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EFFECT OF SURFACTANTS ON THE SURFACE ROUGHNESS OF ELECTROLESS Ni - P COATINGS

Elansezhian R.[1] **and Ramamoorthy B.**[2]
[1]Research Scholar and [2]Professor, Dept. of Mechanical Engineering
Indian Institute of Technology Madras, Chennai -600036, India
E-mail: [1]elansezhianr@yahoo.co.in; [2]ramoo@iitm.ac.in

Kesavan Nair P.
Professor, Department of Metallurgical & Materials Engineering
Indian Institute of Technology Madras, Chennai -600036
E-mail: pkn@iitm.ac.in

Abstract: *Electroless nickel (EN) coatings have gained widespread acceptance as it provides uniform deposit on irregular surfaces, direct deposition on surface activated non – conductors, high hardness and excellent resistance to wear, abrasion and corrosion. The effect of surfactants on the surface roughness of electroless Nickel – Phosphorus surface protective coating obtained from an alkaline bath is presented in this paper. In this study the influence of surfactants sodium dodecylsulfate (SDS) and cetyl trimethyl ammonium bromide (CTAB) on the surface roughness of coated samples were investigated. It was observed that the surface roughness, surface hardness and surface morphology of Ni-P coating were clearly influenced by the addition of surfactants SDS and CTAB. The complete experimental details, results obtained and their analysis are presented in this paper.*

Key words: *Surface roughness, surface morphology, Surfactants, Electroless Ni-P coatings*

1. INTRODUCTION

Good bearing properties in any part are obtained when the surface has large number of irregularities. If the surface is perfectly smooth then seizure would occur due to difficulty of maintaining the lubricating oil film. The rate of wear is proportional to the surface areas in contact and the load per unit area. Thus it is seen that different requirements demand different types of surfaces. All smooth surfaces possess some degree of roughness, even if only at the atomic level. For man-made surfaces, this roughness arises from the manufacturing process which may involve chemical deposition, grinding, polishing, etching or several other commonly used techniques. Correct function of the fabricated component often is critically dependent on its degree of roughness. Every machining operation leaves characteristic evidence on the machined surface. This evidence in the form of finely spaced micro irregularities left by the cutting tool which are termed as surface irregularity or surface roughness (Wolf, 1996). Roughness is sometimes an undesirable property, as it may cause friction , wear , drag and fatigue , but it is sometimes beneficial, as it allows surfaces to trap lubricants and prevents them from welding together.

There are numerous problems caused by surface roughness. Although these problems tend to be application specific, they can be classified into four groups: excess light scatter, mechanical malfunction, environmental instability, and cosmetic acceptability. In optical applications, the primary motivation in measuring surface roughness is to estimate how much the surface will scatter light at the intended wavelength(s) of operation. Excess scatter can result in system nonperformance for sensing optics, imaging optics, laser optics and numerous others (Stover, 1994). In non-optical applications, excess surface roughness can lead to mechanical malfunctions. For example, computer hard disks have a narrow tolerance band for acceptable roughness. If the surface is too smooth, the read/write head may bind to the surface of the disk. If the surface is too rough, the head may be unable to fly over the disk surface on its air cushion in the proper manner (Mason, 1993). Another example of mechanical malfunction can be found in high performance engine machine parts which are required to move or rotate at high speed without wear. Excess surface roughness can lead to unacceptably high levels of frictional heating, causing damage and even failure (Thompson, 2004). Rollers used in almost any application from computer printers and plotters to pressing metals, papers and films in factory environments require careful control of surface quality to ensure the quality of the finished product (Ando, 1998).

Surface roughness can affect cosmetic appearance of a surface. Although this may appear to be the most trivial of the problems caused by surface roughness, it is often important in terms of potential lost revenue (Feist and William, 1994). Hence controlling surface roughness is important in terms of functional and quality aspects. Electroless nickel (EN) coating is a well established surface engineering process that involves deposition of a metal-metalloid alloy coating on various substrates. Although a variety of metals can be electrolessly plated, electroless Ni – P coating has received widespread acceptance as it provides high hardness and excellent resistance to wear, abrasion and corrosion (Mallory and Hajdu, 1991; Riedel, 1991; Baurand, 1994; Gawrilov, 1979; Winowlin et al., 2005). Electroless nickel deposition has become commercially important for finishing steel, aluminium, copper, plastics and many other materials (Mallory and Hajdu, 1991). In this process, metal deposition is driven by the catalytic oxidation of the reductant on the substrate surface (Ridel, 1991). Major advantages over the electrodeposition process include the formation of a uniform deposit on irregular surfaces, direct deposition on surface activated non – conductors and the formation of less porous, more corrosion resistant deposits (Baurand, 1994). Electroless deposition of metals has many applications in micro- and nanotechnologies. In order to improve the surface finish of electroless nickel deposits, surfactants are added into the electrolyte bath and their effects are studied in this paper.

Surfactants are surface active agents that lower the surface tension of a liquid, allowing easier spreading, and lower the interfacial tension between two liquids. Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface. Many surfactants assemble in the bulk solution into aggregates known as micelles . The concentration at which surfactants begin to form micelles is known as the critical micelle concentration or CMC. A surfactant can be classified by the presence of formally charged groups in its head. A nonionic surfactant has no charge groups in its head and an ionic surfactant carries a net charge. If the charge is negative, the surfactant is called anionic; if the charge is positive, it is called cationic (Calbo, 1986).

Many attempts have been made to find out the effect of surfactants on the roughness of electrodeposited Ni–P coatings (Tripathy, Das, Hefter and Sing, 1997; Wheeler, Moffat and Fadden, 2004; McFadden et al., 2003). Alsari, (2001) studied the effect of sodium dodecyl sulfate (SDS) solutions as gelation media on the formation of polyethersulfone (PES) membranes and reported that the roughness of membranes increased with an increase in SDS concentration. Valtierra et al., (2007) studied the influence of cetyltrimethyl ammonium bromide (CTAB) on the roughness of titania sol –gel films and reported that the sol-gel films prepared with surfactant showed a granular microstructure and are composed of irregular particles on the surface and enhanced the photocatalytic activity. However, limited data are available concerning the effects of anionic surfactant sodium dodecyl sulfate (SDS) and cationic surfactant cetyltrimethyl ammonium bromide (CTAB), on the electroless nickel deposits. In this study, the effect of surfactants SDS and CTAB addition was investigated on the surface roughness, and microstructure of EN coated samples.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of the substrates

In this work, mild steel specimens of about 24 mm diameter and 7 mm thickness were prepared from rod stock to be used as substrates. All the specimens were then solutionised at 800^{0}C for 2 hrs and furnace cooled to ensure uniform initial conditions. The samples were then finished by grinding followed by disc polishing and the typical surface finish values measured using a stylus instrument of the finished samples is as follows: Ra = 0.57 µm, Rt = 4.5 µm, Rmax = 3.77 µm and Rz = 3.03 µm. The step-by-step cleaning procedure employed prior to plating consists of cleaning the substrate with acetone, rinsing with distilled water, ultrasonic cleaning in methanol, acid pickling for 1 min. [8% H_2SO_4 by volume], rinsing in distilled water followed by a methanol wash.

2.2 Plating bath and Operating conditions

The composition of the plating bath for electroless Ni-P deposits was taken as: Nickel chloride (30 g/l) as the source of nickel, sodium hypo-phosphite (40 g/l) as the reducing agent, sodium citrate (25 g/l) as the stabilizer and ammonium chloride (50 g/l) as the complexing agent. The surfactant sodium dodecyl sulfate (SDS) was added into solution before electroless nickel deposition with various concentrations ranging from 0.15 g/l to 1.5 g/l and cetyltrimethyl ammonium bromide (CTAB) was added with concentrations ranging from 0.15 g/l to 1.8 g/l. Temperature of the plating bath was maintained at 87^{0}C ($\pm 1^{0}$C). The pH of the bath was maintained between 9 and 10 by addition of sufficient quantity of ammonia solution as and when required. The electrolyte was heated indirectly by an electrically heated oil bath whose temperature was regulated by a Proportional Integral Derivative (PID) controller. The temperature of the oil medium was controlled and the corresponding temperature of the electrolyte was monitored using a thermometer. The coating was proceeded for a period of 2 hours with total volume of the plating bath restricted to 150 ml (unless otherwise mentioned). The bath compositions used for EN deposits are presented in Table 1.

2.3 Analysis of deposits

Surface roughness of EN deposits were measured using a stylus instrument. The microstructures of the electroless nickel deposits were observed using a high resolution scanning electron microscope. The amount of phosphorous and nickel contents on the EN deposits were analyzed using EDAX.

3. RESULTS AND DISCUSSIONS

3. 1. Surface roughness of electroless Ni-P Deposits

The variation of average roughness value with respect to surfactant concentration is shown in Figs. 1 (a) and 1 (b). At lower concentration of surfactants, the average surface roughness value is higher and when concentration reaches to 0.6 g/l and above, the roughness value gets stabilized and it ranges from 1.579 µm to 1.884 µm for SDS and the mean average value is 1.796 µm which is less than the average roughness value of ENi-P deposit without surfactant addition. The average roughness value of E Ni-P deposit without surfactant is 1.885 µm. Fig. 2 shows the surface morphology of SEM images of ENi –P deposited with various SDS concentrations. In Figs. 2 (b), (c) and (d) the Ni-P deposits changes the surface topography from a smooth state to non-smooth state as the amount of nickel particles deposited on the coating surface is increased.

At lower concentration of SDS, the nickel fine particles produced inside the electrolyte bath are entrapped by hydrogen gas to the top surface of bath and then they are deposited on the coating surface. As the SDS concentration is increased, the surface is smoother than that for conventional deposit. The reason being at higher concentration of SDS the contact angle is reduced and this leads to the better wettability of Ni-P deposit. It is apparent that SDS addition during Ni-P deposit reduced the roughness. Researchers Lin and Duh (2006) and Chen et al., (2000) and Young et al., (2001) reported that adding SDS during electrodeposition of Ni-P modified the surface roughness and surface morphology of deposit for under bump metallization (UBM) in microelectronic industry. Wheeler et al., (2004) and Fadden et al., (2003) reported that the surface of electroplated Ni-P deposited with SDS addition was smoother at higher concentrations. This result matches with our experimental result.

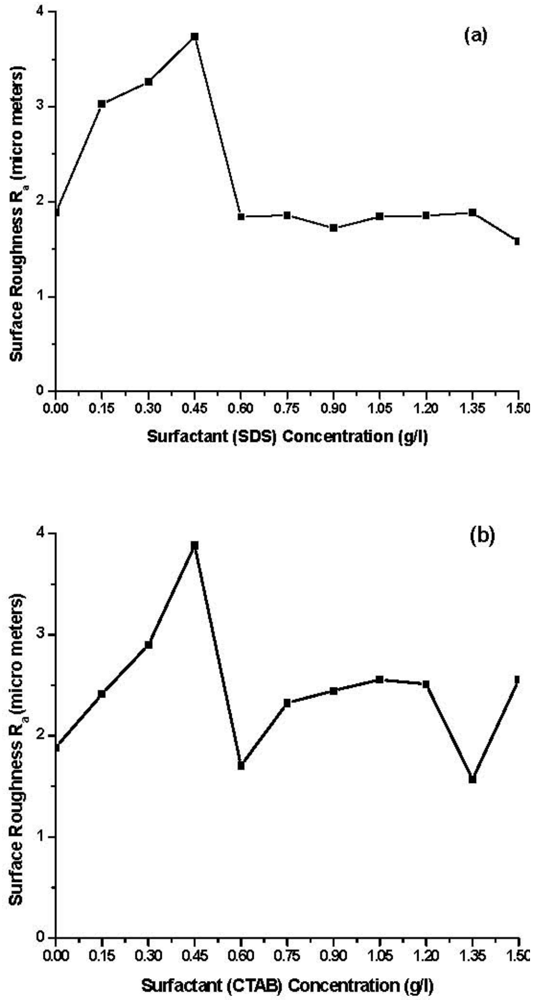

Fig. 1. Average surface roughness of ENi-P deposits vs. concentration of surfactant (a) SDS, (b) CTAB

When surfactant CTAB is added the electrolyte bath, at lower concentration the average surface roughness value is higher and when concentration reaches to 0.6 g/l and above, the roughness value gets stabilized and it ranges from 1.569 µm to 2.557 µm and the mean average value is 2.238 µm. Fig. 3 show the surface morphology of SEM images of ENi –P deposited with various CTAB concentrations. In Figs. 3 (b), (c) and (d) the Ni-P deposits changes the surface topography from a smooth state to coalescence of nickel particles deposited on the coating surface. Addition of CTAB as a surfactant promotes the fusion of nickel particles into a blend at lower concentration. As the CTAB concentration is increased, the surface is smoother as of conventional deposit. This result matches with Kajihara et al., (1998) and Zhao et al., (1996) who studied the influence of CTAB surfactant on the roughness of titania sol-gel film.

4. CONCLUSIONS

Based on the experimental results and analysis, the following conclusions have been drawn which clearly indicate that there is a possibility of a significant improvement in the average surface roughness of ENi – P deposited layers.

1. The surface finish of the coated layer significantly improved when the concentration of the surfactant exceeds 0.6 g/l. But at the lower levels of concentration the surface finish was poor.
2. With SDS, fine nickel particles have dispersed uniformly on the substrate surface resulting in smoother surface finish of the deposited layers.
3. In the presence of CTAB, at lower concentrations, coalescence of nickel particles have been deposited on the substrate surface and at the higher concentration uniformly improved surface finish of the deposited layer is resulted.

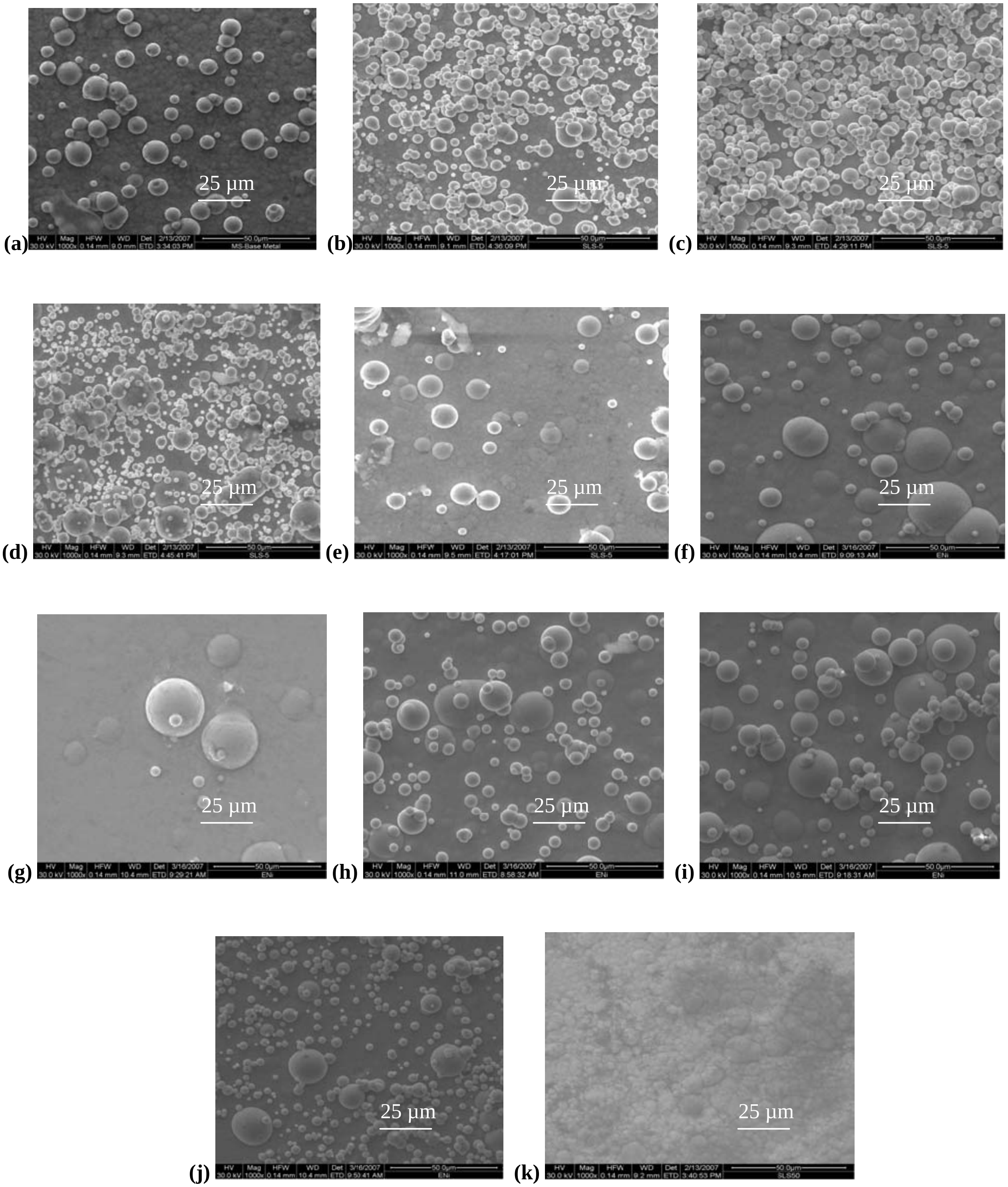

Fig. 2. SEM micrographs (1000X) of ENi – P deposited with various SDS concentrations: (a) without SDS addition (b) 0.15 g/l (c) 0.3 g/l (d) 0.45 g/l (e) 0.6 g/l (f) 0.75 g/l (g) 0.9 g/l (h) 1.05 g/l (i) 1.2 g/l (j) 1.35 g/l (k) 1.5 g/l

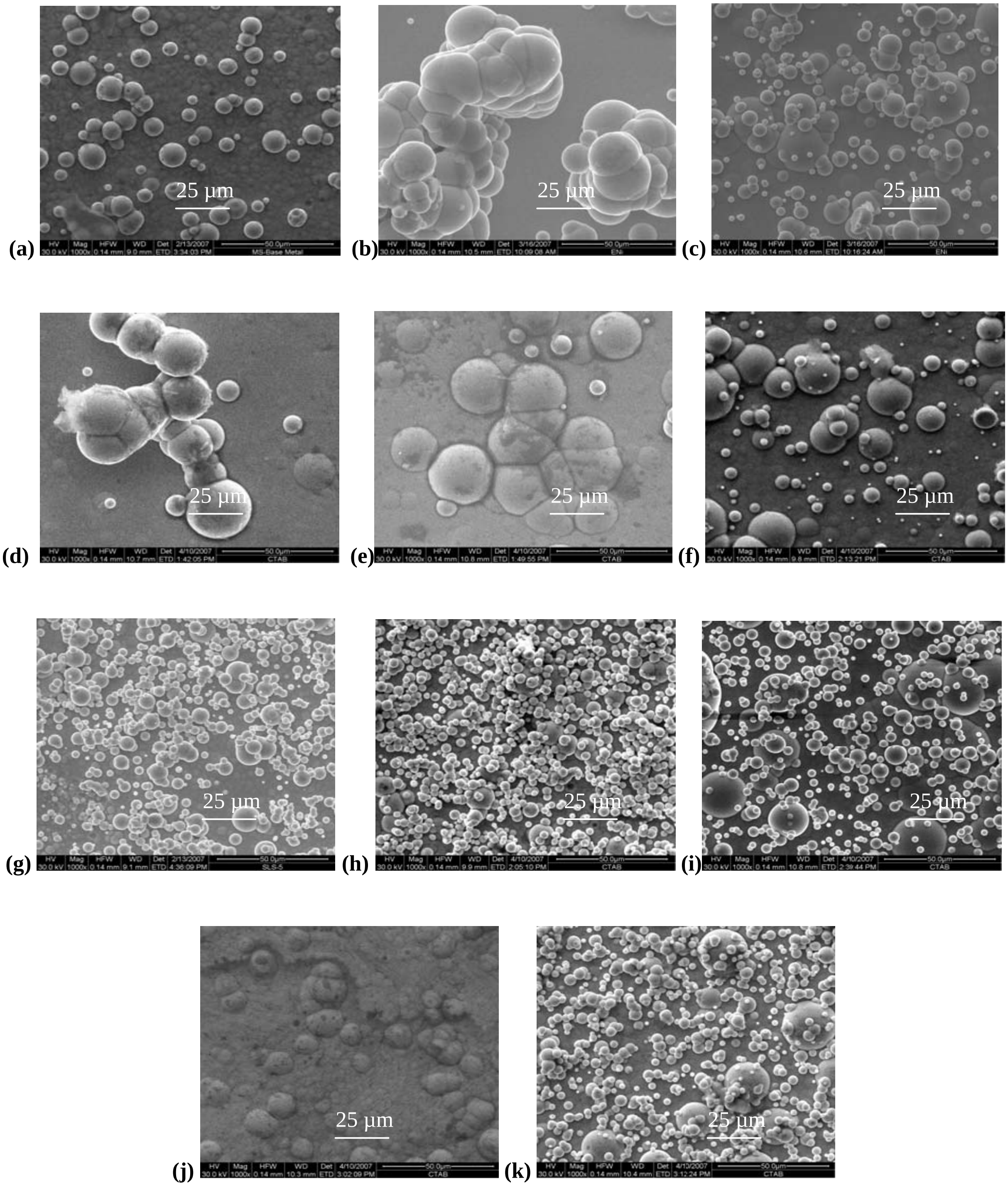

Fig. 3. SEM images of ENi – P deposited with various CTAB concentrations: (a) without SDS addition (b) 0.15 g/l (c) 0.3 g/l (d) 0.45 g/l (e) 0.6 g/l (f) 0.75 g/l (g) 0.9 g/l (h) 1.05 g/l (i) 1.2 g/l (j) 1.35 g/l (k) 1.5 g/l

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