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Investigation of Electrical Characteristics of Composites Produced by Electroless Ni Plating of Si_3N_4

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ABSTRACT

The microstructure. dielectric properties and electrical characteristics of Ni plated Si_3N_4 powders were investigated using specimens produced by tube furnace sintering at 800-1200°C temperature. A uniform nickel layer on Si_3N_4 powders was deposited prior to sintering using electroless plating technique. A composite consisting of binary additions. a metallic phase. Ni within a matrix of Ni has been prepared under Ar shroud and then tube furnace sintered. XRD. SEM (Scanning Electron Microscope). Empedans Phase Analyzer were used to obtain structural data and to determine electrical properties such as dielectric and conductivity at the temperature range of 25-500C. The ferromagnetic resonance varied from 10 Hz to 1 GHz and measurements were employed to characterize the properties of the specimens. Experimental results carried out for composition $(33Si_3N_4)66Ni$ at 1200°C suggest that the best properties as 75.81HB and permittivity were obtained at 1200°C

Keywords: *Powder metallurgy. Electrical Proporties. Composite and Electroless Nickel Plating*

1. INTRODUCTION

The ability to reinforced fine particulate such as ceramic particles within metal matrix by electroless plating method has lead to the development of composite coatings. These coatings exhibit superior properties compared to the plain electroless Ni plating. Composite coatings containing micron size second phase hard particles such as diamond, SiC, Al_2O_3, Si_3N_4, etc. and soft particles namely MoS_2, graphite etc. have been successfully codeposited in Ni matrix [1]. These composite platings find number of applications. For example the useful life of molds for plastics, rubber, etc., has been improved by coating them with Ni-SiC [2]. Electroless Ni plating ceramics offer non-stick, non-galling, high dry lubricity, low friction, precise and uniform torque and tension, good wear and corrosion resistance. The applications for these composite platings have been in the fields include moulds for rubber and plastic components, tools for pumps, valves and butterfly valve for oil and gas industry, fasteners, precision instrument parts, aluminium air cylinders, carburetors, choke shafts, etc. [3]. Ni plating ceramics composite are applied to improve the wear resistance of tools. Some examples are contact heads of honing heads, broaching tools for graphite, valves for viscous rubber masses and thread guides for use in textile machines and friction texturizing disks [4]. Silicon nitride (Si_3N_4) based ceramics have been studied intensively for more than 40 years and used in numerous applications as structural and functional ceramic materials due to its superior properties. such as high-temperature strength. good oxidation resistance. and low thermal expansion coefficient [5–7].The ability to reinforce fine particulate matter such as hard ceramic or soft lubricious particles within metal matrix by electroless plating method has lead to the development of composite coatings. These coatings exhibit superior properties compared to the plain electroless Ni-P coatings. Composite coatings containing micron size second phase hard particles such as diamond. SiC.

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Al_2O_3. Si_3N_4. etc. and soft particles namely MoS_2. HBN. graphite etc. have been successfully co deposited in Ni matrix [8]. These composite coatings find number of applications. For example the useful life of molds for plastics. rubber. etc.. has been improved by coating them with Ni-P-SiC [9]. Ni-P-diamond composite coatings are applied to improve the wear resistance of tools[10]. In general. electroless codeposition processes of second phase particle take place at low temperature and the chemical interaction is not favored between the particles and the matrix. The particles are only physically entrapped in the Ni matrix. Therefore heat treatment of these coatings is necessary in order to promote phase transitions which will influence their properties. Several investigators have successfully co deposited hard particles (like WC. SiC) in electroless Ni-P matrix [11-13]. Electroless NiP micro- and nano-composite coatings containing SiC and Si_3N_4 particles were prepared and characterized for their structure and tribological properties [14]. Metallic materials with small grains exhibiting a high strength are interesting from both theoretical and experimental point of view. Further enhancement of their mechanical properties is possible due to reinforcement by ceramic particles [15-16].

Electroless nickel composite coatings containing submicron silicon nitride particles. To prepare the composite coating the selection of second phase particles is also equally important. Silicon nitride is well known for its superior wear resistance. low coefficient of friction. higher hot hardness. good resistance to high temperature oxidation as well as to aqueous corrosion. Hence. systematic studies were carried out to prepare Ni-Si_3N_4 composite coatings by electroless deposition method. Plain Ni coatings were also prepared for comparison. Deposits were characterized for their structure. morphology. phase transformation behavior and micro hardness at various heat treatment temperatures. At crystallization temperatures deposits were heat treated and analysis was carried out to find out the phases formed. Grain size has also been calculated for as-deposited and heat treated coatings at crystallization temperatures.

2. EXPERIMENTAL METHOD

Starting powders employed in this study were as follows: the purity of 99.8% for Si_3N_4 powders with a particle size lower than 40 μm. and Si_3N_4 ceramic-metal composite was produced by electroless Ni plating of Si_3N_4 powders.

Ni plating was achieved by suspending the starting Si_3N_4 powders in a Ni containing solution ($NiCI_2.6H_2O$) at 90-95°C and by adding Hydrazine Hydrate ($N_2H_4.H_2O$) and 35 vol.% Ammonia solution while keeping the pH at 9-10. With increasing temperature. Ammonia evaporation rate increased rapidly. therefore. a dripper was used to add more ammonia for adjusting pH of the plating solution. In the mean time. the solution was continuously stirred and the pH was constantly monitored by using a Philips PW 9413 Ion-Activity Meter. Combination Ion selective electrodes are available. Ion selective measurements can be made using these combination ISE electrodes from Sensorex. ISE types available: Fluoride (F-), Chloride (Cl-), Ammonium (NH4+), Postassium (K+) and Nitrate (NO3-). All are vailable as lab style 12mm units or can be used on-line for simple installations

The reaction was allowed to continue until sufficient Ni was added for plating all the Si_3N_4 powders. then. Ni plated Si_3N_4 powders were filtered out of the solution by using a paper filter and repeatedly washed off by distilled water and then oven dried at 105°C. and then followed by sintering at 800-1200ºC for 2h using a tube furnace. Composition of the electroless nickel plating bath and its operating conditions were given in Table 1.

Table 1. The chemicals of Nickel plating bath and their ratios

Chemicals	Conditions
Si_3N_4 powders	5g
Nickel Chloride ($NiCI_2.6H_2O$)	40g
Hydrazine Hydrate ($N_2H_4.H_2O$)	%20
Distile Water	%80
Temperature (°C)	90-95°C
pH Value	9-10

The purity of 99.9% for Si_3N_4 powders with a particle size lower than 40μm. The composition of was calculated according to formula 33%Si_3N_4+Ni. that is. 33% Si_3N_4+Ni. specimens were prepared in 5g cylindrical compressed pre-form. The mixture was shaped by single axis cold hydraulic pressing using high strength steel die. A pressure of 300 Bar was used for the compacting all the powder mixtures. The cold pressed samples underwent for a sintering at 800-1200°C for 2 hour in a tube furnace using Argon gas atmosphere. The specimens were cooled in the furnace after sintering and their hardness and shear strengths measurements were carried out using METTEST-HT (Brinell) hardness tester and Shimadzu Autograph AG-IS 100KN universal tensile tester machine. standard metallurgical specimen preparation was made to reveal the microstructure of the joints and powder compacts.

Shimadzu XRD-6000 X-Ray Diffraction analyzer was operated with Cu K alpha radiation at the scanning rate of 2 degree per minute. LEO 1430 VP model Scanning Electron Microscope fitted with Oxford EDX analyzer was used for microstructural and EDX compositional analysis and Nova Control Alfa Empedans Phase Analyzer operated between 1Hz-10MHz with a temperature range of 0-1400°C with a power rated at 1.5KW. produced by Hundsangen/Germany. was used for measuring electrical properties.

The volumetric changes of 33%Si_3N_4+Ni composite material after sintering were calculated by using (d=m/V) formula (Figure 1). The volume of pre-sintered and post-sintered samples was measured with Archimedes principle. F= $\rho g V$

Where, F = Buoyant force of a given body,
V = Volume of the displaced fluid
g = acceleration due to gravity

We know that density $\rho = \rho f - \rho g$. Here ρf is the density of the fluid and ρg is density of the body. Hence the formula can also be given as . F= $(\rho f - \rho g).g.V$

All the percentages and ratios are given in weight percent unless stated otherwise.

3. RESULTS AND DISCUSSION

3.1. Characterization of specimens

In the study. the samples prepared and shaped (pressed) were sintered at temperatures ranging at 800-1200ºC in tube furnace and made ready for physical. mechanical and metallographic analyses. Density-composition change curve is shown in Figure 1 The highest sintered density was achieved at 1200°C as 4.15gr/cm^3 Theoretical density of the composite $(33Si_3N_4)66Ni$ was calculated as 6.17 gr/cm^3

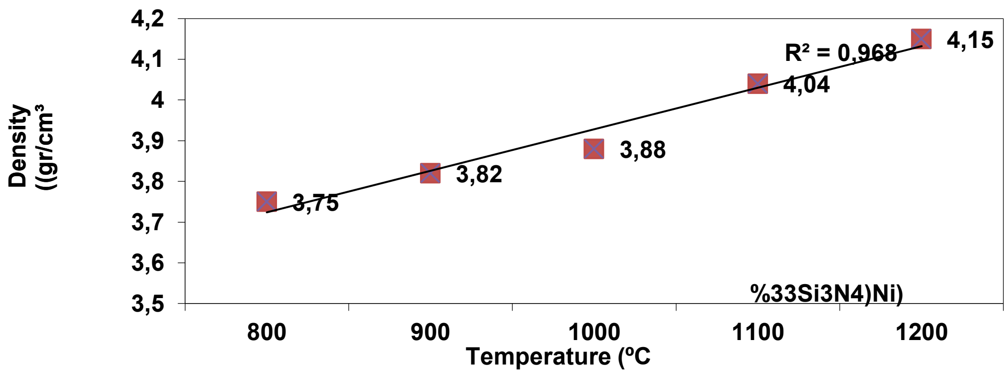

Figure 1. The density change with respect to sintering temperature

The hardness-composition change diagram is shown in Fig. 2. The hardness values of the composite samples produced using tube furnace sintering technique within the temperature range 1200°C from powders obtained as a result of plating $(Si_3N_4)Ni$ powders through electroless Ni plating method in tube furnace were given. According to this. the highest hardness value in the composite samples produced using electroless plating method was observed to be 75.81HB at 1200°C

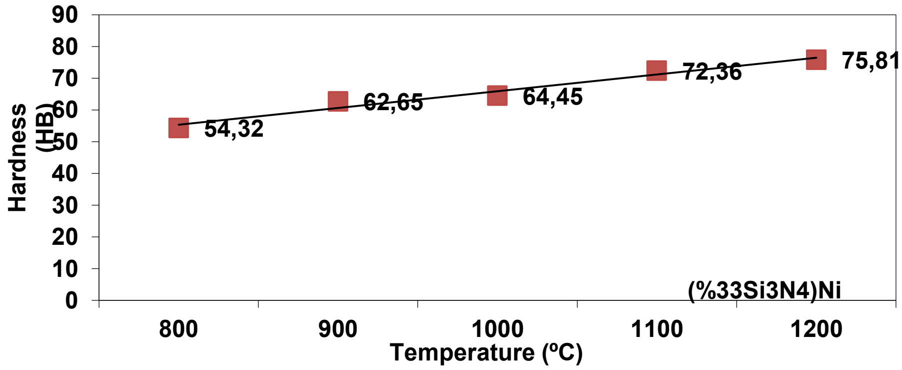

Figure 2. The hardness change with respect to sintering temperature

The dielectric coefficient of composite made of Ni coated $\%33Si_3N_4$ powders was investigated using impedance phase analyzer. The dielectric coefficient was found to be decreasing with frequency and it becomes zero at 1MHz frequency. The dielectric coefficient increased at frequencies lower than 1MHz. The permittivity values increased rapidly with respect to temperature up to 10KHz above which it became constant. The coefficients of specimens that were produced at 1200C was lower than those of produced at 800C. It can be concluded that there are more ions available in grain boundaries of specimens produced at 1200C.

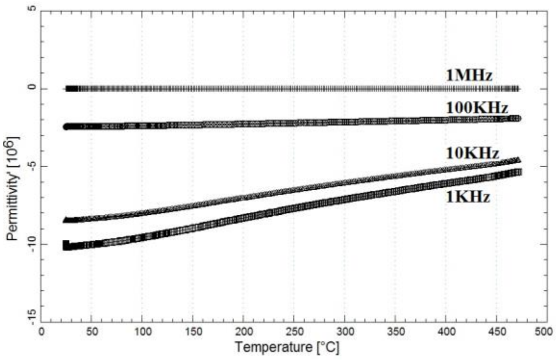

Figure 3 APA graphs of the temperature-dependent change in permittivity -received %66Ni Plated Si_3N_4 Composite at 800°C sintered.

The produced at 800 °C composite showed similar electrical characteristics. Sintered at 1200 °C increased the electrical conductivity of the sample is less porous. The dielectric coefficient was found to be decreasing with frequency and it becomes zero at 1MHz frequency. The dielectric coefficient increased at frequencies lower than 1MHz. The permittivity values increased rapidly with respect to temperature up to 10KHz above which it became constant.

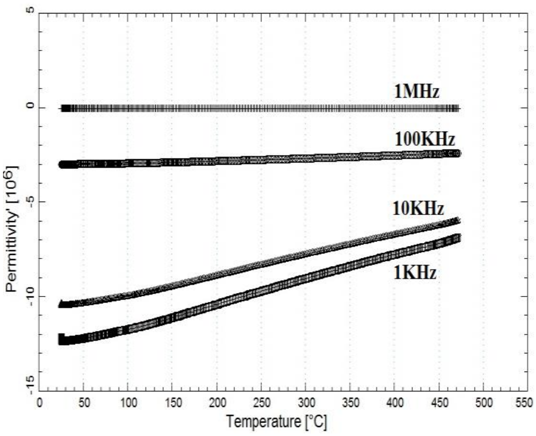

Figure 4 APA graphs of the temperature-dependent change in permittivity -received %66Ni Plated Si_3N_4 Composite at 1200°C sintered.

Ni Plated Si_3N_4 based composite sintered at 800°C has dielectric (permittivity) coefficient of 0.28 S/cm which is lower than that of sintered at 1200°C. This may be related to the amount of porosity inside the specimens such that the porosity in specimens sintered at 800°C was very high. The porosity in composite may hinder the conductivity of the specimens. For both specimens. conductivity linearly decreases down to 10^5Hz and then an experience sharp fall and reaches the zero value at 10^6 Hz. For both specimens the conductivity band is about 10 kHz wide and it sharply goes down from 10 KHz to 1 MHz at which it becomes zero.

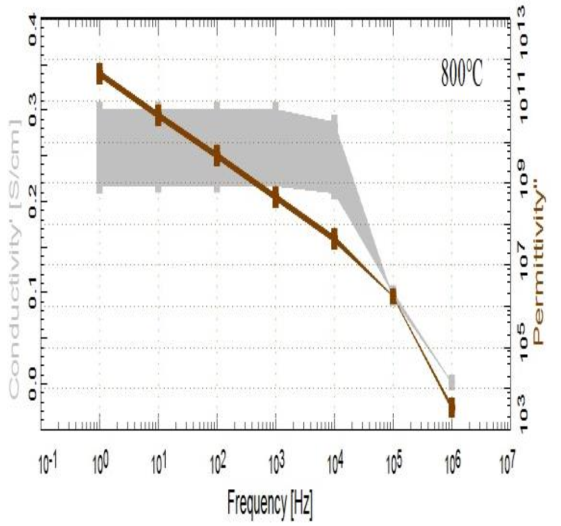

Figure 5 APA graphs of the temperature-dependent change in conductivity and Permittivity -received %66Ni Plated Si_3N_4 Composite at 800°C sintered.

Ni Plated Si_3N_4 based composite sintered at 1200°C has dielectric (permittivity) coefficient of 0.34 S/cm The porosity in composite may hinder the conductivity of the specimens. The specimens. conductivity linearly decreases down to 10^5Hz and then an experience sharp fall and reaches the zero value at 10^6 Hz.

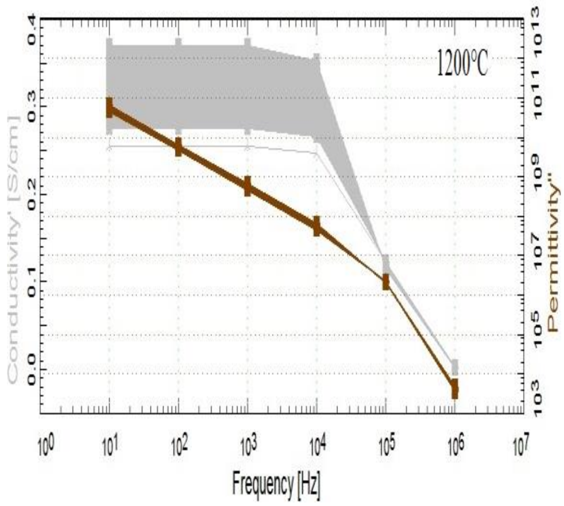

Figure 6 APA graphs of the temperature-dependent change in conductivity and Permittivity -received %66Ni Plated Si_3N_4 Composite at 1200°C sintered

3.2. Structural analysis

After nickel plating process. whether the plating was achieved in Si_3N_4 powders or not was examined through SEM analysis. It was observed that grains were bonded to each other and the particles grew larger. In addition. there were pores exhibiting homogeneous dispersion among the grains.

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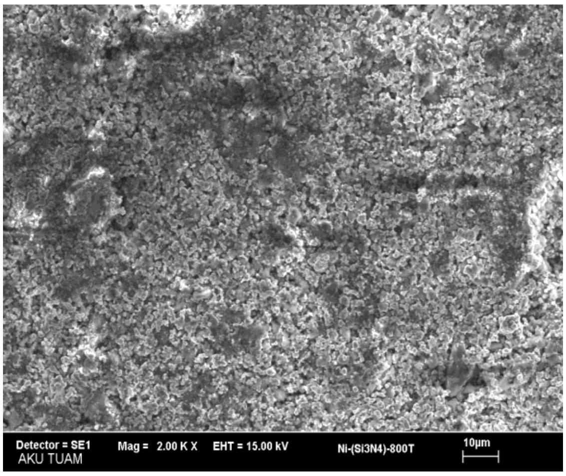

Figure 7 SEM micrographs of as-received Ni Plated Si_3N_4. Mag.2kX 800ºC

Scanning Electron Microscopy (SEM) and XRD analyses were carried out on the specimens to reveal the effect of Ni plating and characterize the phases present within the specimen. Figure 8 shows Ni plated particles having a layer of Ni with low density of porosity before sintering process.

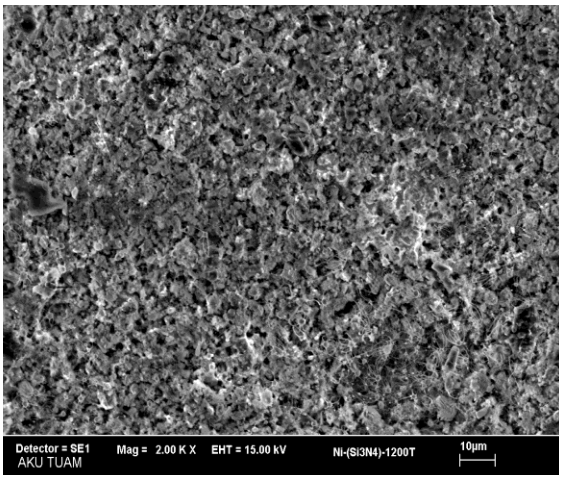

Figure 8 SEM micrographs of as-received Ni plated Si_3N_4. Mag.2kX 1200ºC

In Figure 9 NiSi. Ni_2Si. and Ni_3Si peaks can be seen in the XRD analysis from (Si_3N_4)Ni composite sintered in tube furnace at 1200°C.

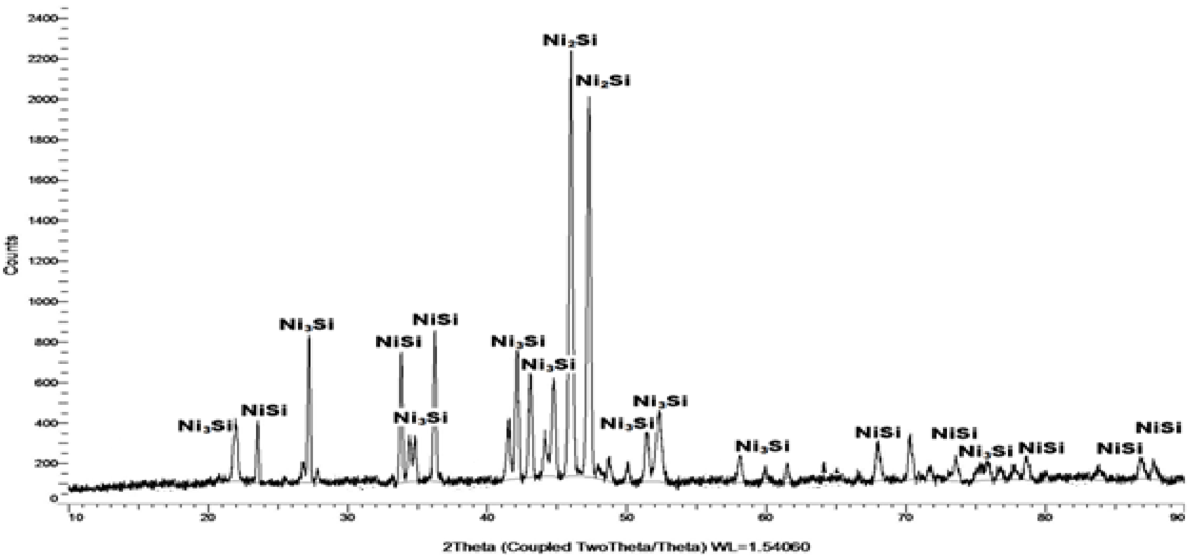

Figure 10 X-ray diffraction patterns of the (Si_3N_4)%66Ni sintered at 1200ºC

4. CONCLUSION

Electroless Ni plating containing micron silicon nitride particles were successfully prepared using a hydrazine reduced bath.There is a direct relationship between theoretical and experimental permittivity that has been obtained from Impedance Phase Analyzer. A permittivity measurement could be made up to 100 KHz above which the permittivity was unreadable. The Electrical conductivity decreases rapidly at higher frequencies of 10 kHz. Whereas the magnetic permittivity decreased linearly with increasing frequency. Up to 10 kHz electrical conductivity varies as a linear tape. Rapidly dropped to zero from 10 kHz up to 1MHz. SEM metallographic structure has led to changes in the linear electrical properties of the pics to be homogeneous. Ni coating are preferred due to sintering of Si_3N_4 ceramic powders makes it easier by providing a homogeneous coating. It also prevents oxidation.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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