Science Press

ARTICLE

Synthesis of Nickel powders by Hydrazine Hydrate Reduction of Nickel Hydroxide

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Abstract: Fine nickel powders with a narrow particle size distribution was prepared by reducing nickel hydroxide in an aqueous solution. The study analyzed nickel powder formation and reduction pathways, discussing the effects of the molar ratio of hydrazine hydrate to nickel hydroxide, hydrazine concentration, and the amount of surfactant PEG6000 on particle size, surface morphology, and dispersion. X-ray diffraction (XRD), scanning electron microscopy (SEM), and laser particle size analysis revealed that nickel particle nucleation occurred on the nickel hydroxide surface, which gradually dissolved during the reaction. Increasing the molar ratio of hydrazine to nickel hydroxide initially decreased and then increased the nickel particle size. Higher hydrazine concentrations reduced particle size. A small amount of PEG6000 improved dispersion, while higher amounts preserved the morphology of nickel hydroxide. Adjusting the surfactant amount allowed control of the average particle size between 1-2μm.

Key words: Nickel hydroxide; liquid-phase reduction; dispersibility; surfactant

Extensive study has been performed over the past two decades on the production of micro/nano nickel powder due to its potential applications in Absorbing Materials, Multi-layer Ceramic Capacitors (MLCC), catalyst and electrode material[1-7]. Several procedures have been used to produce nickel powder including vapor phase method[8,9], spray pyrolysis[10], micro-emulsion[11], polyol process[12-15], and liquid-phase reduction[16-22].

Among these options, liquid-phase reduction has become well recognized for its ability to precisely manipulate the composition, size, and shape of nickel powder. An example approach involves the reduction of nickel salts (such as $NiCl_2$ and $NiSO_4$) using hydrazine hydrate in alkaline conditions[23,24]. Acidic solutions cause the standard reduction potential of hydrazinium ion $N_2H_5^+$ to be -0.23V. The reaction can be represented as follows:

$$N_2 + 5H^+ + 4e^- \rightarrow N_2H_5^+ \tag{1}$$

Hydrazine (N_2H_4) exhibits a standard reduction potential of -1.16 V in alkaline solutions.

$$N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^- \tag{2}$$
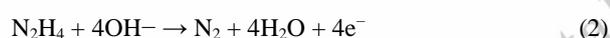
Conversely, the conventional reduction potentials for Ni^{2+} and $Ni(OH)_2$ as sources of nickel are -0.25 V and -0.72 V, respectively[25].

$$Ni^{2+} + 2e^- \rightarrow Ni \tag{3}$$

$$Ni(OH)_2 + 2e^- \rightarrow Ni + 2OH^- \tag{4}$$

This indicates that reducing nickel hydroxide requires a higher overpotential and is more challenging than reducing nickel ions. While extensive research has been conducted on the effect of hydrazine in alkaline environments on the size and shape of nickel powders from nickel salts, no literature has yet reported on the direct reduction of nickel hydroxide in aqueous solution using hydrazine. This paper presents the preparation of nickel powder via the direct reduction of nickel hydroxide with hydrazine and explores its reduction pathways.

1 Experiment

1.1 materials

The utilized materials included $Ni(OH)_2$, 80% $N_2H_4 \cdot H_2O$, and polyethylene glycol 6000 (PEG6000). All

reagents used were of analytical quality and did not necessitate additional purification.

1.2 Preparation of Nickel Powder

The molar ratio of hydrazine hydrate to nickel hydroxide is denoted as K, hydrazine concentration as C, and surfactant amount as X. To study the reduction process of $Ni(OH)_2$ in hydrazine, a composition ratio of K=5 and C=1.5 was chosen. At 60℃, 1.58g of $Ni(OH)_2$ was mixed with a certain amount of water and stirred. $N_2H_4 \cdot H_2O$ was then added to react, with sampling at different times to elucidate the transformation process of $Ni(OH)_2$ during reduction. Depending on reaction time, the powder color varied from green to dark green to black. To investigate the effects of different K, C, and X values, the mixture was thoroughly stirred for 3-5 hours to ensure complete reaction. The resulting powders were then washed three times with deionized water and anhydrous ethanol by centrifugation and filtration, followed by drying at 60℃ in a ventilated oven for 24 hours.

1.3 Characterization

The nickel powder was subjected to phase analysis using X-ray diffraction (Rigaku, D/Max−2000). The morphology and dispersity of the powder were analyzed using scanning electron microscopy (SEM). Particle size and size distribution were analyzed using a laser particle size analyzer (Malvern2000, measurement range: 0.01 – 1000μm).

2 Results and Discussion

2.1 Formation of Nickel Particles and Their Reduction Pathways

According to traditional methods, the equation representing the reaction of hydrazine reducing nickel salts in an alkaline environment is as follows[26]:

$$2Ni^{2+} + N_2H_4 + 4OH^- \rightarrow 2Ni + N_2 + 4H_2O \qquad (5)$$
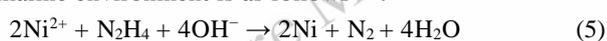
In addition, two side reactions also take place[26]:

$$N_2H_4 \rightarrow N_2 + 2H_2 \qquad (6)$$

$$3N_2H_4 \rightarrow N_2 + 4NH_3 \qquad (7)$$

Nevertheless, the mechanisms by which hydrazine is reduced and nickel nucleates when nickel hydroxide is employed as the source of nickel are still unidentified. The X-ray diffraction patterns of samples obtained at reaction times of 30min, 45min, 60min, 75min, and 90min are shown in Fig.1. The diffraction peak labeled with (◆) signifies the presence of the hexagonal phase of $Ni(OH)_2$, whereas the peak labeled with (♣) corresponds to the face-centered cubic metallic Ni phase. When the reaction time is 30 minutes, there is no evidence of nickel nucleation, indicating that there is a period of induction in the reduction of nickel hydroxide by hydrazine. After a duration of 45 minutes, the diffraction peak of nickel becomes perceptible, albeit it exhibits a rather weak intensity. This suggests that certain nickel particles have entered the in-

duction period and begun nucleation. After a period of 60min, the amplitude of the diffraction peak for nickel particles amplifies, while the amplitude of the diffraction peak for nickel hydroxide diminishes. This indicates a significant time of nickel nucleation. After 75min of processing, only nickel diffraction peaks are observed, while those of nickel hydroxide are not present. This suggests that the nickel particles generated in the earlier stage are starting to increase in size, and the nickel hydroxide has been entirely reduced. Upon reaching a duration of 90 minutes, the diffraction peaks indicate the existence of a distinct nickel phase without impurities.
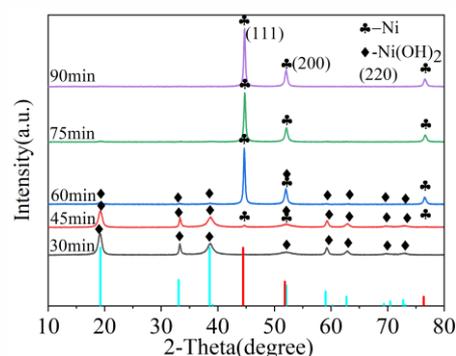
Fig.1 XRD patterns of samples at reaction times of 30 min, 45 min,60min, 75 min, and 90 min

Fig.2 depicts the physical structure of nickel powder that was produced through the direct reduction of nickel hydroxide using hydrazine hydrate. After 30 minutes, the nickel is still in the induction period and has not yet formed nuclei. The scanning electron microscope (SEM) image simply displays nickel hydroxide. As the reaction period lengthens, minute particles start to form on the surface of the nickel hydroxide. These particles, as indicated by the X-ray diffraction patterns, are nickel particles generated during reduction. During the course of the reaction, additional nickel particles are produced. The majority of these particles stick to the surface of the nickel hydroxide, creating a core-shell structure composed of nickel and nickel hydroxide. However, a portion of the particles separate from the sur-face of the nickel hydroxide. Following the reaction, the SEM pictures no longer show any trace of nickel hydroxide, suggesting that it has been fully reduced by hydrazine.

Additionally, the nickel particles have suffered some degree of agglomeration. The agglomerates maintain some features of the nickel hydroxide in terms of shape and particle size, as a result of the formation and enlargement of nickel particles on the surface of the nickel hydroxide, followed by the aggregation caused by van der Waals forces.

This implies that the process of reducing nickel hydroxide with hydrazine involves the interaction between hydrazine and nickel hydroxide on the surface of the latter. Nickel atoms form clusters on the surface of the nickel hydroxide instead of being dispersed in the solution. Throughout the reaction, the

nickel hydroxide gradually dissolves and vanishes, while the nickel nuclei undergo growth and agglomeration as a result of van der Waals forces and magnetic attraction. The equation representing the reaction between hydrazine and nickel hydroxide in this approach is as follows:

$$2Ni(OH)_2 + N_2H_4 \rightarrow 2Ni + N_2 + 4H_2O \qquad (8)$$
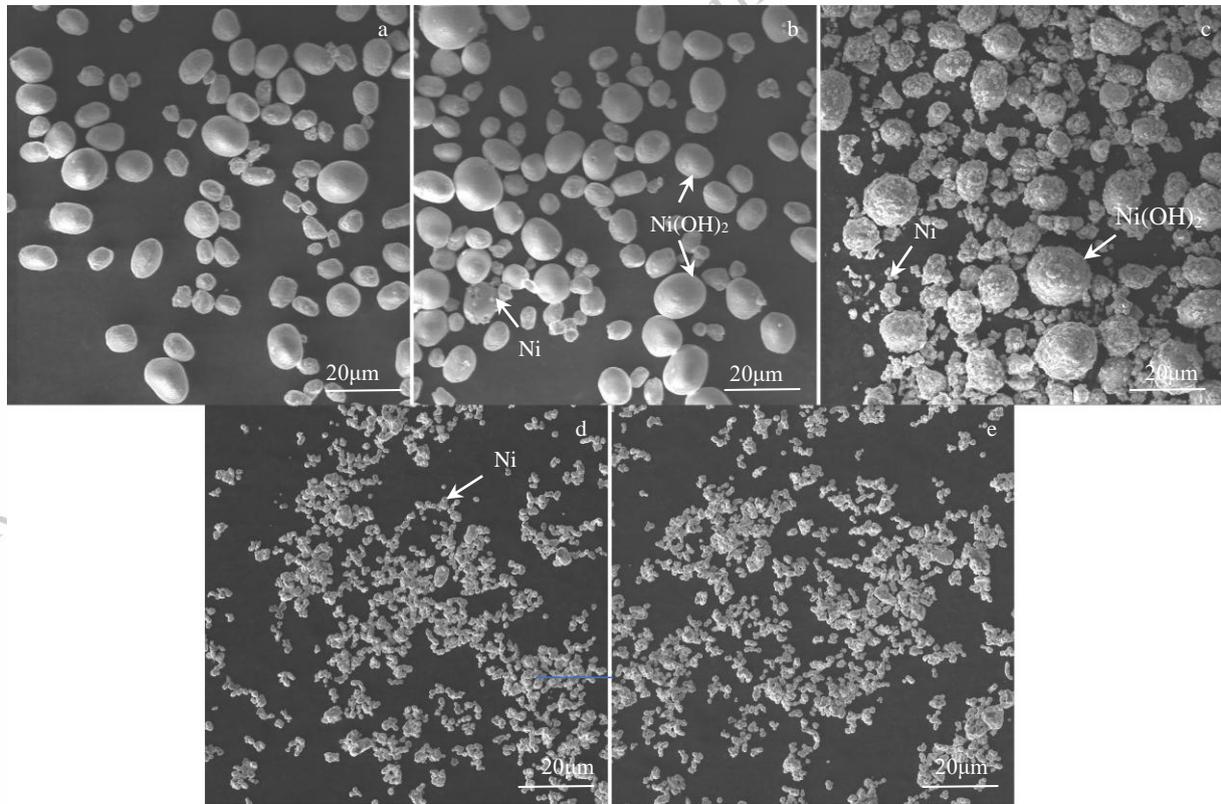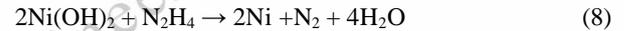
Fig.2 SEM micrographs of samples at reaction times (a) 30 min; (b) 45min; (c) 60 min; (d) 75 min; (e) 90 min
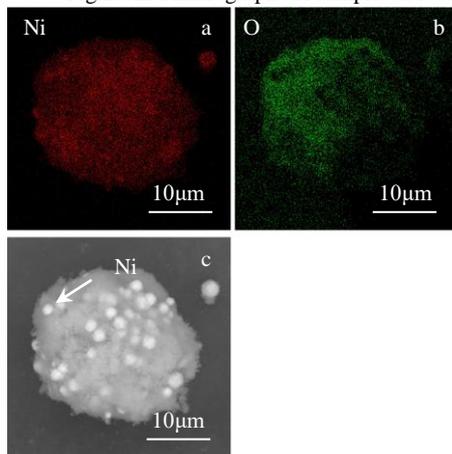
Fig.3 EDS element mappings (a–b) and SEM image (c) of a reaction time of 60 min

To further investigate the product variations during the reduction process, a map scan was performed on the mixed powder after a reaction time of 60 minutes, as shown in Fig 3a-c. The Ni element represents the reduced Ni, while the O element corresponds to nickel hydroxide. The results indicate distinct enrichment and depletion regions for Ni and O elements, with Ni-enriched regions aligning with O-depleted areas. Combined with XRD and SEM analyses, this confirms that nickel nucleates on the surface of nickel hydroxide rather than in the solution.

2.2 Effect of the Molar Ratio of Hydrazine Hydrate to Nickel Hydroxide

Equations (3) and (4) demonstrate that hydrazine hydrate necessitates a lesser potential for the reduction of nickel hydroxide in comparison to nickel salts.

Fig.4 displays the X-ray diffraction (XRD) patterns of nickel powders that were made using different molar ratios of hydrazine hydrate to nickel hydroxide. These ratios are represented by the symbols K=3, 4, 5, 6, and 7, respectively. The diffraction peaks labeled with (♣) correspond to the face-centered cubic (fcc) metallic nickel (Ni) phase. Equation (8) indicates that the minimal molar ratio should be 0.5. However, the presence of side reactions (equations (6) and (7)), which are catalyzed by nickel and cause the decomposition of hydrazine hydrate, substantially raises this ratio. The peaks observed at 44.35℃ (111),51.91℃ (200), and 76.42℃ (220) in Fig.4 correspond to the standard diffraction data. These peaks confirm the formation of pure elemental nickel powder at various molar ratios ranging from 3 to 7.

Fig.5 depicts the physical structure of nickel particles that were produced using various ratios of reactants. The molar ratios of the reactants are denoted as K=3, 4, 5, 6, and 7, which match to Figure 5a-e. The Ni powder formed by directly re-

ducing nickel hydroxide with hydrazine hydrate has a primary particle size of around 0.5-2μm.
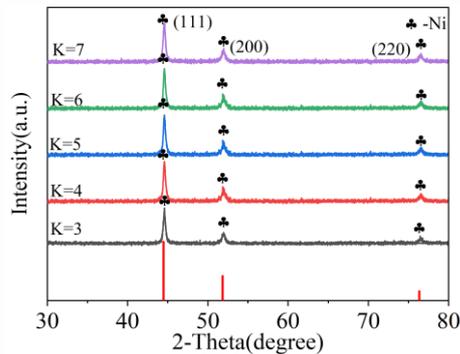
Fig.4 XRD patterns of samples prepared at molar ratios of 3, 4, 5, 6, and 7

The primary particles agglomerate to generate secondary particles. As the molar ratio of the reactant increases, the primary particle size of the resultant Ni powder initially falls and subsequently increases. When the molar ratio of reactants is less than or equal to 4, both the rate of nucleation and the number of nuclei for Ni are low, leading to a comparatively larger primary particle size. Simultaneously, the sluggish reaction rate prevents the Ni particles from separating from the nickel hydroxide surface and forming connections with one another during particle development. When the molar ratio of reactants is equal to or greater than 5, the reaction proceeds rapidly, resulting in the formation of a significant number of nickel nuclei during the initial stage of the reaction. These nuclei detach off the surface of nickel hydroxide. Following separation, the size of the primary Ni particles reduces and the process of agglomeration becomes less pronounced.
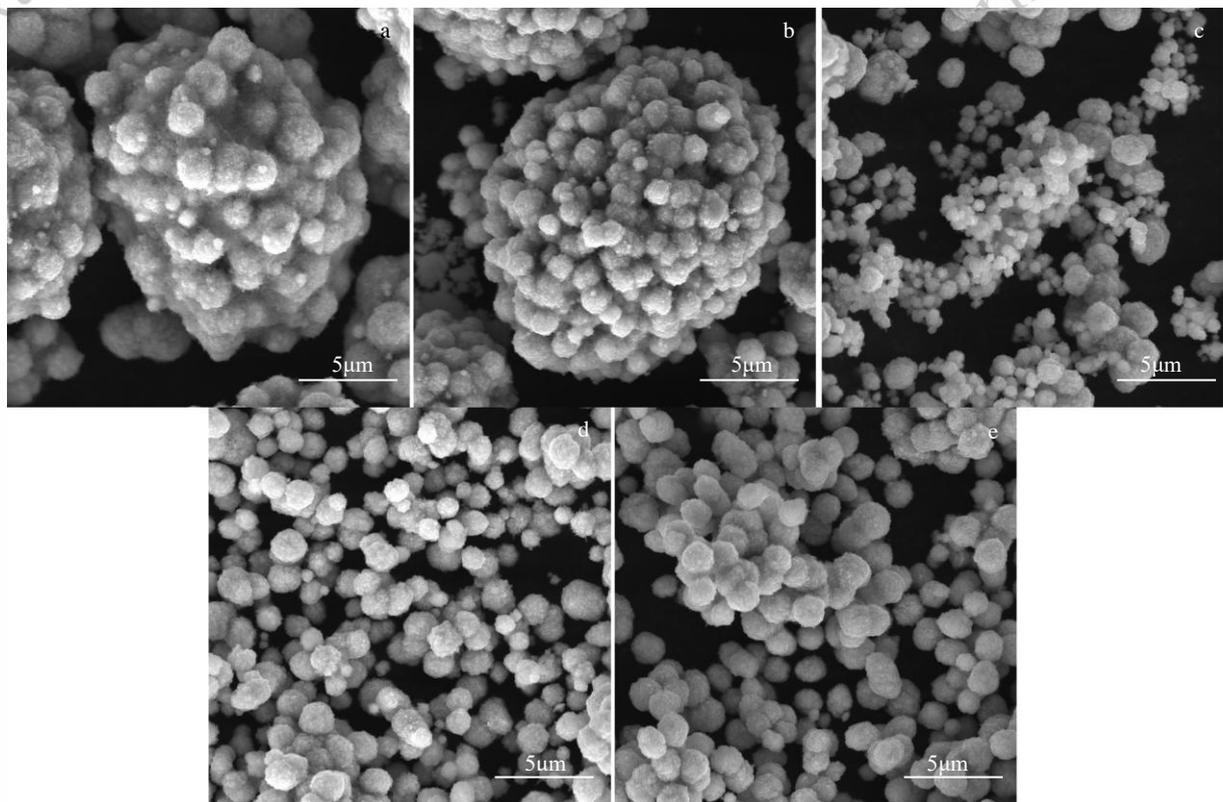
Fig.5 SEM micrographs of samples prepared at molar ratios of 3, 4, 5, 6, and 7. (a) K=3; (b) K=4; (c) K=5; (d) K=6; (e) K=7

Fig.6 depicts the trends in the average particle sizes D10, D50, and D90 of nickel powder manufactured at different molar ratios. The average size of the nickel particles initially decreases and subsequently increases as the molar ratio increases. The minimum values for D10, D50, and D90 are achieved when the molar ratio is 5. The laser particle size analysis results are consistent with the observations acquired using the scanning electron microscope (SEM).
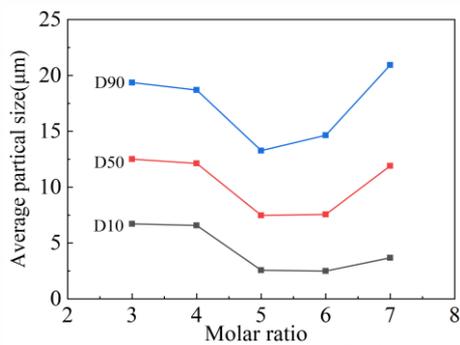
Fig.6 Trends in the average particle sizes of nickel powder
prepared at various molar ratios

Fig.7 XRD patterns of samples with Hydrazine Hydrate Concentration at 1, 1.5, 2, 3, and 4

2.3. Effect of Hydrazine Concentration

With a fixed reaction molar ratio of 5, Fig.7 illustrates the X-ray diffraction patterns for nickel powder prepared with hydrazine hydrate concentrations of 1mol/L, 1.5mol/L, 2mol/L, 3mol/L, and 4mol/L, denoted as C=1mol/L to C=4mol/L, respectively. The diffraction peaks marked with (♣) correspond to the face-centered cubic metallic Ni phase. From Fig.6, it is evident that each concentration yields nickel single-phase powders upon re- action completion. This indicates that varying the hydrazine hydrate concentration does not affect the endpoint of the reaction. When sufficient hydrazine is present, the final reaction product is independent of its relative concentration.

Fig.8 shows micrographs of nickel particles prepared at different hydrazine hydrate concentrations. From Figures 8a to 8e, the primary particle size of nickel powder produced by direct reduction of nickel hydroxide with hydrazine ranges from approximately 0.5 to 5µm. These primary particles tend to agglomerate into secondary particles. As the hydrazine hydrate concentration increases, the primary particle size decreases. This occurs because at lower concentrations, fewer nickel particles nucleate after the induction period, allowing subsequent nucleation and growth more readily on existing particles, resulting in larger primary particles. When the concentration is C 1.5, the slower reaction rate allows nickel particles to grow and fuse on the nickel hydroxide surface, forming larger secondary agglomerates. At concentrations C 2, the reaction rate is rapid, causing many nickel nuclei to form early and detach from the nickel hydroxide surface. These detached nickel particles cannot grow effectively, leading to smaller primary particle sizes and reduced agglomeration, with only van der Waals and magnetic forces contributing to weak aggregation.
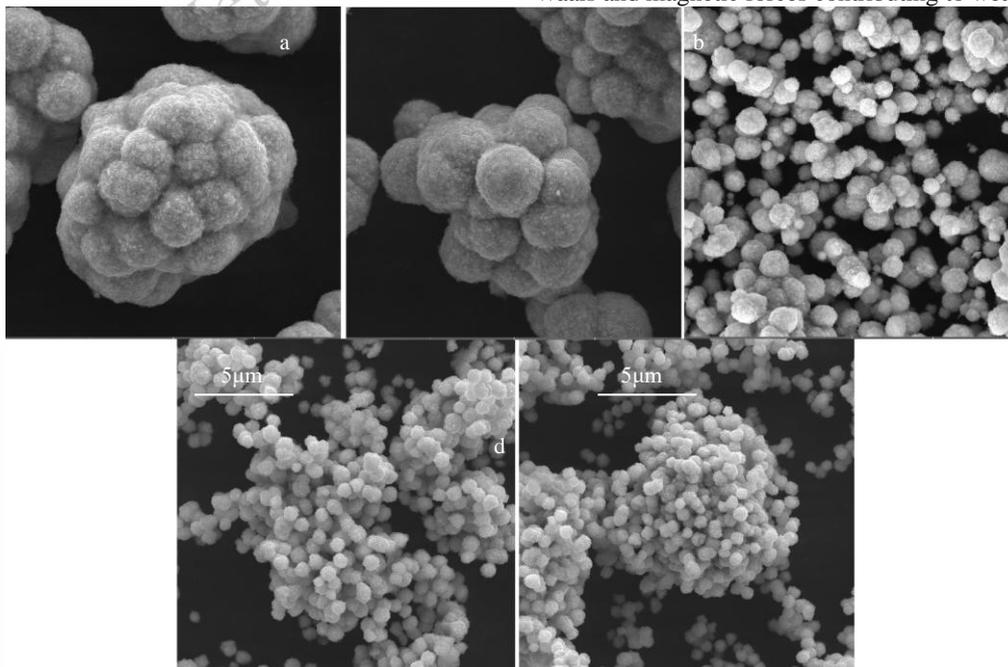
Fig.8 SEM micrographs of samples with hydrazine hydrate concentrations:(a) C=1; (b) C=1.5; (c) C=2; (d) C=3; (e) C=4

Fig.9 illustrates the trend in average particle size (D10, D50, D90) of nickel powder at various hydrazine hydrate
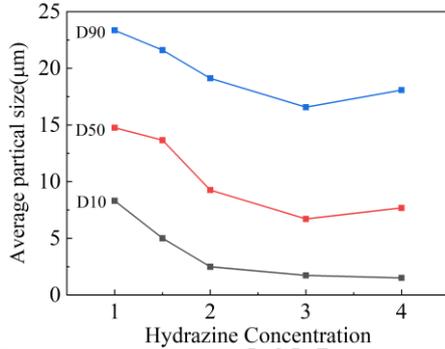
concentrations.

Fig.9 Trend of average particle size of nickel powder at varying hydrazine hydrate concentrations

The average particle size decreases initially with increasing hydrazine concentration and then increases, reaching a minimum at C=3.The laser particle size analysis results align with the SEM observations.

2.4. Effect of Surfactant Addition Dosage

The dosage of clustering of nickel powders formed during the reaction can be modified by adjusting various molar ratios and relative concentrations in the process. Huang et al.[27] conducted a study on the influence of several surfactants on the reduction of nickel salts using hydrazine hydrate in alkaline conditions. The findings revealed that the nonionic surfactant polyethylene glycol 6000 (PEG6000) shown effective dispersion capabilities inside the reaction system. The predetermined stoichiometric ratio was K=5, and the concentration of hydrazine hydrate was C=3mol/L. Fig.10 displays the X-ray patterns of nickel powders that were generated with different dosages of surfactant addition, specifically at mass ratios of 0.25. Fig.10 illustrates that the inclusion of surfactants has no impact on the phase composition of the resulting reaction product.
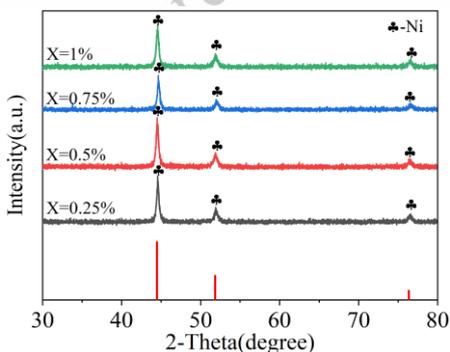
Fig.10 XRD patterns of samples with surfactant addition dos age of 0.25%, 0.5%, 0.75%, and 1%

Fig.11 illustrates the micrographs of nickel powders that were created using varying degrees of surfactant addition.Fig.11a-d depict two distinct results resulting from the direct reduction of nickel hydroxide using hydrazine hydrate in the presence of a surfactant. Fig.12 illustrates the impact of several dosage of PEG6000 addition. When the concen-

tration of X is less than or equal to 0.5%, a minimal quantity of surfactant is found in the solution system, with a portion attaching to the surface of nickel hydroxide. During the initial stages of the reaction, a large number of nickel particles separate from the surface of nickel hydroxide due to fast reaction rates. These particles are then isolated by PEG6000 in the solution system, which effectively prevents them from aggregating due to van der Waals and magnetic forces. When the concentration of X is equal to or more than 0.75%, a significant quantity of PEG6000 is present in the solution system, forming connections with one another. Prior to the reaction, every particle of nickel hydroxide is completely surrounded with PEG6000.Upon initiation of the reaction, nickel particles promptly emerge within the nickel hydroxide coating and are unable to disengage and enter the solution. Consequently, the aggregates that are produced following the reaction maintain the size and shape properties of the original nickel hydroxide, leading to smaller individual particles and considerably bigger aggregate particles.

Fig.13 depicts the changing patterns of the average particle size (D10, D50, D90) of nickel powder when varying dosages of surfactant are added during preparation. The mean diameter of nickel powders initially drops and subsequently increases as the amount of surfactant added increases. At an increase of X=0.5%, the values of D10, D50, and D90 all reach their minimum dosages. The laser particle size analysis findings align with the scanning electron microscope (SEM) results.
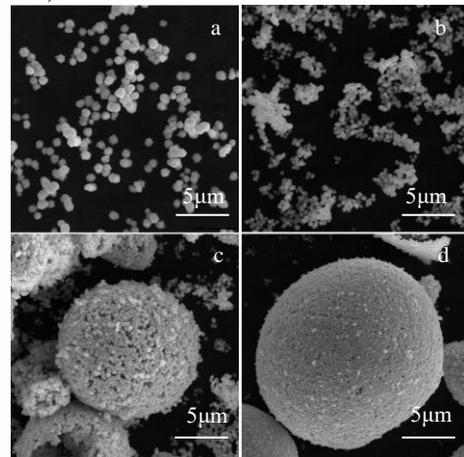
Fig.11 SEM micrographs of samples with surfactant addition dosage of 0.25%, 0.5%, 0.75%, and 1%: (a) X=0.25%;(b) X=0.5%; (c) X=0.75%; (d) X=1%
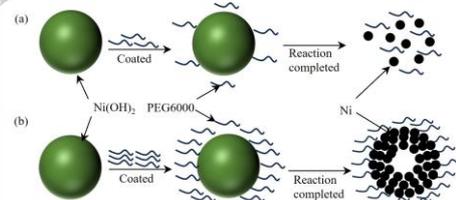
Fig.12 Pathways of the impact of different surfactant addition dosage: (a) X=0.25%; (b) X=1%
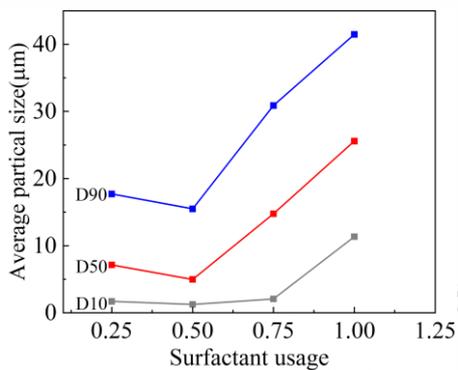
Fig.13 Variation trend of average particle size of nickel powder with different surfactant usage dosage

3. Conclusion

1) Nickel is nucleated on the surface of nickel hydroxide by reduction with hydrazine hydrate.

2) The optimum technological parameters for preparing the ultrafine nickel powder with high purity and spherical shape are as follows: reaction temperature of 60°C, the molar ratio of hydrazine hydrate to nickel hydroxide is 5, the concentration of hydrazine hydrate is 3mol/L, the surfactant addition dosage is 0.5%.

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水合肼还原氢氧化镍合成镍金属颗粒

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摘　要： 用氢氧化镍在水溶液中被还原制备了窄粒度分布的微细镍粉，分析了镍颗粒的形成和还原途径，讨论了水合肼与氢氧化镍摩尔比、水合肼浓度和表面活性剂 PEG6000 的添加量对镍颗粒的粒径大小、表面形貌和分散性的影响。通过 X 射线衍射（XRD）、扫描电子显微镜（SEM）和激光粒度分析，发现镍颗粒在氢氧化镍表面完成形核，反应过程中氢氧化镍逐渐溶解。随着水合肼与氢氧化镍反应摩尔比的提高，镍颗粒的粒径先变小后变大；随着水合肼浓度的提高，镍颗粒的粒径变小；表面活性剂 PEG6000 的少量添加使镍颗粒的分散性得到改善，更高的表面活性剂添加量使镍一次颗粒趋于保留氢氧化镍的形貌。通过调节表面活性剂添加量可以使平均粒径控制在 1-2μm。

关键词： 氢氧化镍、液相还原、分散性、表面活性剂