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Effect of Temperature on the Synthesis of Nano-Nickel Particles

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Abstract The focus of this study is to observe the effect of temperature on the size and morphology of nano-nickel particles. Nano-nickel particles have been prepared by a simple polymer-surfactant interaction of a cationic polymer poly vinyl pyrrolidone (PVP) with an anionic surfactant, sodium-dodecyl-sulphate SDS at different temperatures i.e. 60°C, 80°C and 100°C. Nano-sized nickel particles were synthesized by using nickel chloride as the precursor, hydrazine as the reducing agent in the presence of SDS and PVP in a strong basic medium (pH-10.2). Our research shows that the rate of reduction increases as the reaction temperature was increased from 60°C to 100°C. Finer particles of diameters less than 10nm were formed as the temperature was increased from 60 to 100°C. The morphology of the synthesized nano-nickel particles also varied as the temperature was increased. The concentration of nickel chloride and SDS/PVP was kept constant in all these experiments. The nano-sized nickel particles synthesized were characterized by using SEM and HRTEM.

Keywords Morphology, Hydrazine, Reduction, SEM, TEM

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1. Introduction

In the past two decades, considerable attention has been devoted to the synthesis of metallic nano-particles specially nano-nickel particles because of their unusual properties that differ from either the bulk or single atoms. During the 19th century and the first half of the 20th century the preoccupation with metal colloids was essentially confined within the academic communities as these materials offered excellent models for studying the relationships between the size, shapes and structure of the individual particles and their unique properties, such as , catalytic, optical, electrical and magnetic. During the second part of the last century, however, many of these properties have found applications in several fields of technology and as a result metallic particles ranging in size from few nanometres to ten of micrometers are today used extensively in electronics[1-4], catalysis[5-8], pigments[9] and metallurgy[10]. Several others applications such as bio-sensing[11-14], antimicrobial, non linear optics[15], high density magnetic storage[16], transparent conductive coatings[17] etc are still in early stages of development, but are expected to evolve rapidly within the next few years. More so than the traditional applications, these new technological fields require materials with controlled size, size distribution, morphology, composition, internal structure and surface characteristics. Consequently there is a renewed interest in the development of preparation techniques capable of tailoring these properties needs to support the technical progress of the existing applications and meet the challenges of the emerging ones.

There are three different processes used for the synthesis of metallic nano-particles[18,19]. First process is “phase breakdown” in which by supplying energy necessary to increase the specific surface area of the dispersed matter, the size of the bulk metal can be reduced to the desired dimensions. This can be done by the mechanical breakdown of the solid metals using ball milling or by dividing the molten metal in to droplets, which are subsequently solidified by rapid cooling. These two methods are not capable of generating uniform or mono dispersed metallic particles. Second process is “phase transformation method” in which metal compounds are converted into finely divided metallic particles by thermal decomposition (thermolysis or pyrolysis) or chemical reduction. By this process it is possible to prepare uniform metal particles of different shape. Third process is “phase build-up”, in this process metallic particles are constructed from their building blocks i.e. metal atoms. This may be in a gas phase i.e. chemical or physical vapour deposition or in a liquid phase i.e. chemical precipitation. Different techniques have been used to prepare the metal nano-particles, such as reduction of metal oxides and metal salts[20], sonochemical and thermal decomposition of metal complexes[21] and reduction in solution by strong reducing agents[22].

We report here synthesis of nano-nickel particles by a phase transformation method in which $NiCl_2$ is converted to nano sized Ni particles through a chemical reduction process

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using hydrazine as a reducing agent along with a cationic polymer and an anionic surfactant in a basic medium. Surfactants-covered water pools offer a unique microenvironment for the formation of nano-particles. They do not only act as micro reactors for the processing reactions but also inhibit the excess aggregation of the particles because the surfactants could adsorb on the surfaces of the particles when the particle size approaches that of water pool. As a result, the particles obtained in such a medium are generally very fine and monodispersed.

2. Experimental

Materials used for the synthesis of nano-nickel particles were nickel chloride analytical grade, sodium dodecyl sulphate, poly vinyl pyrrolidone, hydrazine hydrate solution sodium carbonate; de-ionized distilled water was used in the preparation of all the solutions. Instruments used for the preparation and characterization of nano-nickel particles were thermostatically controlled hot plate with magnetic stirrer, four necked round bottom flask, Condenser.

Nano-sized agglomerated Ni particles were synthesized by dissolving 8.78g of $NiCl_2$ (40 mmol) in a glass beaker containing 100ml of de-ionized distilled water at 40°C. The pH of the solution was maintained at 10.2 by adding Na_2CO_3 solution to the reacting solution. At this point the temperature of the solution was raised to 60°C and 30 mL of hydrazine was added to the solution. In order to study the effect of temperature on the formation of nano-nickel particles, same experiment was carried out at 80°C and 100°C.We observe that at 60°C as the reaction continues, the 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 ion reduction to reach completion. The particles from bottom of the reaction vessel were collected, centrifuged (4000 rpm), washed with distilled water and ethanol for three times, and finally desiccated at room temperature before characterization. Scanning Electron Microscope (SEM) FEI–NOVA 200Nanolab with EDAX and High Resolution Transmission Electron Microscope (HRTEM) JEOL - JEM 2100F had been used to characterize these synthesized nickel particles and elucidated results are discussed.

3. Results and Discussion

Metal atoms are formed by transferring of electrons from a reducing agent (Red^{m-}) to the oxidized metallic species M^{n+}

$$M^{n+} + Red^{m-}M^0+Ox^{m-n} \qquad (1)$$

where M^0 = metal atom produced by the gaining of electron from the reducing agent, Ox^{m-n} = species produced from the reducing agent after transferring electron to the metal ion, m and n are the charges. Transfer of electrons from the reducing agent to the metal ions mainly depends on the value of standard redox potential associated with the reaction ΔE^0.

For the information about mechanism of the reduction reaction, the value of ΔE^0 is also an excellent predictor of the rate of the chemical reaction. Generally an increase in its value is associated with a more rapid generation of atoms in the liquid phase. E^0 of equation (1) in a basic medium is -0.26 and for the equation (2) is -1.16. So the value of ΔE^0 then becomes -0.26 - (-1.16) = +0.939 V. The value of ΔE^0 for the reduction of by hydrazine in a basic medium is +0.939V, so it is possible to reduce ion by hydrazine in the basic medium. Ni^{2+} ion can be reduced as follows:

$$Ni^{2+} + 2e \rightarrow Ni \qquad (2)$$

In a basic medium hydrazine acts as a very strong reducing agent

$$N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e \qquad (3)$$

So the overall reaction for the reduction of Ni^{2+} by hydrazine in a basic medium is as follows:

$$Ni^{2+} + N_2H_4 + OH^- \rightarrow Ni + N_2 + H_2O \qquad (4)$$

In order to increase the pH to10.2 concentrated sodium carbonate solution was added to the $NiCl_2$ solution. However, as the sodium carbonate dissolves in water it forms NaOH which then react with $NiCl_2$ and form $Ni(OH)_2$

$$Na_2CO_3 + H_2O = NaOH + H_2CO_3 \qquad (5)$$

$$NaOH + NiCl_2 = Ni(OH)_2 + NaCl \qquad (6)$$

Hence, the Ni^{2+} ions from the compound $Ni(OH)_2$ are reduced to Ni atoms as shown in equation (4).

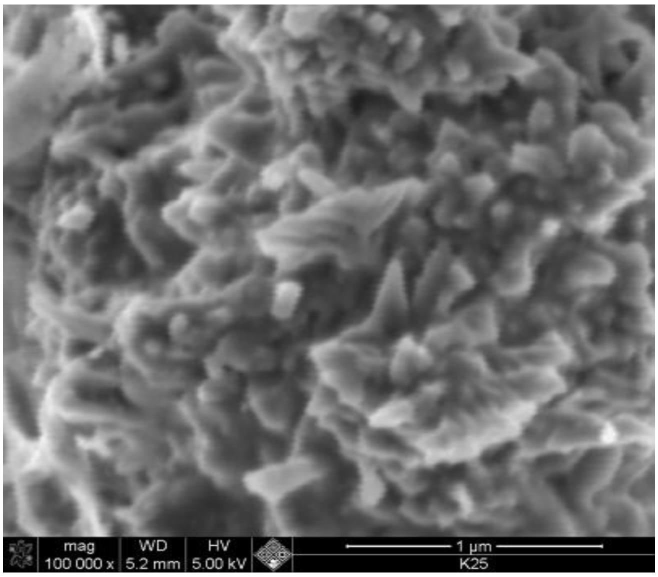

Figure 1. SEM image nano nickel particles synthesized at 60°C, mag x100,000

Figure 1 shows SEM image of the nano-nickel particles that was synthesized using hydrazine with SDS and PVP at a reaction temperature of 60°C. The SEM image shows the presence of spherical shaped particles.

Fig 2 shows SEM image of nano nickel particles synthesized using hydrazine with SDS and PVP at a reaction temperature of 80°C. SEM image shows that the particles have both spherical and little spiky shaped.

Fig 3 shows SEM image of the nano-nickel particles which were synthesized using hydrazine with SDS and PVP at a reaction temperature of 100°C. Here the SEM image shows that the particles have a kind of spiky morphology and there is a presence of hexagonal shaped structure. Experimental results show that by increasing the reaction temperature morphology of the synthesized nano-nickel particles changes from spherical, spherical spiky and to a combination of mixed hexagonal and spiky structures. As the temperature of the reaction is increased the kinetics of reaction is likely to increase with time. More newborn particles are nucleated by the reduction process and hence much finer particles can be expected to be formed.

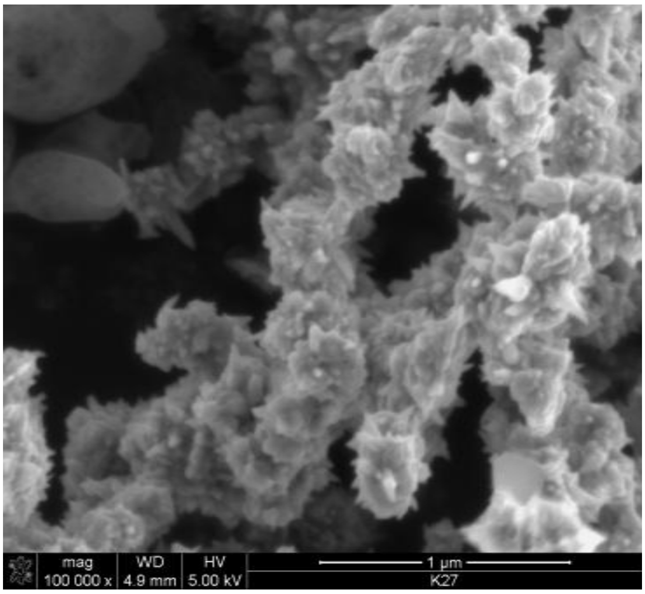

Figure 2. SEM image of nano nickel particles synthesized at 80°C mag x 80,000

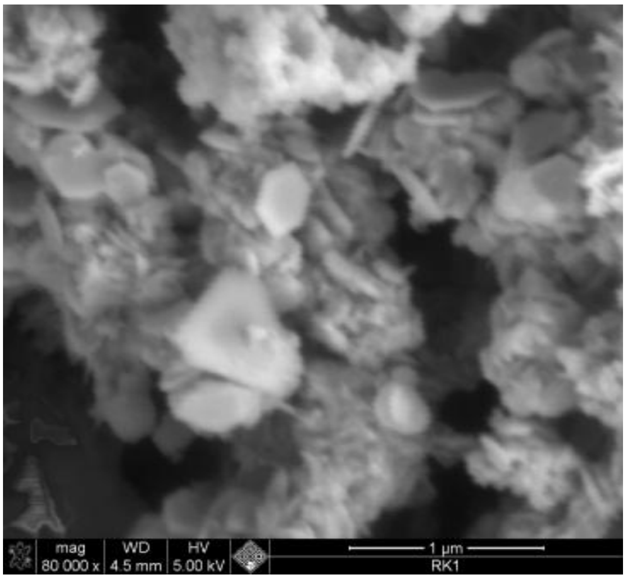

Figure 3. SEM image of nano nickel particles synthesized at 100°C mag x80,000

Figure 4 shows TEM image of the nano-nickel particles synthesized using hydrazine with SDS and PVP at a reaction temperature of 60°C. Figure 4 shows that synthesized nano-nickel particles are around 31nm in diameter. Size of the nickel nano-particles were determined using the scale bar at the bottom left of the figure 4. Fig 5 shows image of the nano-nickel particles synthesized using hydrazine with SDS and PVP at a reaction temperature of 80°C. Figure 5 shows that synthesized nano-nickel particles are around 20nm in diameter. Size of the nickel nano-particles are determined using the scale bar at the bottom left of the figure 5.

Fig 6 shows TEM image of the nano-nickel particles that were synthesized using hydrazine with SDS and PVP at a reaction temperature of 100°C. The image shows that synthesized nano-nickel particles are around 10nm in diameter. Size of the nickel nano-particles are determined using the scale bar at the bottom left of the figure 6.

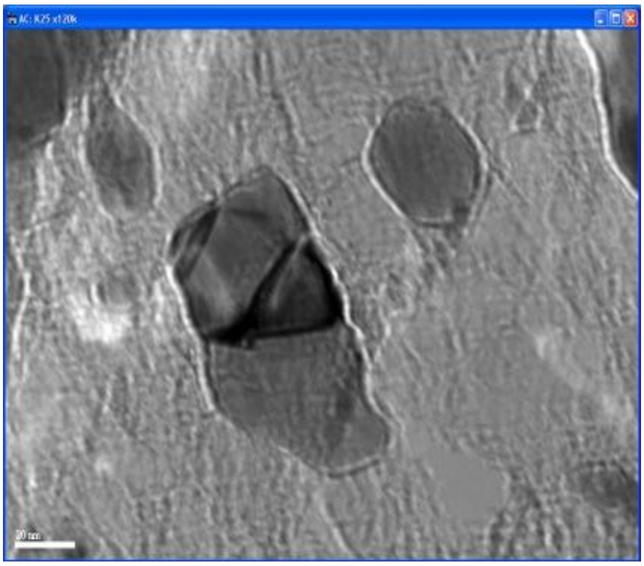

Figure 4. TEM image of nano-nickel particles synthesized at 60°C

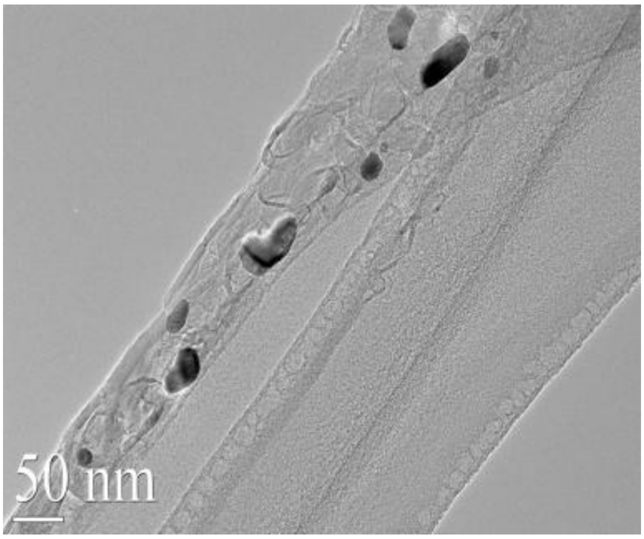

Figure 5. TEM image of nano-Ni particles synthesized at 80°C

TEM images also show quite clearly that the diameter of the nickel particles had decreased considerably as the reaction temperature was increased from 60 to 100^0C. At increased temperatures not only the rate of nucleation would increase but one would also expect these Ni particles to have higher energy and hence move around with higher speed. Therefore we expect these particles would rather move around until they lose all the energy and as a consequence they would not get enough time to be agglomerated.

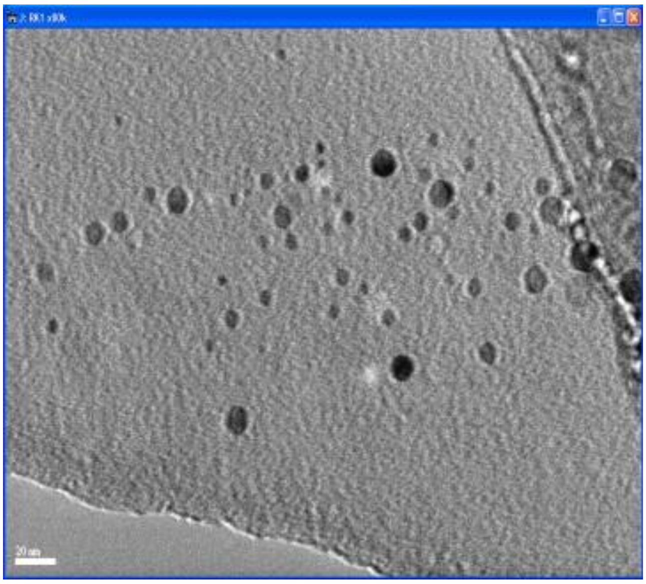

Figure 6. TEM image of nano-Ni particles synthesized at 100°C

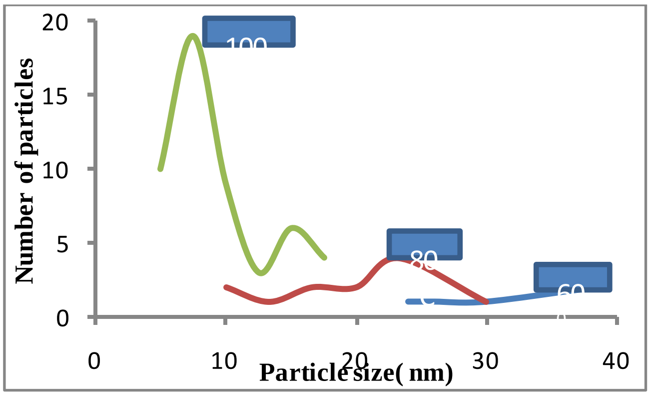

Figure 7. Plot of Particle size versus number of particles at different temperature

Figure 7 is the plot of particle size versus number of particles at different temperature. This plot shows the particle size distribution at different temperature and finest Ni particles were formed when SDS was used with PVP at a reaction temperature of 100°C. The particle size formed were less than 10 nm in diameter (Fig 6). Ni particles synthesized at a reaction temperature of 80°C were around 20 nm in diameter (Fig 5). Ni particles synthesized at a reaction temperature of 60°C are around 31nm in diameter (Fig 4). These results are summarized in Table 1.

Table 1. Effect of Temperature on the particle size

Temperature	Average Particle size	Range
60°C	31 nm	14
80°C	19 nm	23
100°C	10 nm	13

Nano-crystalline nickel has been synthesized by a chemical reduction process in which $NiCl_2$ is converted to nano sized Ni particles through a chemical reduction process using hydrazine as a reducing agent along with a cationic polymer and an anionic surfactant in a basic medium. Temperature has been found to play a significant role in the synthesis of nano-Ni particles. As the reaction temperature was increased from 60 to 100^0C, the particle size decreased. Smallest particles were formed at 100^0C. As the reaction continued these particles did not combine with neighbouring atoms and molecules to form clusters/agglomerates. It seems that the anionic surfactant had been able to provide the unique microenvironment required for the formation of nano-particles. This surfactant was able to minimize or inhibit the formation of excessive clusters/agglomerates of Ni atoms which were not able to form large scaled Ni particles/agglomerates. Using this chemical reduction process it has been possible to obtain nickel particles which were as fine as 10nm. Among currently available nano-particles, magnetic variants are used in a wide range of research area, including catalysis, biomedicine and magnetic resonance imaging (MRI), generally on the basis of their functional versatility. Nickel particles synthesized in this project has been used in the synthesis of NiCrAl alloy particles for aerospace applications.

4. Conclusions

Nano-sized nickel particles have been prepared by using a "phase transformation" method by using a chemical reduction process. In order to study the effect of temperature on the particle size, experiments were carried out at different temperatures i.e. 60, 80 and 100°C. SEM characterization showed that Ni particles synthesized at lower temperatures were almost spherical but as the temperature was increased particles showed very spiky morphology. However, finest Ni particles of less than 10nm in diameter were formed at 100^0C. TEM characterization confirmed this inverse relationship i.e. Ni particle size decreased as the reaction temperatures were increased from 60 to 100^0C. The focus of this study is in the applications of nano-Ni particles in aerospace and medical/biological applications.

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