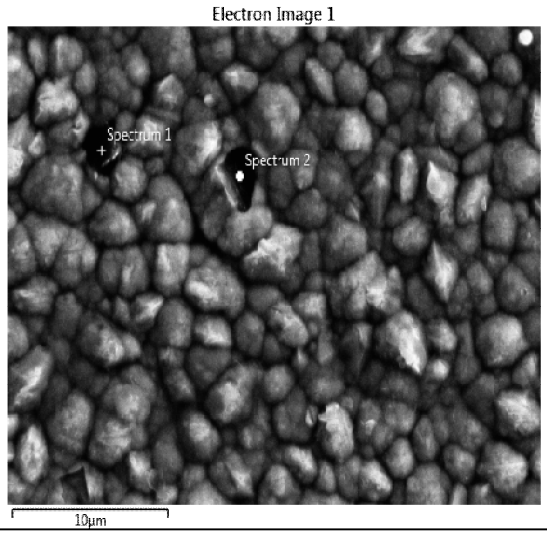
3. OBSERVATIONS AND RESULTS –

Experimental parameter I – 3 µm diamond, (5 g/L), 60 ml solution , 30 min prior to sonication , 3 min deposition + 3 min sonication , Temperature 50-55 degree Celsius 21 cycles intermittent (electrodes kept dipped while sonication intervals) no deposition while sonication

FIG. 3.1 & 3.2*-The images on the right hand side are the S.E.M images of the equiaxed nanocrystalline deposited nickel (with uniformly deposited 3µm diamond particles over the matrix) on the annealed Cu substrate at magnification of 10 µm and 2 µm .*







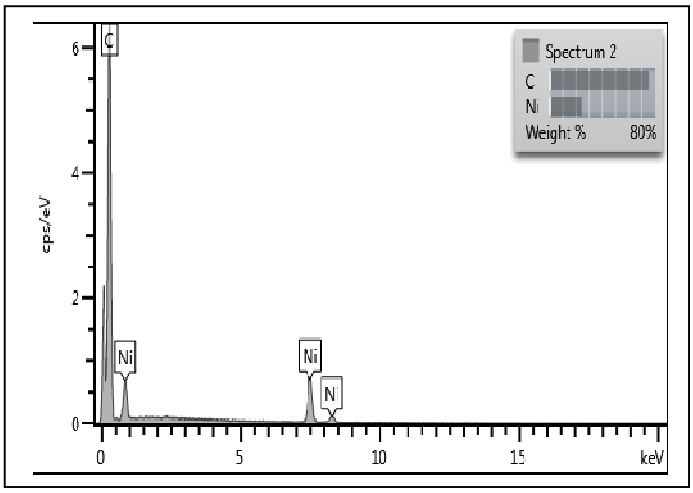
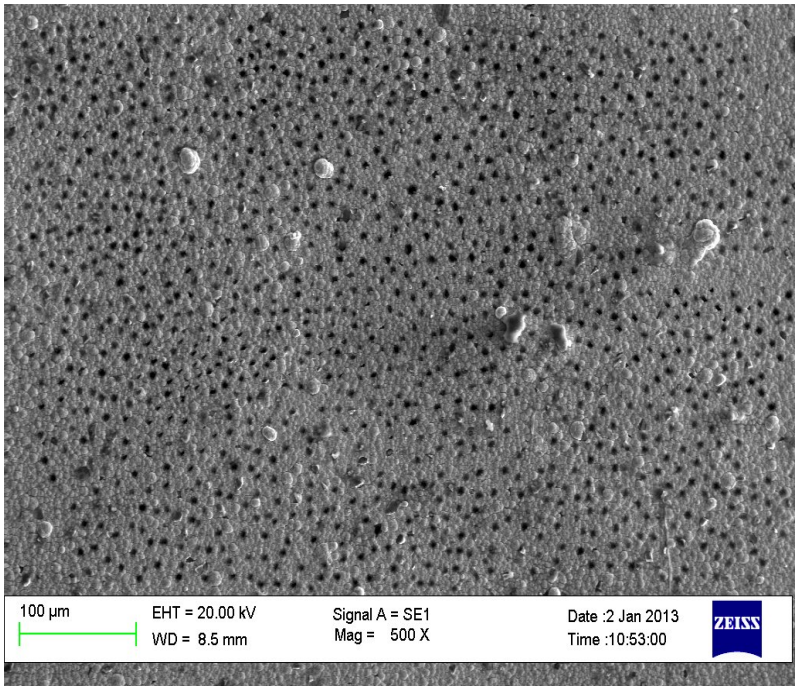


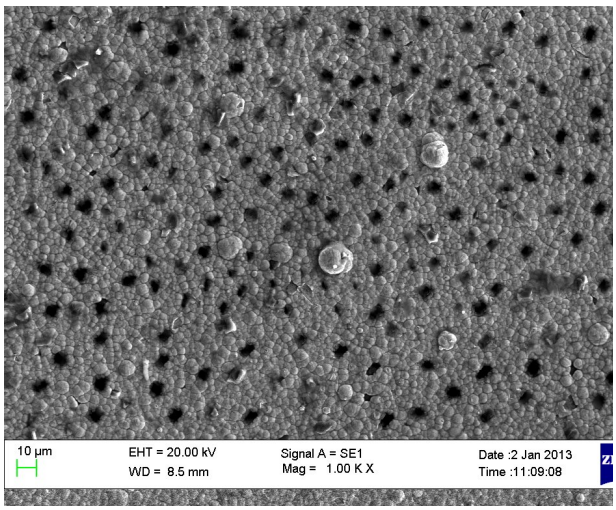
Fig.3.3 & 3.4-ABOVE SHOWN IS THE ELEMENTAL MAPPING which shows two spectrums viz: SPECTRUM 1 and SPECTRUM 2. From elemental mapping we can clearly see that the CARBON WEIGHT % at SPECTRUM 2 is very high around 80 % and presence of very low Ni % which indicates and proves the presence of diamond particle over there.

Experimental parameter II – 6 µm diamond, (5 g/L), 60 ml solution , 30 min prior to sonication , 3 min deposition + 3 min sonication , Temperature 50-55 degree Celsius
21 cycles intermittent (electrodes kept dipped while sonication intervals) no deposition while sonication

Fig. 3.5 -6 µm DIAMOND 21 cycles



S.E.M image of the uniformly deposited equiaxed nanocrystalline Ni (with 6µm diamond particles embedded over the matrix) on the annealed Cu substrate at magnification of 2 µm . It also shows the uniform deposition of the diamond particles as well.



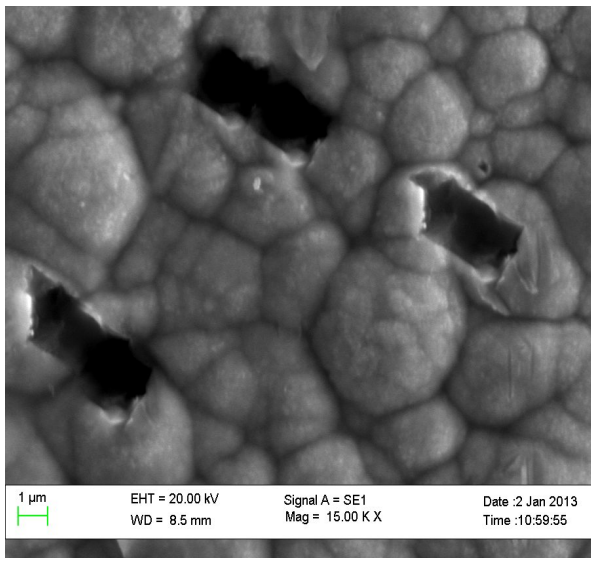


Fig.3.6 & 3.7(above)-S.E.M image of the uniformly deposited equiaxed nanocrystalline Ni (with 6µm diamond particles embedded over it) on the Cu substrate at different magnifications of 10 &1 µm .

Experimental parameter III –1 µm diamond, (5 g/L), 60 ml solution , 30 min prior to sonication , 3 min deposition + 3 min sonication , Temperature 50-55 degree Celsius
21 cycles intermittent (electrodes kept dipped while sonication intervals) no deposition while sonication

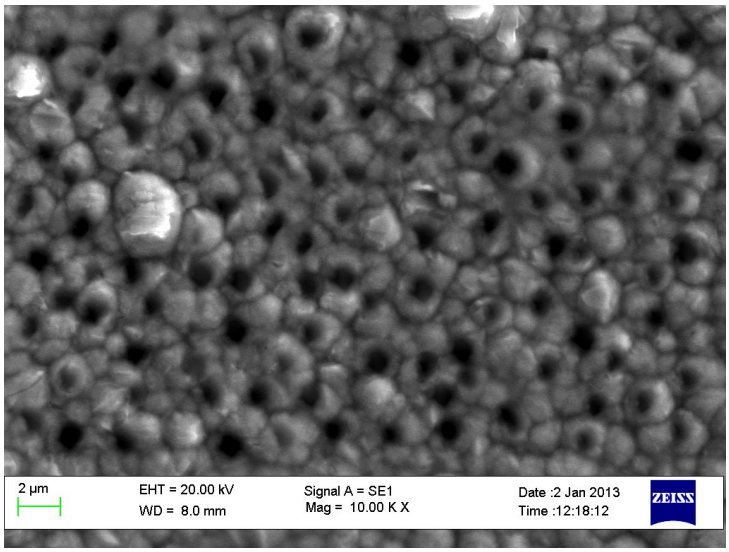


Fig 3.8(Left Hand Side) - S.E.M image of the uniformly deposited equiaxed nanocrystalline Ni (with 1µm diamond particles embedded over the matrix) on the annealed Cu substrate at magnification of 2 µm . It also shows the uniform deposition of the diamond particles as well.

TABLE 4.1 – Evaluation of the Vicker's Hardness Of the samples

ANNEALED COPPER SAMPLE (Hv0.01)	Ni- 1 MICRON DIAMOND COATING 21 CYCLES (Hv0.01)	Ni- 3 MICRON DIAMOND COATING 21 CYCLES (Hv0.01)	Ni- 6 MICRON DIAMOND COATING 21 CYCLES (Hv0.01)
108.5	433.8	469.8	481.7
108.3	435.6	475.2	485.6
112.6	439.2	468.5	489.6
109.7	439.6	472.5	488.6
111.8	443.3	478.1	489.3
Average =110.18 Hardness	Average =438.3 Hardness	Average = 472.82 Hardness	Average = 486.96 Hardness

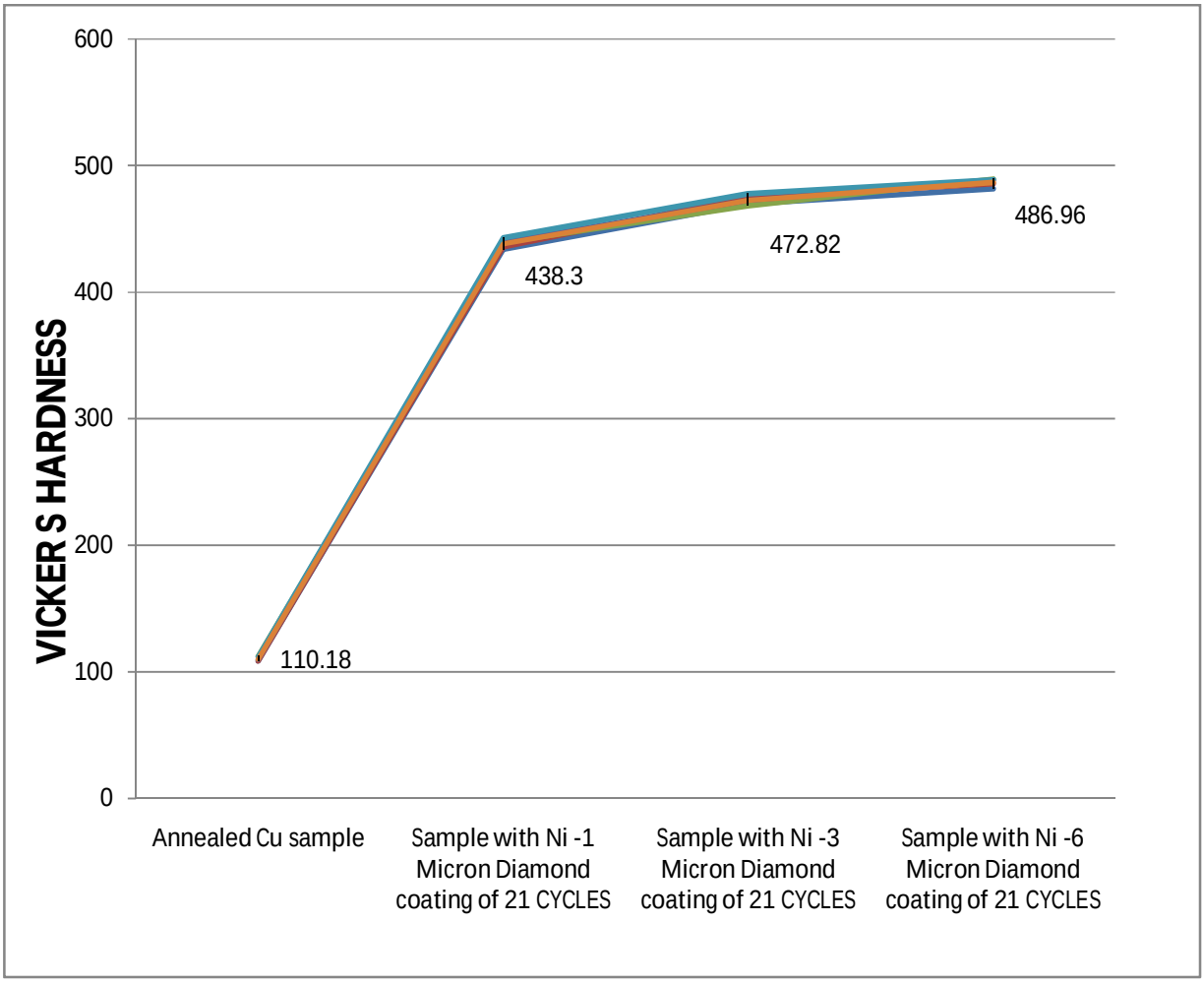


CHART 4.1 -Variation in the value of VICKER'S hardness of the annealed copper sample on the electrodeposition of nanocrystalline nickel embedded with various micrometer sized diamond.

5.CONCLUSION –

The enhanced content of nanocrystalline Ni with increased current density of around 200 mA/cm^2 allows achieving enhanced hardness in comparison to that of low Ni deposits.
The ultrasonication of the bath before the electrodepostion process did not allowed the diamond particles to settle down very early during the electrodeposition process and hence allowed better deposition of diamond particles on the nanocrystalline nickel matrix .
Tremendous increase in the value of Vicker's hardness (as shown in Table 4.1) of the annealed copper substrate is noticed on the electrodeposition of nanocrystalline film of Ni coated with micron sized diamond particles . The best result of the increased values of hardness(486.96Hv0.01**)** was found with 6 µm diamond embedded nanocrystalline Ni film on the annealed copper sample (Chart 4.1).

So Superior Ni-Diamond coatings, with improved corrosion resistance and hardness, can been developed on an annealed copper substrate

These coatings can be used in single and multilayer electronic packaging, enhancing mechanical properties of surfaces, mining, and ship building
However, it is important to note that superior corrosion resistance can only be possible when the nano crystalline films are dense and defect free.

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