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PREPARATION OF NICKEL POWDERS IN NONAQUEOUS MEDIA

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Precipitation of nickel powder is usually carried out in aqueous media. Nonaqueous solvents such as ethanolamines offer several advantages. The effective temperature range extends to the higher temperatures needed for the reduction of nickel at atmospheric pressure, a reaction that is also facilitated by the basicity of the medium. Tests were carried out for the preparation of submicrometre nickel powders by the reduction of metal salts using various ethanolamines (monoethanolamine – MEA, diethanolamine – DEA, and triethanolamine - TEA) as solvents. Hydrazine (N_2H_4) was used as the reducing agent. The basicity, polarity, viscosity and boiling point of the reaction medium all affect the reactions. By changing the reaction conditions and the anionic component of the precursor salt, it was possible to alter the purity and morphology of the nickel powders obtained and the average particle size, except in the case of MEA where no reduction occured. The products were subsequently characterised by chemical analysis and by scanning electron microscopy.

1. Introduction

There are many physical and chemical methods for the production of metal powders of particle size below one micrometre. Among the chemical methods, the reduction of a metal salt or oxide by an appropriate reducing agent is frequently employed. The properties of the product largely depend on the properties of all components of the system, e.g. the metallic precursor, the reducing agent and the solvent medium. The potential of the reducing agent and the reduction potential of the cation also significantly influence the progress of the reactions [1-3]. The most commonly used solvent is water, due to its availability and low cost. Its substitution with a new reaction medium is justified because of better control of the chemical reaction, the subsequent change in the reaction conditions, and thus also in the properties of the product.

A system of nickel acetate (chloride and sulphate), hydrazine and ethanolamine was selected for the study. Acetate was employed as the nickel precursor (in most of the experiments) on the grounds that during the reaction it decomposes to gaseous products and does not contaminate the end product or filtrate. Hydrazine is a highly potential reducing agent and, in a similar way to acetate, its decomposition products do not interfere with the quality of the product. Ethanolamines were chosen for their high boiling points and basicity, both of which facilitate the reduction of nickel. The use of a series of ethanolamines enabled a range of reaction temperatures from 171 °C to 335 °C and viscosities from 30.9 to 613.6 mPas (at 20 °C) at atmospheric pressure. The objective of the experiments was the acquisition of basic knowledge concerning the behaviour of such systems and the properties of the end products, as a possible alternative for the production of nanosize nickel powders.

Research on similar systems has been published earlier [4,5], but ethanolamine was added to an aqueous solution as a complexing agent in addition to the reducing agent, and the experiments were conducted at higher pressures in an autoclave. A different approach has also been tried [6] through the isolation of a nickel complex with monoethanolamine, followed by a subsequent thermal decomposition to nickel powders in an electric furnace in the absence of a reducing agent.

2. Experimental

Reactions in the nickel precursor/hydrazine/ethanolamine system were carried out in glass beakers equipped with a stirrer. A solution of nickel salt in ethanolamine was firstly prepared, along with a solution of hydrazine in ethanolamine. The nickel solution was then heated to 185 °C and the hydrazine solution added. After several minutes nickel powder precipitated from the solution. The metal powder was then filtered, washed in ethanol, filtered again and dried in vacuum at room temperature.

In the majority of experiments $Ni(CH_3COO)_2 \times 4H_2O$ (Carlo Erba, p.a.) was used, except when determining the effect of the anionic component of the nickel salt on reaction efficiency and product purity, when the salts $NiSO_4 \times 7H_2O$ (Carlo Erba, p.a.) and $NiCl_2 \times 6H_2O$ (Carlo Erba, p.a.) were tested. The anhydrous hydrazine solution was prepared by the thermal decomposition of hydrazido–carbonic acid (N_2H_3COOH) in ethanolamine [7].

3. Results and discussion

Chemical reduction/precipitation is a frequently used method for the preparation of metal powders. Submicrometre metal particles are prepared most easily from very dilute solutions, as individual nuclei cannot grow to larger sizes due to the restrictions of mass balance in such a batch system. In this research higher concentrations of nickel were used, bearing in mind the potential applications of the process. Concentrations of nickel available to all three ethanolamines (MEA, DEA and TEA) were selected, thus enabling a comparison of results. The solubility of nickel acetate in TEA was the limiting factor, as it proved to be the lowest for this solvent. Particle size and purity were taken to be the most important properties of the product, in conjunction with the yield of the reaction. The residual concentration of nickel in the filtrate is not just an indicator of the reaction yield, but also of the ability of the solvent to form complex nickel ions, thus keeping them in the solution.

Although the research was designed to compare the effect of all three solvents, in the case of MEA the reduction did not take place at the boiling point of the solvent (171 °C).

3.1. Influence of nickel precursor on the properties of nickel metal powder

The solutions of nickel (II) acetate, sulphate and chloride hydrates in DEA and TEA were used. The initial concentration of nickel (II) ions was 5 g/l for all salts and both solvents. The molar ratio of hydrazine added to nickel (II) ions was 2.42. The results are summarized in Table 1.

TABLE 1.
Results of nickel precipitation for different nickel salts.

Nickel salt	Nickel content in product %		Conc. of Ni^{2+} in filtrate (g/l)	
	DEA	TEA	DEA	TEA
$Ni(CH_3COO)_2 \times 4H_2O$	95.09	99.41	1.47	2.49
$NiSO_4 \times 7H_2O$	97.01	98.48	0.73	0.88
$NiCl_2 \times 6H_2O$	96.05	99.81	0.73	0.81

In TEA the products were purer than in DEA, regardless of the anionic component of the metal salt. This can be ascribed to the greater polarity of the TEA molecule ($\mu = 3.57$ D), in comparison to the DEA molecule ($\mu = 2.81$ D) [3]. The polarity of a molecule serves as a rough estimate of its solubility in a different polar solvent, in this case ethanol, which was used for rinsing the product after the end of the reaction. Ethanol removes a more polar solvent from the surface of the nickel to a greater extent. Presumably, it is not possible to remove organic solvents from pores of the product due to surface tension and viscosity of the solvent.

Table 1 shows that the efficiency of the reduction (a lower concentration of nickel (II) ions in the filtrate) in DEA was higher than in TEA, as TEA forms a stronger initial complex with nickel ions than DEA. The stronger the initial complex, the harder it is for a molecule of the reducing agent to replace the ligand (DEA, TEA) in the complex and start the reduction. This was also confirmed by Bjerrum, who proposed a linear relationship between the basicity of the amine and the strength of the complex formed between the metal and the ligand [8]. The higher the basicity of the ligand, the stronger its complex with metals. The basicities (pK_B) of ethanolamines DEA and TEA are 5.12 and 6.25, respectively [3]. To initiate reduction, hydrazine must penetrate the ligand sphere surrounding the cation and partially or completely replace the ethanolamine.

3.2. Influence of the initial concentration of nickel ions on product characteristics

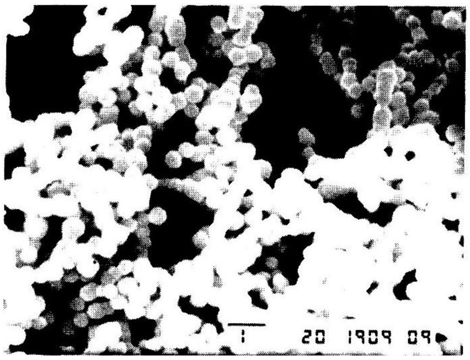
The initial solutions for this experiment were prepared from nickel (II) acetate tetrahydrate with concentrations ranging from 1.25 to 20 g/l. For both solvents the reducing agent N_2H_4 had a concentration of 6.4 g/l.

TABLE 2.
Results of nickel reduction/precipitation reactions.

Initial conc. of Ni^{2+} ions (g/l)	Nickel content in product (%)		Conc. of Ni^{2+} in filtrate (g/l)		d_{SEM} (μm)	
	DEA	TEA	DEA	TEA	DEA	TEA
1.25	96.15	99.77	0.03	0	0.49	0.33
2.5	95.79	99.14	0.1	0.73	0.74	0.42
5	95.09	98.97	1.47	2.05	0.76	0.52
10	82.42	98.55	7.63	4.4	0.88	0.5
20	81.77	97.37	13.98	12.77	1.12	0.62

The higher concentrations of metal ions in the TEA filtrate could be the result of formation of a stronger metal cation/TEA complex and a greater difficulty of access on the part of the reducing agent to the central nickel cation.

The average size (d_{SEM}) of the nickel powder particles was measured using photographs obtained by SEM at a magnification of 10000, as measurements of particle size by the scattering of laser light proved impossible due to the high degree of agglomeration of particles. The results show that the particles were bigger when DEA was used, which can be explained by the lower viscosity of DEA (Fig. 1) [3]. Due to the better mobility of atoms in a less viscous medium (DEA), the resulting particles are bigger than in TEA (Fig. 2) [2].



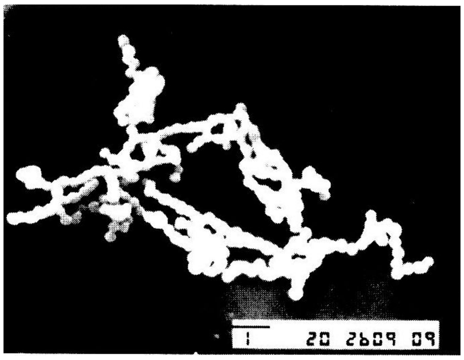


Fig. 1. Nickel powder prepared in DEA.

Fig. 2. Nickel powder prepared in TEA (right).

Particle size decreased with the initial concentration in both solvents, which is consistent with the mass balance of the system. The higher the concentration of the initial solution, the more substance is available for the growth of individual crystals, and the larger the particles obtained. These particles combine into agglomerates.

4. Conclusion

The experiments demonstrated that by selection of a reaction medium and by controll of the conditions of nickel precipitation, the morphological properties and chemical composition of the products can be altered. The size of particles was in the range 0.33 to 1.12 μm (Table 2). When TEA was used, the particles were always smaller than in the products obtained using DEA as a solvent. This can be attributed to the higher basicity and viscosity of the medium. The efficiency of the reduction reaction is greater in the case of DEA, which can be explained by the formation of a weaker complex between nickel (II) ions and DEA than that with TEA. A precise description of the mechanism of the reduction reactions in both solvents is difficult, due to the different effects of individual properties of the solvents (viscosity, basicity, polarity, polarisability, etc.) and their influence on the reducing agent. Nevertheless, after some additional research and refinements, this process could be an alternative in the preparation of nickel powders by reduction of nickel salts from solutions at atmospheric pressure.

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PRIPREMA NIKALNOG PRAHA U NEVODENIM SREDSTVIMA

Precipitacija Ni praha obično se radi u vodenim otopinama. Međutim, otapala poput etanolamina pružaju više prednosti. Pripreman je submikrometarski prah nikla redukcijom metalnih soli, upotrebljavajući razne etalomine kao otapala. Redukcija je načinjena pomoću hidrazina. Bazičnost, polarnost, viskoznost i točka vrenja otopine znatno utječu na reakcije. Prahovi su istražvani kemijskom analizom i pomoću SEM.