African Journal of Pure and Applied Chemistry Vol. 4(5), pp. 58-63, May 2010
Available online at http://www.academicjournals.org/AJPAC
ISSN 1996 - 0840 © 2010 Academic Journals

Full Length Research Paper

Synthesis of nano-nickel by a wet chemical reduction method in the presence of surfactant (SDS) and a polymer (PVP)

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Accepted 4 March, 2010

Nano-sized nickel particles have been synthesized by a bottom-up approach, using hydrazine as the reducing agent in the presence of an anionic surfactant - sodium-dodecyl sulphate (SDS). The effect of adding a cationic polymer -polyvinylpyrrolidone (PVP) with an anionic surfactant has been studied at two different temperatures; the rate of reduction increased as the reaction temperature was increased from 60 to 100°C. These nano-aggregated nickel particles were characterized by using SEM with EDX facilities, TEM and XRD. TEM characterization showed the presence of spherical Ni particles as fine as 10 nm in diameter. However, the SEM images showed a very spiky morphology; very small spherical shaped objects were clearly observed within these spiky structures. XRD studies show that the nickel crystals have fcc structure. The combination of SDS/PVP reaction produced nano-sized nickel particles which were much finer than the reactions where SDS was used on its own. PVP has shown some dispersion power and was found to be capable of preventing nickel particles from gradual agglomeration.

Key words: Bottom-up, SDS, PVP, 10 nm.

INTRODUCTION

There is a continuous exploitation and exploration of nano-materials which have unusual properties that differ from either the bulk or single atom. Consequently nano-metals find applications in diverse fields, such as homogeneous and heterogeneous catalysis (El-Sayed, 2001; Thomas et al., 2003) fuel cell catalysis (Cui and Lieber, 2001; Sun et al., 2000), electronics (Cui and Lieber, 2001) optics (Eychmuller, 2001) magnetism (Puntes et al., 2001), material sciences (Rao, 2000) and even in medical and biological sciences (Niemeyer, 2001). While the design of nano-materials endowed with size dependant functions is gaining much importance, the synthetic strategies have matched their application needs, making a “made to order” relationship possible. These newer tunable synthetic methodologies offer not only an option of preparing any desired bi- and multi-metallic compositions, but it is also possible to control the size and the inner structure of the resulting nano-metals.

Nano-structured materials can be produced by two different approaches, namely, “top down” and “bottom up” approach. The top down approach is the process of breaking down the bulk metals and subsequent stabilization of the resulting nano-sized metal particles of colloidal protecting agents (Hussain and Haque, 2008). The bottom up approach on the other hand is the wet chemical nano-particle preparation, which relies on building nano-particles from the atom level of the metal. The interaction between polymers and surfactants in aqueous solutions has been very popular due to applications of mixed polymer-surfactant systems in various materials systems, such as detergents, hair care products, foams, emulsions, mineral oil recovery and in gene-therapy DNA-lipid complexes. We report here a synthetic method of preparing nano-structured Ni particles by bottom up approach, that is, a wet chemical nano-particle preparation

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through which we shall be able to prepare nano-nickel particles as small as 10 nm in diameter at low cost.

Nano nickel particles synthesis has been studied extensively over the past decade due to their unique properties and applications in various fields. In recent years research involving nano particles and nano scale materials has generated a great deal of interest from engineers and scientists of nearly all disciplines. Nano-sized nickel particles have found many applications including catalysts, batteries and in super alloys. Finer the size of the catalysts, higher is the catalytic activity. For example, using 30 nm nickel particles as catalyst to synthesize optical active 3-hydrobutyric methyl ester, the yield rate has been found to be as high as to 85% and the reaction speed was also found to be 15 times more compared with that of normal nickel catalyst. They can also be used for the preparation of porous metallic ensembles and as fillers for polymers.

The electric and magnetic properties of nano nickel particles are strongly dependent on the morphology and shape of the particles (Cordente et al., 2001). Therefore nickel nano particles with different morphology and shape, such as nano spheres, hollow sphere, nano rod, nano belt and core-shell structure, have been synthesized by various methods (Ni et al., 2005; Li and Komarneni, 2006; Bao et al., 2003). In fact, nanometer-sized crystallites are often the primary product in precipitation from solution. Such dispersions are inherently unstable and the so-formed nanoscale crystallites become aggregated to form larger particles. Ni and co-workers have reported a chainlike nickel wire formed by self-assembly of small nickel crystallites in a soft template (Ni et al., 2007).

Many different techniques have been used in the preparation of nano-sized particles, for example, the reduction of metal oxide salts (Kimijima and Sugimoto, 2005), decomposition of carbonyls and reduction in solutions by strong reducing agents (Petit et al., 1993). Reducing agents used include potassium borohydrides, sodium hypophosphite and hydrazine, which corresponds to the formation of metal borides (Petit et al., 1993). It is now well-known that water-soluble non-ionic macromolecule, such as polyvinylpirrolidone (PVP) or polyethyleneoxide (PEO) interact strongly with anionic surfactant, such as sodium dodecyl sulphate (SDS), in aqueous solution. Above the critical association concentration (cac), surfactant aggregate on macromolecule chains in micellar structure, which is known as bound-micelle.

The size of the alloy powders currently used in the synthesis of thermal barrier coatings (TBC) by thermal plasma spraying is much bigger than 100 um in diameter. The object of this research work was to synthesize nano-sized nickel particles/aggregates. The ultimate aim is to synthesize nano-sized NiCrAlY alloy powders (less than 100 nm in diameter) for high temperature applications in aerospace and power generation industries in bulk quantities (Hussain and Haque, 2008). It is anticipated that the finer nano-sized particles would reduce the high temperature corrosion.

MATERIALS AND METHODS

Materials used in this research work were nickel chloride electro-plating grade; sodium dodecyl sulphate (SDS, LOBA Chemie, India, 92%); polyvinylpyrrolidone (PVP Winlab, UK); hydrazine hydrate solution (LOBA Chemie, India, 80%); Sodium Carbonate (Sigma, 99%); de-ionized distilled water was used in the preparation of all the solutions. A thermostatically controlled hot plate with magnetic stirrer (Yellow Line) was used in this research work. The nano-sized nickel particles were synthesized by dissolving 10 g of $NiCl_2$ in a glass beaker containing 100 mL of de-ionized water which was maintained at 40°C. 20 g/l of SDS and 20 g/l of PVP were added to the solution.

In order to study the effect of PVP on the formation of nano-Ni particles a nickel solution was made by adding 20 g/l of SDS only without any PVP. The pH of the nickel solution was then increased to 10.2 by adding concentrated sodium carbonate solution. 150 mL of hydrazine was added to the solution slowly while stirring was on all the time. Temperature of the Ni solution was increased to 60°C before adding the hydrazine to the Ni solution. Reaction was also carried out at higher temperatures such as 60 and 100°C under reflux conditions. At 60°C as the reaction continues appearance of gray/black precipitates in the beaker meant that nickel particles have started to form.

This reaction is not instantaneous and can take several hours for the nickel reduction to reach completion. However, under reflux condition at 100°C the conversion was very quick (less than 20 min), froth formation was minimized.

While the nickel particles are formed at 60°C there is a huge volume expansion of the reacting solution because we use SDS as surfactant and according to equation 2 nitrogen gas is formed and hence care had to be taken not to spill the solution over the reaction vessel e.g. much bigger beakers were use that could handle the volume expansion of the reacting chemicals. As the reaction proceeded the top of the beaker became covered with thick froth; simultaneously Ni particles were deposited at the bottom of the reaction vessel.

Under reflux condition, however, this volume expansion was very little. The gray/black particles so formed were the aggregated nano-sized nickel particles. The products were collected, centrifuged (4000 rpm), washed with distilled water and ethanol for three times and finally desiccated at room temperature before characterization. The froth also contained a fair amount of fine Ni particles hence these particles were recovered by washing with acetone and water before drying.

It has been observed that hydrazine used from a freshly opened bottle gives much faster reaction. The nickel particles were characterized using, Scanning Electron Microscope (SEM) FEI–NOVA 200Nanolab with EDAX, Transmission Electron Microscope (TEM) JEOL - JEM 2100F and X-ray diffraction (XRD) JEOL JDX – 8030 X-ray Diffractometer System.

RESULTS AND DISCUSSION

Hydrazine is a normal reducer; its reductive ability varies according to the pH value of the solution. In acid medium, φ^{o}_{N2H4} is 0.23V and N_2H_4 is easily oxidized to NH_3. In a basic medium, φ^{o}_{N2H4} is -1.16V and it can be easily oxidized to N_2. At 25°C, $\varphi^{o}_{/Ni^{2+}/Ni}$ is -0.221V, so it is possible to reduce nickel ions in basic medium. The reaction equation between nickel chloride and sodium carbonate

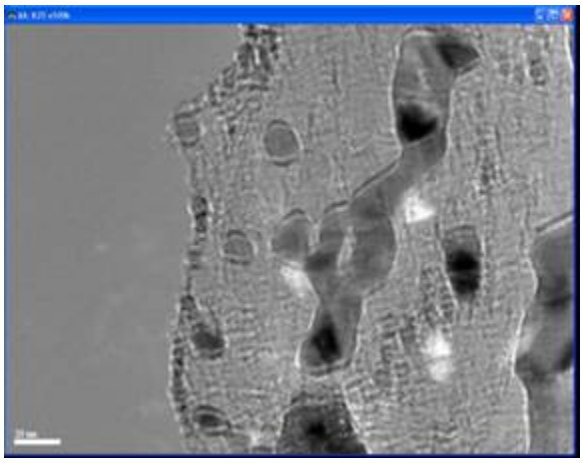

Figure 1. TEM image of Ni particles synthesized using SDS/PVP at 60°C.

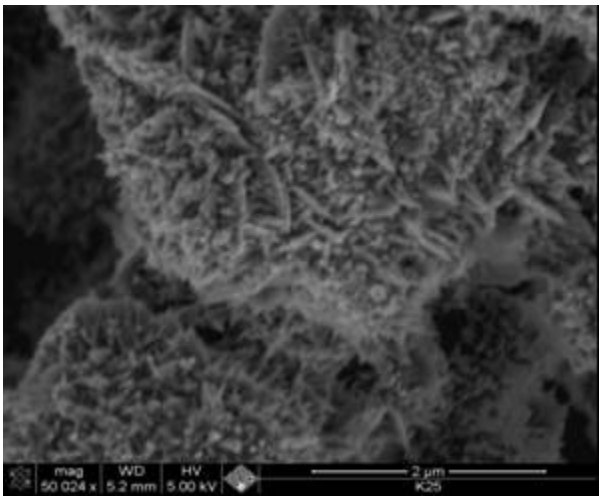

Figure 2. SEM image of Ni particles synthesized using SDS/PVP at 60°C. Magnification ×65,000.

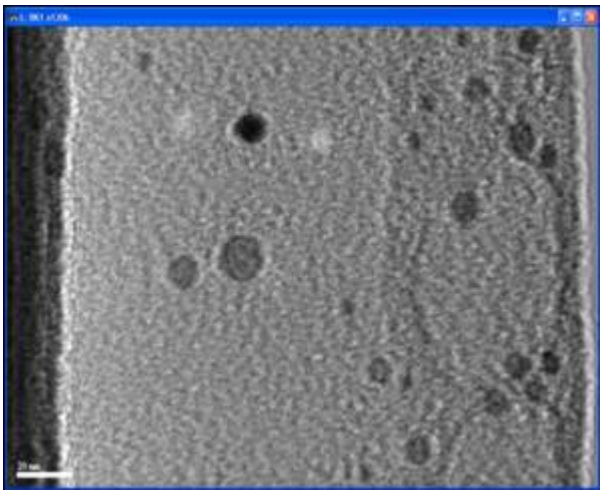

Figure 3. TEM image of Ni particles synthesized using SDS/ PVP at 100°C.

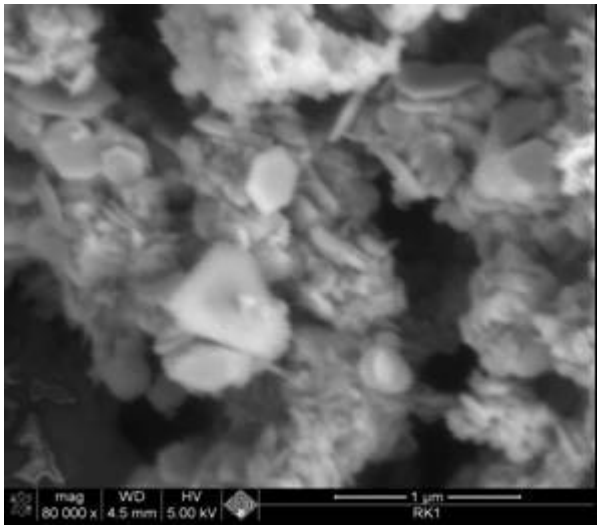

Figure 4. SEM image of Ni particles synthesized using SDS/ PVP at 100°C. Magnification × 80, 000

in aqueous medium can be written as follows:

$NiCl_2(aq) + Na_2CO_3(aq) = Ni(OH)_2(s) + 2NaCl(aq) + CO_2(g)$ …….. (1)

Hydrazine is added to the solution containing nickel carbonate at 60°C to enhance the reaction rate. The reaction equation between nickel and hydrazine is:

$2Ni^{2+} + N_2H_4 + 4OH^- = 2Ni + N_2 \uparrow + 4H_2O$ ……(2)

Figures 1 and 2 show images of nickel powders synthesized by using SDS/PVP at 60°C. Figure1 is a TEM image. Figure 2 is a SEM image of the same nickel powder at magnification of 65,000. TEM image shows (Figure 1) presence of spherical particles which are less than 30 nm in diameter. The SEM image (Figure 2) shows a very spiky morphology of the Ni powders, very small spherical shaped objects can clearly be observed within these spiky structures.

Figures 3 and 4 are images of Ni powders synthesized under reflux conditions at 100°C. Figure 3 is a TEM image of the Ni powders synthesized under reflux conditions at 100°C. Figure 4 shows SEM image of the same Ni powder sample at a magnification of 80,000. The TEM image (Figure 3) shows presence many small and spherical particles with diameters less than the diameter of the particles observed in Figure 1. Measured diameters of these particles are less than 10 nm. Figure 4 is an SEM image at a much higher magnification than that observed in Figure 2. The image shows objects which are very similar to the morphology observed in Figure 2. The

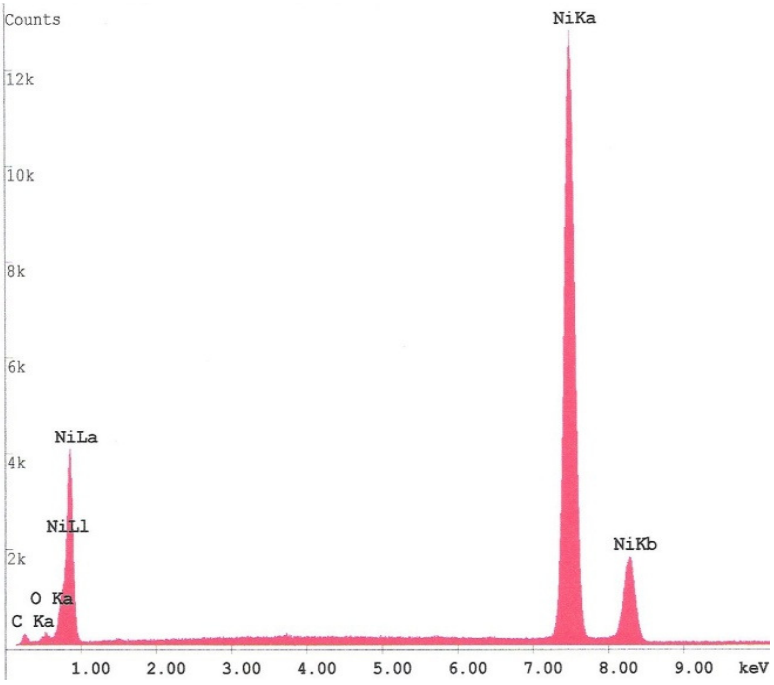

Figure 5. SEM/EDAX patterns of nano-nickel powder samples prepared with SDS/PVP at 60^0C.

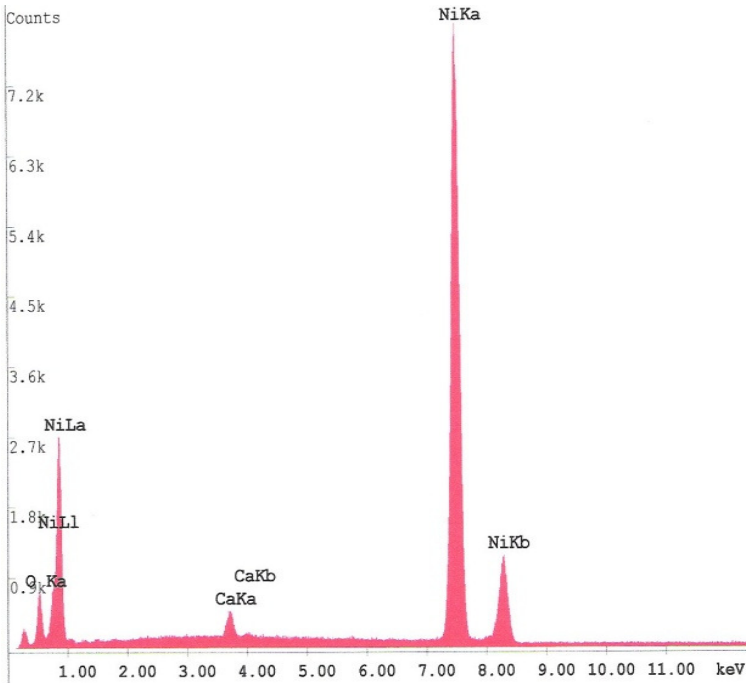

Figure 6. SEM/EDAX patterns of a nano-nickel sample powder which was prepared with SDS/PVP at 100^0C.

structure is still spiky with fine spherical structures still present but the effect is much reduced due to higher magnification. Samples prepared with SDS/PVP at 60℃ powder which was prepared with SDS/PVP at 100℃.

Figures 5 and 6 are SEM/EDAX plots of the Ni powders synthesized at 60 and 100℃ respectively. Both Figures show four clear peaks of Ni that is NiL a, NiL1, NiKa and NIKb. The oxygen and carbon peaks are negligible in

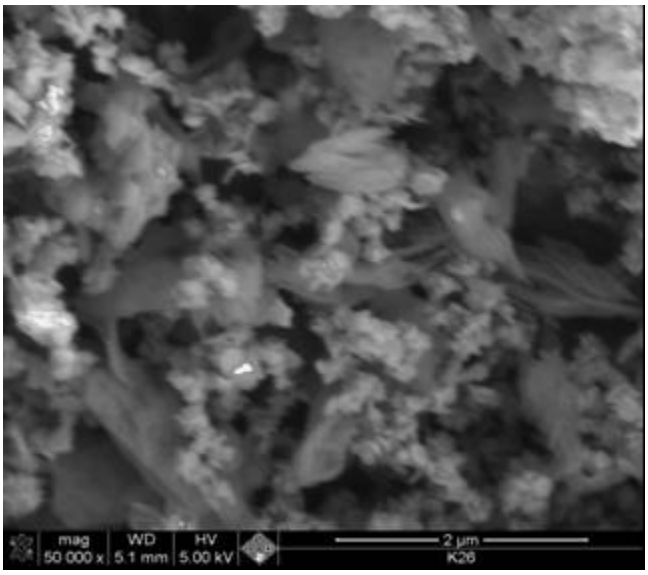

Figure 7. SEM image of Ni particles synthesized using SDS only without PVP at 60°C. Magnification ×50,000.

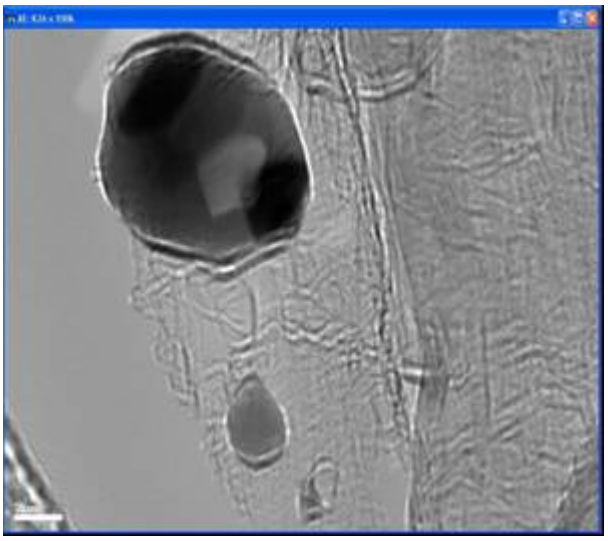

Figure 8. TEM image of Ni particles synthesized using SDS only without PVP at 60°C.

Figure 5, however, the oxygen level observed in Figure 6 shows some prominence. The peak intensity of the Ni sample synthesized under reflux conditions is much reduced than the sample synthesized at 60°C. It seems the reduced intensities of the SEM/EDAX plots is an indiation that the particle size are much finer. The presence of a small Ca peak cannot be accounted for from this expeiental work. Clearly the effect of increasing the temperature from 60 to 100°C has resulted in the refinement of the nickel particles. Figure 3 shows the presence of nickel particles which are as fine as 10 nm in diameter.

Figures 7 and 8 are images of nickel particles which were prepared with SDS only that is, without PVP. The SEM image (Figure 7) does not show the spiky structures as has been observed in the previous images, presence of very small particles are evident. TEM image (Figure 8 shows the particle size is much bigger than Ni-particles produced by SDS/PVP at 100 or even 60°C.

Figure 9 is the X-ray diffraction patterns of products prepared in the presence of SDS-PVP clusters. The angle 2θ at 44.5°, 51.8° and 76.4° are the characteristic absorption of nickel crystal at (111), (200) and (222), it means the products prepared are nickel crystal with face centered (fcc) structure.

Nickel crystals are magnentic at the same time nano-sized particles are known to have very large surface areas, hence these synthesized nano-particles will also have very high surface energy. Consequently these fine nickel crystals will be attracted towards each other and very quickly form aggregated nickel particles in order to reduce their surface energies. We conclude that linear PVP molecule has template effect which means the newborn nickel crystals will be attracted by these PVP templates, with time the newborn nickel crystals will grow along the PVP chains, it may be the reason why these linear nickel crystals formed are linear and spiky as observed in figures 2 and 5. The concept of surfactant-micelle formation could help to deduce the most likely reaction mechanisms for the formation of nano-sized Ni particles would be that these surfactant molecules (SDS) will also have this template effect on the formation of nickel particles. These surfactants reduce the interfacial tension between the newborn particles by adsorbing SDS at the liquid-metal interface so formed.

Our results clearly show that it is possible to synthesize nano-sized Ni-particles by using SDS alone which has some template effect. However, PVP has a definite template effect on the formation and retention of the nano-sized Ni particles; spherical/spiky nickel nano particles are formed due to template effects of PVP and SDS. As the reaction temperature is increased even finer particles are produced with an increase in the rate of particle formation.

In this research work nano-sized nickel particles/ aggregates were synthesized, TEM/SEM images show the presence of Ni particles which were as fine as 10 nm in diameter. The currently used NiCrAlY alloy powder size is much bigger than 100 um in diameter (Hussain et al., 2008). The ultimate aim is to synthesize nano-sized NiCrAlY alloy powders (less than 100 nm in diameter) for high temperature applications in aerospace and power generation industries in bulk quantities (Hussain et al., 2008).

Conclusions

Nano-sized nickel particles have been prepare by a

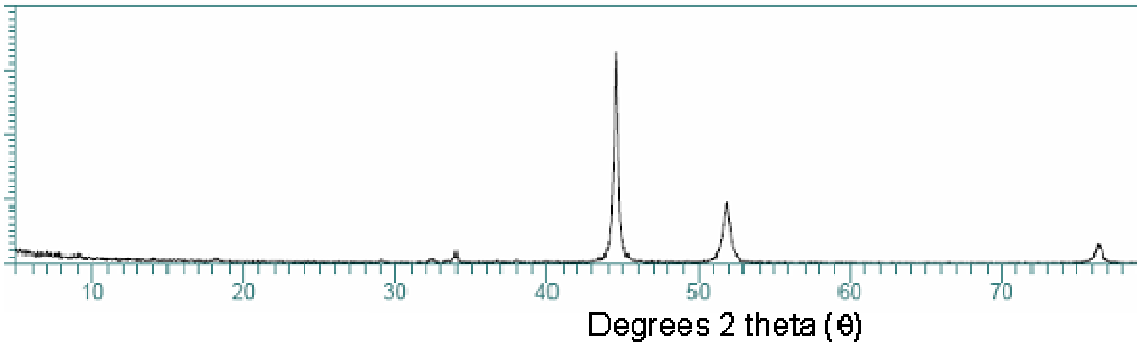

Figure 9. XRD pattern of Ni particles synthesized using SDS and PVP.

simple polymer-surfactant interaction of a cationic polymer polyvinylpyrrolidone (PVP) with an anionic surfactant, sodium-dodecyl-sulphate SDS in a strong basic medium. Our research shows that the rate of reduction increases as the temperature is increased from 60 to 100°C under reflux conditions; under these conditions the particles sizes formed are also much smaller. SEM/EDAX plots indicate when peak heights are reduced this seems like an indication of the presence of even finer particles. XRD studies show that the nickel crystals have fcc structure. The combination of SDS/PVP reaction produced nano-sized nickel particles which were much finer than the reactions where SDS was used on its own. PVP has shown some dispersion power, it has been found to be capable of preventing nickel particles from gradual agglomeration.

ACKNOWLEDGMENT

We thankfully acknowledge the technical support provided by National Nanotechnology Center at KACST. We would also like to thank Abdul Rahman Al Ghihab and Muath Ahmed Ababtain, National Nanotechnology Center at KACST for their co-operation and assistance with SEM and TEM work.

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