

## Effect of surfactants on dispersion property and morphology of nano-sized nickel powders

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**Abstract:** Fine face-centered cubic (FCC) nickel powders were synthesized by liquid phase reduction with different surfactants. The products were investigated by scanning electron microscopy (SEM), laser particle size analyzer and X-ray powder diffraction (XRD). The results indicate that the type, dosage and relative molecular mass of surfactants significantly impact the purity, dispersion property, particle size, size distribution and morphology of the products. The nonionic surfactants poly ethylene glycol (PEG) and polyethylene glycol sorbitan monostearate (Tween) showed better dispersing ability in the reaction system than the others. The optimal mass ratios of surfactant to Ni are 100 mg/g and 150 mg/g for PEG-600 and Tween-40, respectively. The products obtained in the optimal conditions have ideal morphology and narrow size distribution. Moreover, study on the relative molecular mass effect revealed that with the increase of the relative molecular mass of Tween, the morphology of nickel powders changed from sphere to spiny ball.

**Key words:** nickel powder; surfactant; dispersion; morphology; synthesis

### 1 Introduction

Due to the high surface activity, low resistivity, great thermal and electrical conductivities, nano-sized nickel powder has been widely used as magnetic material [1–3], electrical conductive paste [4,5], catalyst [6–8], electrode material [9] and binder for cemented carbide [10]. With respect to the application of nano-materials, a frequently encountered problem is the aggregation of the nano-sized particles, especially when the particle size decreases to a considerably small extent. During the past decades, many efforts have been directed to the development of nickel powders with well-defined morphology and favorable dispersion property.

Till now, several synthetic methods, such as laser-driven synthesis [11,12], spray pyrolysis [13,14], micro-emulsion [15], polyol process [16–18], vacuum pyrolytic decomposition [19,20], hydrothermal method [21] and liquid phase reduction [22–24], have been developed to prepare the nickel powders. Among these methods, liquid phase reduction has been intensively investigated because of its better control of the composition, low reaction temperature and simple

procedure. For this method, amphiphilic surfactants like poly vinyl pyrrolidone (PVP) and poly ethylene glycol (PEG) have been widely used as dispersing agents to control the dispersion and morphology of the products [25–29]. The reason lies on the following two aspects. On the one hand, amphiphilic surfactants have unique ability to self-organize in solution, which can modify the interfacial property and enhance the compatibility between particles of different characteristics. On the other hand, amphiphilic surfactants dissolved in water are inclined to form thermodynamically stable supramolecular assemblies such as micelles and microemulsions, which can be used as nano-reactors for nickel particles with certain shapes and size distributions. Hence, the systematical research on the effect of surfactants on the dispersion property and morphology of nickel powder is much required.

In this work the effect of surfactants on the synthesis of nano-sized nickel powders was studied. The nickel powders were synthesized by reducing nickel sulfate in aqueous hydrazine solution with a variety of surfactants including cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl sulfate (SDS), PVP, PEG, poly oxyethylene tert-octylphenyl (Trion X-100),

triethanolamine (TEA) and polyethylene glycol sorbitan monostearate (Tween). The influence of surfactants on the purity, dispersion property, particle size and distribution of the nickel products was investigated. Meanwhile, the relationship between the relative molecular mass of surfactants and the morphology of the product was discussed.

## 2 Experimental

### 2.1 Materials and reagents

All reagents were analytical grade.  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (The relative molecular mass ( $M_r$ ) is 262.85), 85%  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  ( $M_r=50.06$ ) and  $\text{NaOH}$  ( $M_r=40.00$ ) were used as source materials. And CTAB ( $\text{C}_{19}\text{H}_{42}\text{BrN}$ ,  $M_r=364.45$ ), SDS ( $\text{C}_{12}\text{H}_{25}\text{NaO}_4\text{S}$ ,  $M_r=288.38$ ), TEA ( $(\text{HOCH}_2\text{CH}_2)_3\text{N}$ ,  $M_r \approx 149.19$ ), PVP ( $(\text{C}_6\text{H}_9\text{NO})_n$ , average  $M_r \approx 30000$ ), PEG-600 ( $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ , average  $M_r \approx 600$ ), Triton X-100 ( $\text{C}_{14}\text{H}_{22}\text{O}(\text{OCH}_2\text{CH}_2)_n$ , average  $M_r \approx 646.86$ ), Tween-40 ( $\text{C}_{62}\text{H}_{122}\text{O}_{26}$ ,  $M_r=1283.62$ ), Tween-60 ( $\text{C}_{64}\text{H}_{126}\text{O}_{26}$ ,  $M_r=1311.65$ ) and Tween-85 ( $\text{C}_{100}\text{H}_{188}\text{O}_{28}$ ,  $M_r=1838.54$ ) were used as surfactants.

### 2.2 Preparation of nano-sized nickel powders

The method of preparing fine nickel powders by liquid phase reduction has been described in our previous work [30,31]. Nickel sulfate (6.57 g) and an appropriate amount of surfactant were dissolved in deionized water to obtain 50 mL solution, and it was transferred into a flask (250 mL); then, hydrazine (5.89 g) and  $\text{NaOH}$  (2.00 g) were mixed with deionized water to obtain the other 50 mL solution, and it was added dropwise into the flask under stirring at 60 °C. However, when the influence of different types of surfactants on the preparation of nickel powders was investigated, the dosages of all of the source materials were cut down a half. And the pH value of reaction system was controlled at 13.0–14.0 through adding a handful of saturated  $\text{NaOH}$  solution. In order to ensure Ni-ions to be reduced completely, the amount of hydrazine was 4 times of the theoretical value.

### 2.3 Characterization

The crystal phases of samples were characterized by X-ray diffraction (XRD) (Rigaku, D/Max-2000) using  $\text{Cu K}\alpha$  radiation with graphite monochromator. The primary grain sizes of the samples were calculated by the Debye-Scherrer formula. The morphology and dispersion were examined by scanning electron microscope (SEM) (JEOL, JSM 4500). The particle size and size distribution were analyzed by the laser particle size analyzer (Malvern 2000, measurement range: 0.01–1000  $\mu\text{m}$ ).

## 3 Results and discussion

### 3.1 Effect of different types of surfactants

To find the influence of different types of surfactants on the preparation of nickel powders, seven kinds of surfactants including CTAB (cationic type), SDS (anionic type) and five other nonionic ones, i.e. PVP, PEG-600, Triton X-100, TEA and Tween-40, were employed in the reduction reaction and the dosage of each surfactant (versus Ni) is 100 mg/g. The XRD patterns of the products are shown in Fig. 1. The diffraction peaks marked with (\*) can be indexed as face-centered cubic (FCC) metallic Ni phase (JCPDS card No. 03-065-2865), and those marked with (#) can be indexed as hexagonal phase of  $\text{Ni}(\text{OH})_2$  (JCPDS card No. 00-014-0117). It can be seen that nickel powders with high purity were obtained using any of the nonionic surfactants. In contrast, the reduction systems with ionic surfactants CTAB and SDS resulted in incompletely reduced products which were mixed with  $\text{Ni}(\text{OH})_2$  impurity. This may be explained as follows. The Ni-ions are positively charged in the reaction solution. The cationic surfactant CTAB cannot effectively coat the Ni-ions due to the electrostatic repulsion. However, the intermediate products  $\text{Ni}(\text{OH})_2$  are neutral species, which are prone to be cladded by the CTAB micelles. This prevents further reduction of  $\text{Ni}(\text{OH})_2$  to attain the nickel powders. Regarding the anionic-type surfactant, it is known that SDS is also a foaming agent. A great amount of bubbles were formed in the reaction solution, which made it difficult to control the reduction conditions. So the products in SDS-emulsified system were also obtained with less purity.

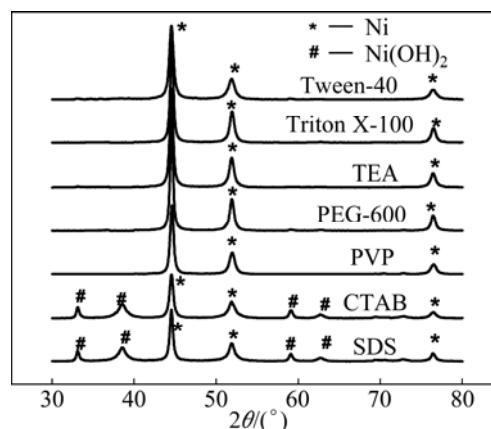
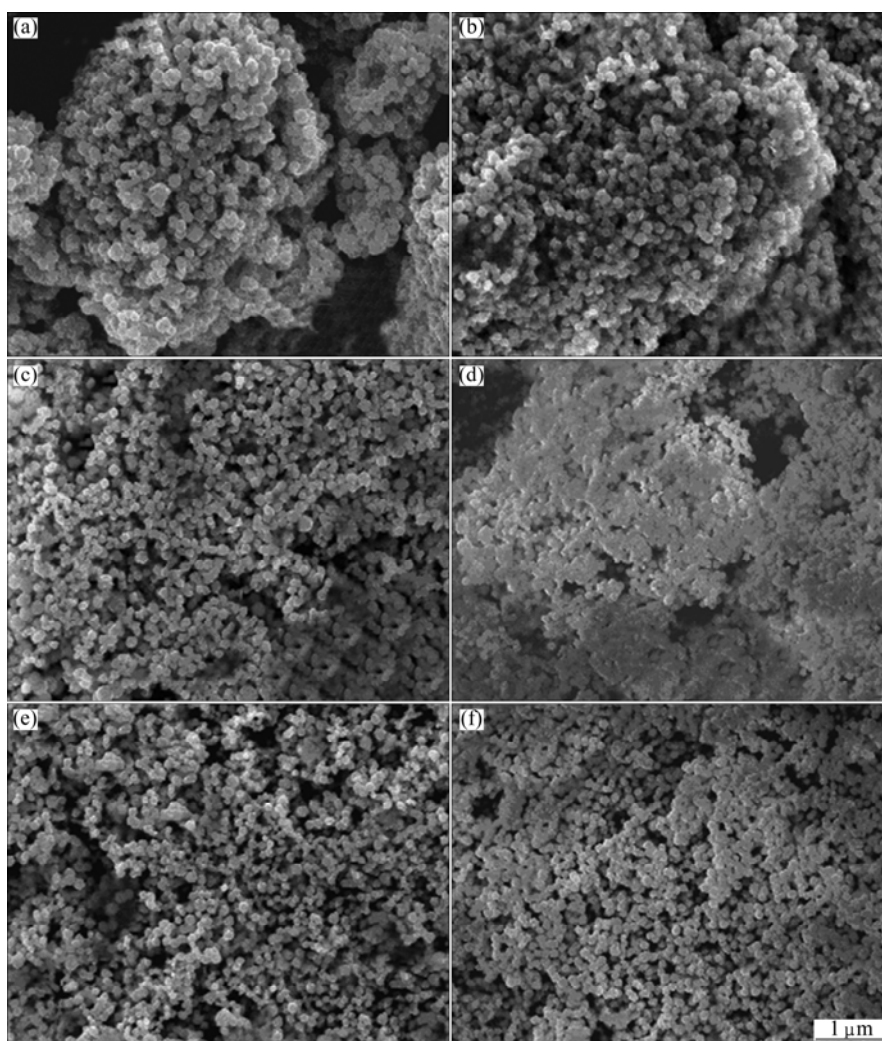


Fig. 1 XRD patterns of Ni powders prepared with different surfactants

The morphology of pure Ni particles is shown in Fig. 2. Reference samples prepared without surfactants (Fig. 2(a)) easily agglomerate because of the van der



**Fig. 2** SEM images of samples prepared with nonionic surfactants: (a) Nothing; (b) PVP; (c) PEG-600; (d) TEA; (e) Triton X-100; (f) Tween-40

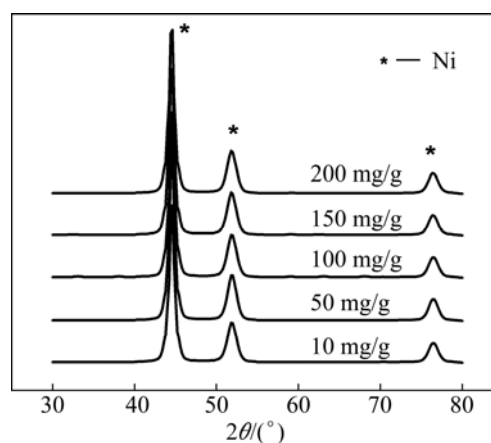
Waals force and magnetic attraction. However, the introduction of nonionic surfactants, especially PEG-600 (Fig. 2(c)) and Tween-40 (Fig. 2(f)), obviously improve the dispersion property of the nickel particles. This can be attributed to the favorable stability of the nonionic surfactant micelles in aqueous solution, which results in a better interaction with the nickel particles and prevent the aggregation of the products.

### 3.2 Effect of dosage of surfactants

The dosage of surfactants is also an important factor influencing the properties of the nano-sized nickel products. Due to the excellent dispersing ability, PEG-600 and Tween-40 were chosen as representatives for the investigation of dosage effect. The synthesis experiments were performed with different mass ratios of surfactant to Ni varying from 10 mg/g to 200 mg/g.

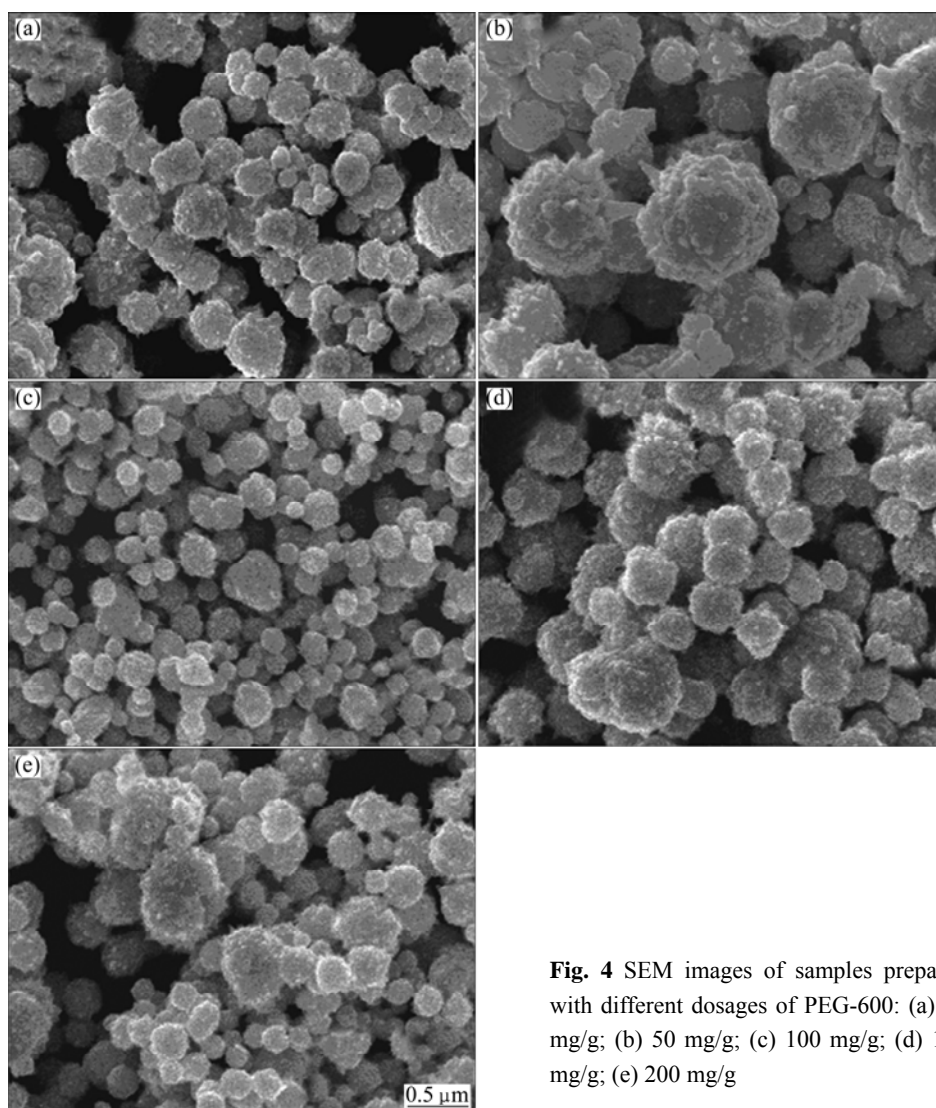
#### 3.2.1 Effect of dosage of PEG-600

The XRD patterns of samples prepared with different dosages of PEG-600 are shown in Fig. 3. The diffraction peaks marked with (\*) can be indexed as FCC



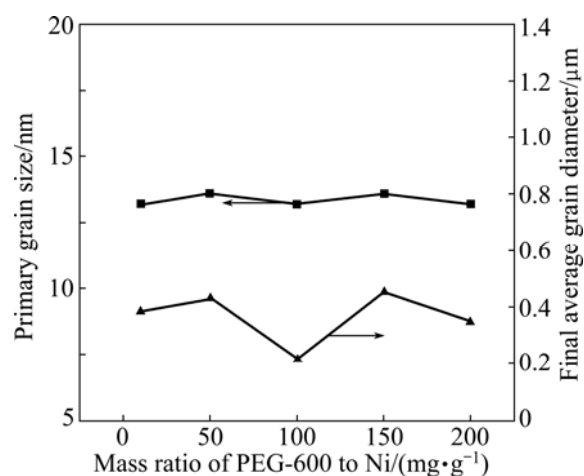
**Fig. 3** XRD patterns of Ni powders prepared with different dosages of PEG-600

nickel phase and it indicates that pure nickel powders were obtained. And the morphology of the corresponding samples is spherical and less-agglomerated, which is shown in Fig. 4. In addition, based upon the calculation by the Debye-Scherrer formula, all of the primary grain



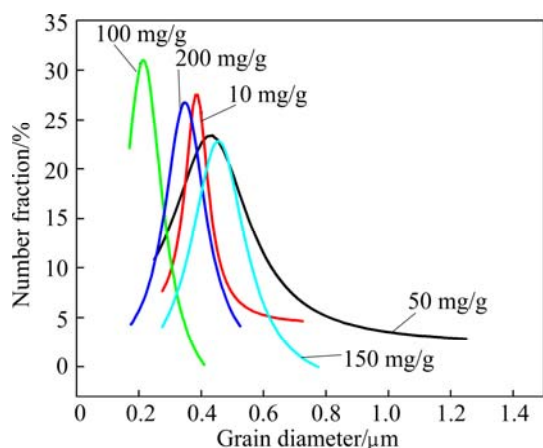
**Fig. 4** SEM images of samples prepared with different dosages of PEG-600: (a) 10 mg/g; (b) 50 mg/g; (c) 100 mg/g; (d) 150 mg/g; (e) 200 mg/g

sizes of nickel powders in different conditions are about 13 nm (Fig. 5). It is claimed that the dosage of PEG-600 almost does not affect the primary grain size of product. However, as the dosage of PEG-600 increased from 10 mg/g to 200 mg/g, the average particle size of samples first decreased from 430 nm to 214 nm, and then increased to 455 nm (Fig. 5). Moreover, the amount of PEG-600 could obviously affect the size distribution of the nickel particles. Figure 6 shows that too little (10 mg/g ~ 50 mg/g) or too much (150 mg/g– 200 mg/g) surfactant resulted in a wide size distribution. The optimal mass ratio of PEG-600 to Ni is 100 mg/g. Such phenomenon is understandable. A small amount of PEG-600 is not sufficient to coat the nickel particles, which may aggregate together in the reaction mixture. However, too much surfactant in the solution will increase the viscosity of the system, as well as the difficulty to control the morphology of the nickel particles. Both the situations cannot lead to a favorable result. Only under the optimal experimental conditions,



**Fig. 5** Primary grain sizes and average particle sizes of samples prepared with different dosages of PEG-600

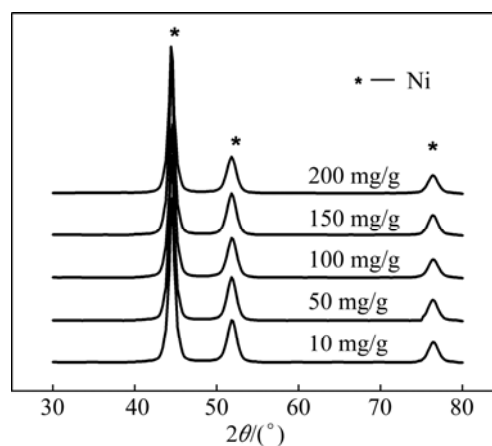
nickel powders with narrow size distribution ranging from 170 nm to 410 nm and average particle size of 214 nm were obtained.



**Fig. 6** Size distribution of samples prepared with different dosages of PEG-600

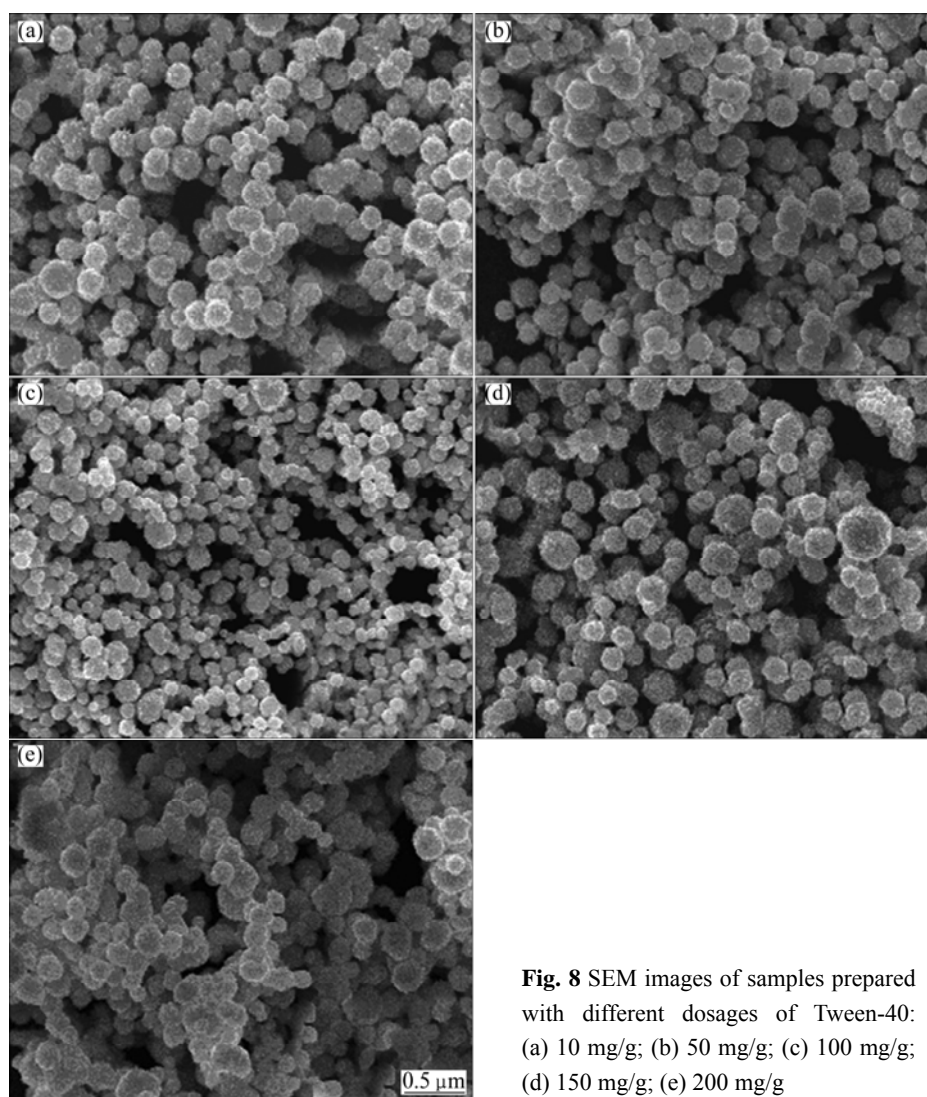
### 3.2.2 Effect of dosage of Tween-40

XRD patterns of the samples prepared with different dosages of Tween-40 are shown in Fig. 7. The diffraction peaks are marked as Fig. 3 and pure FCC nickel powders



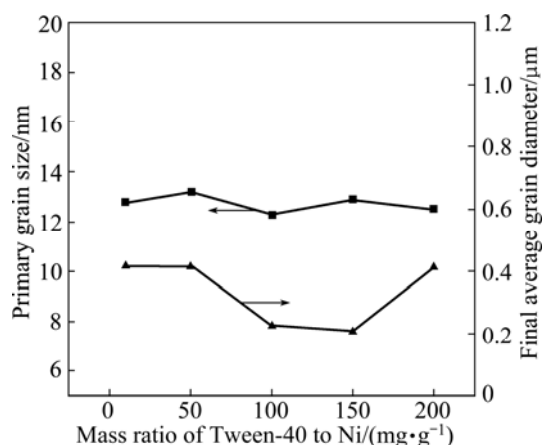
**Fig. 7** XRD patterns of Ni powders prepared with different dosages of Tween-40

were also obtained. The products have a spherical or near-spherical morphology, which is shown in Fig. 8. Primary grain size of the samples calculated based on the Debye-Scherrer formula was between 12–14 nm (Fig. 9),



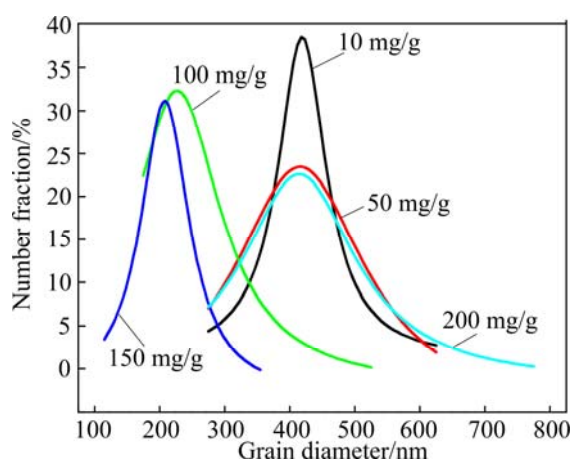
**Fig. 8** SEM images of samples prepared with different dosages of Tween-40: (a) 10 mg/g; (b) 50 mg/g; (c) 100 mg/g; (d) 150 mg/g; (e) 200 mg/g





**Fig. 9** Primary grain sizes and average particle sizes of samples prepared with different dosages of Tween-40

suggesting that the dosage of Tween-40 has no evident influence on such parameter, which was similar to the situation of PEG-600. Meanwhile, similarity was also found in the dosage effect on the average particle size and the size distribution. When the mass ratio of Tween-40 to Ni increased from 10 mg/g to 200 mg/g, the average particle size of the nickel products decreased from 420 nm to 208 nm, followed by an increase to 415 nm (Fig. 9). For the size distribution, an optimal mass ratio of Tween-40 to Ni was found to be about 150 mg/g. In this condition, the nickel particles showed a narrow size distribution ranging from 100 nm to 350 nm. And the average particle size was found to be 208 nm (Fig. 10). Too much surfactant (200 mg/g) resulted in a wide size distribution of the product. The great similarity in the dosage effect of PEG-600 and Tween-40 is ascribed to the similar dispersion mechanism of the nonionic surfactants.

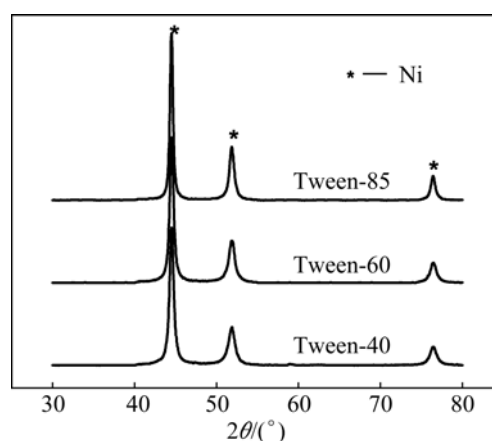


**Fig. 10** Size distributions of samples prepared with different dosages of Tween-40

### 3.3 Effect of relative molecular mass of surfactants

The effect of relative molecular mass of Tween

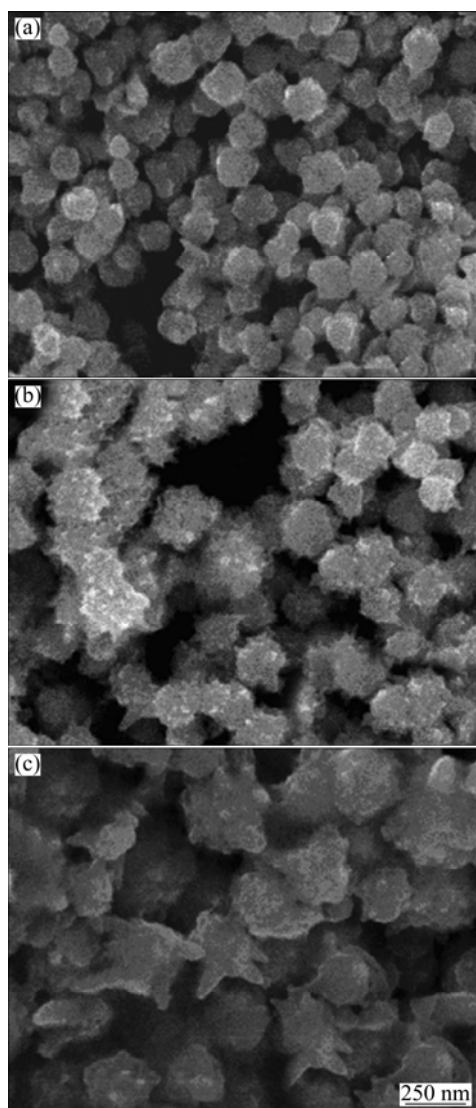
surfactant (Tween-40, Tween-60 and Tween-85) on the morphology of nickel powders was investigated. The XRD patterns of the samples are shown in Fig. 11. The diffraction peaks match well with the peaks in Fig. 3, so all of the samples are pure FCC nickel powders. With the increase of relative molecular mass of Tween surfactants, the morphology of particles changed from fine sphere to irregular shape like spiny ball (Fig. 12). The evolution can be explained by the larger viscosity and steric hindrance resulting from the use of Tween surfactant with higher relative molecular mass. In such circumstance, it is more difficult to form ideal cladding of surfactant micelles to the nickel particles, and the crystal nuclei can not grow up at the same rate in all directions. This produces nickel particles with irregular shape.



**Fig. 11** XRD patterns of Ni powders prepared with different relative molecular mass of Tween surfactants

## 4 Conclusions

High-purity FCC nickel powders with favorable dispersion property were prepared by liquid phase reduction. A variety of surfactants were employed for the investigation of the effect of surfactants on the dispersion and morphology of the products. Among them, the nonionic surfactants PEG-600 and Tween-40 were found to show better performance. The detailed study revealed that the dosage of the two surfactants almost had no influence on the primary grain sizes of the products, but obviously affected the particle size and distribution. The optimal mass ratio of the surfactant to Ni was 100 mg/g and 150 mg/g for PEG-600 and Tween-40, respectively. Under the optimized conditions, nickel powders with ideal morphology and narrow size distribution could be obtained. Besides, the study on the effect of relative molecular mass showed that Tween surfactant with lower molecular mass was more inclined to result in nickel products with fine sphere morphology.



**Fig. 12** SEM images of Ni powders prepared with different relative molecular mass of Tween surfactants: (a) Tween-40; (b) Tween-60; (c) Tween-85

## References

- [1] TZITIOS V, BASINA G, GJOKA M, ALEXANDRAKIS V, GEORGAKILAS V, NIARCHOS D, BOUKOS N, PETRIDIS D. Chemical synthesis and characterization of hcp Ni nanoparticles [J]. *Nanotechnology*, 2006, 17(15): 3750–3755.
- [2] HAN M, LIU Q, HE J H, SONG Y, XU Z, ZHU J M. Controllable synthesis and magnetic properties of cubic and hexagonal phase nickel nanocrystals [J]. *Advanced Materials*, 2007, 19(8): 1096–1100.
- [3] CORDENTE N, RESPAUD M, SENOCQ F, CASANOVE M J, AMIENS C, CHAUDRET B. Synthesis and magnetic properties of nickel nanorods [J]. *Nano Letters*, 2001, 1(10): 565–568.
- [4] PHETSINORATH S, ZOU Jian-xin, ZENG Xiao-qin, SUN Hai-quan, DING Wen-jiang. Preparation and hydrogen storage properties of ultrafine pure Mg and Mg–Ti particles [J]. *Transactions of Nonferrous Metals Society of China*, 2012, 22: 1849–1854.
- [5] LEE J Y, LEE J H, HONG S H, LEE Y K, CHOI J Y. Coating BaTiO<sub>3</sub> nanolayers on spherical Ni powders for multilayer ceramic capacitors [J]. *Advanced Materials*, 2003, 15(19): 1665–1658.
- [6] PARK J, KANG E, SON S U, PARK H M, LEE M K, KIM J, KIM K W, NOH H J, PARK J H, BAE C J, PARK J G, HYEON T. Monodisperse nanoparticles of Ni and NiO: Synthesis, characterization, self-assembled superlattices, and catalytic applications in the Suzuki coupling reaction [J]. *Advanced Materials*, 2005, 17(4): 429–434.
- [7] UMEGAKI T, YAN J M, ZHANG X B, SHIOYAMA H, KURIYAMA N, XU Q. Preparation and catalysis of poly (N-vinyl-2-pyrrolidone) (PVP) stabilized nickel catalyst for hydrolytic dehydrogenation of ammonia borane [J]. *International Journal of Hydrogen Energy*, 2009, 34(9): 3816–3822.
- [8] KAPOOR S, SALUNKE H G, TRIPATHI A K, KULSHRESHTHA S K, MITTAL J P. Radiolytic preparation and catalytic properties of nanophase nickel metal particles [J]. *Materials Research Bulletin*, 2000, 35(1): 143–148.
- [9] XIA X H, WANG X L, MAI Y J, SHI S J, TANG Y Y, GU C G, TU J P, ZHANG Y Q. Three-dimensional porous nano-Ni supported silicon composite film for high-performance lithium-ion batteries [J]. *Journal of Power Sources*, 2012, 213: 106–111.
- [10] LEE K B, PARK S, MIRKIN C A. Multicomponent magnetic nanorods for biomolecular separations [J]. *Angewandte Chemie–International Edition*, 2004, 43(23): 3048–3050.
- [11] HE Y Q, LI X G, SWIHART M T. Laser-driven aerosol synthesis of nickel nanoparticles [J]. *Chemistry of Materials*, 2005, 17(5): 1017–1026.
- [12] WANG F, ZHANG Z C, CHANG Z Q. Effects of magnetic field on the morphology of nickel nanocrystals prepared by gamma-irradiation in aqueous solutions [J]. *Materials Letters*, 2000, 55(1–2): 27–29.
- [13] XIA B, LENGGORO I W, OKUYAMA K. The role of ammonia and ammonium bicarbonate in the preparation of nickel particles from nickel chloride [J]. *Journal of Materials Research*, 2000, 15(10): 2157–2166.
- [14] XIA B, LENGGORO I W, OKUYAMA K. Preparation of nickel powders by spray pyrolysis of nickel formate [J]. *Journal of the American Ceramic Society*, 2001, 84(7): 1425–1432.
- [15] NI X M, SU X B, YANG Z P, ZHENG H G. The preparation of nickel nanorods in water-in-oil microemulsion [J]. *Journal of Crystal Growth*, 2003, 252(4): 612–617.
- [16] YU K N, KIM D J, CHUNG H S, LIANG H. Dispersed rodlike nickel powder synthesized by modified polyol process [J]. *Materials Letters*, 2003, 57(24–25): 3993–3997.
- [17] LEE J Y, HONG S H, LEE J H, LEE Y K, CHOI J Y. Coating of TiO<sub>2</sub> nanolayer on spherical Ni particles using a novel sol–gel route [J]. *Journal of Materials Research*, 2004, 19(6): 1669–1675.
- [18] CHEN D H, WU S H. Synthesis of nickel nanoparticles in water-in-oil microemulsions [J]. *Chemistry of Materials*, 2000, 12(5): 1354–1360.
- [19] FANG D L, WANG Z B, YANG P H, LIU W, CHEN C S, WINNUST A J A. Preparation of ultra-fine nickel manganite powders and ceramics by a solid-state coordination reaction [J]. *Journal of the American Ceramic Society*, 2006, 89(1): 230–235.
- [20] WU Chong-hu. Preparation of ultrafine Co<sub>3</sub>O<sub>4</sub> powders by continuous and controllable combustion synthesis [J]. *Transactions of Nonferrous Metals Society of China*, 2011, 21: 679–684.
- [21] AHN J G, HAI H T, KIM D J, PARK J S, KIM S B. Direct synthesis of nickel powders from NiO slurry by hydrothermal hydrogen reduction process [J]. *Hydrometallurgy*, 2010, 102(1–4): 101–104.
- [22] BAI L Y, ZHANG H B, JIN H C, YUAN F L. Synthesis of nickel powders: From spheres to monodispersed clusters [J]. *Journal of Cluster Science*, 2012, 23(2): 357–364.
- [23] KIM K M, LEE J H, YOON S M, LEE H C, LEE Y K, CHOI J Y. Preparation of mono-disperse Ni powders via the reduction of

- hydrazine complexes: The effect of source materials and impurities [J]. Journal of Electroceramics, 2006, 17(2–4): 339–343.
- [24] XIA Ji-yong, TANG Mo-tang, CHEN Cui, JIN Sheng-ming, CHEN Yong-ming. Preparation of  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> from bismuth powders through low-temperature oxidation [J]. Transactions of Nonferrous Metals Society of China, 2012, 22: 2289–2294.
- [25] RANE S B, SETH T, PHATAK G J, AMALNERKAR D P, DAS B K. Influence of surfactants treatment on silver powder and its thick films [J]. Materials Letters, 2003, 57(20): 3096–3100.
- [26] MARZAN L, TOURIN I T. Reduction and stabilization of silver nanoparticles in ethanol by nonionic surfactants [J]. Langmuir, 1996, 12(15): 358–3589.
- [27] PAL T, SAU T K, JANA N R. Reversible formation and dissolution of silver nanoparticles in aqueous surfactant media [J]. Langmuir, 1997, 13(6): 1481–1485.
- [28] HOU Y L, GAO S. Monodisperse nickel nanoparticles prepared from a monosurfactant system and their magnetic properties [J]. Journal of Materials Chemistry, 2003, 13(7): 1510–1512.
- [29] WU S H, CHEN D H. Synthesis and stabilization of Ni nanoparticles in a pure aqueous CTAB solution [J]. Chemistry Letters, 2004, 33(4): 406–407.
- [30] HUANG Guo-yong, XU Sheng-ming, XU Gang, LI Lin-yan, ZHANG Li-feng. Preparation of fine nickel powders via reduction of nickel hydrazine complex precursors [J]. Transactions of Nonferrous Metals Society of China, 2009, 19: 389–393.
- [31] HUANG Guo-yong, XU Sheng-ming, XU Gang, LI Lin-yan, CHEN Song-zhe. Preparation and characterization of mono-disperse spherical nickel particles [J]. The Chinese Journal of Process Engineering, 2007, 7(6): 1126–1131. (in Chinese)

## 表面活性剂对超细镍粉分散性及形貌的影响

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**摘要:** 采用液相化学还原法制备超细镍粉时, 颗粒容易团聚, 需加入合适且适量的表面活性剂进行改进。通过 SEM、XRD、激光粒度分析仪等表征手段, 考察表面活性剂种类及用量对超细镍粉分散性的影响, 并研究表面活性剂相对分子质量大小对颗粒形貌的影响。结果表明: 非离子型表面活性剂 PEG-600 和吐温(Tween-40)能明显地改善超细镍粉的团聚现象, 且其相对镍理论产量的最佳用量分别为 100 mg/g 和 150 mg/g; 并发现随着 Tween 相对分子质量的增大, 镍粉颗粒由光滑的球形变成不规则形状。

**关键词:** 镍粉; 表面活性剂; 分散; 形貌; 合成

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