

THERMAL PROPERTIES AND REACTIVITY DETERMINATION OF MICRO- AND SUBMICROMETER NICKEL POWDERS

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Abstract

Monodispersed fine metal nickel powders of uniform shape and high purity are increasingly required for specific uses in many technological areas, especially in the preparation of electronic materials such as the manufacture of conductive inks and pastes and the formation of catalysts. Metallic nickel powders were prepared in ethylene glycol by the reduction of a nickel solution. Hydrazine was used as a reducing agent. Metal powders were characterized by chemical analysis, scanning electron microscopy (SEM), thermogravimetry (TG), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC). Particle size distributions were determined using laser light scattering. The reactivity and purity of these fine nickel powders were tested by repeated oxidation and reduction of nickel powders in oxidative and reductive atmospheres.

Keywords: nickel powders, oxidation, thermal analysis

Introduction

There are many physical and chemical methods for the production of metal powders with dimensions around and below one micrometer. Among chemical methods, the reduction of metal oxide by hydrogen or carbon monoxide is frequently employed. Reduction of a metal salt solution by an appropriate reducing agent enables better control of product characteristics. In general the properties of products obtained by this route depend on the properties of all components of the system, e.g. the metallic precursor, the reducing agent and the solvent medium as well as on the reaction conditions [1]. Fine nickel and other metal particles are used in many areas of technological importance (e.g. microelectronics, magnetic disks, sintered magnets and catalysts). In microelectronics conductive inks and pastes are used in the thick film technique for producing electronic components such as the conductive networks of hybrid microcircuits and for internal electrodes of multilayer ceramic capacitors [2]. Metal nickel catalysts are also applied in such reactions as alkylation, aromatization, and hydrogenation, in Fischer-Tropsch synthesis [3]. For possible future applications, understanding the behavior of products exposed to heat treatment under oxidation and reduction conditions is of great importance. This can cause significant chemical and morphological variations and changes to the fine

metal powders. Sequential and cyclic treatments of oxidation and reduction can produce microstructural changes in metal, oxide film and multiphase interactions in the sample. Cyclic oxidation and reduction can also alter catalytic properties and affect the active sites on the surface of metallic nickel [4].

A system of nickel chloride, hydrazine and ethylene glycol (EG) was selected for this research. Hydrazine is a high potential reducing agent and its decomposition products do not interfere with the quality of the product. EG was used as a solvent for the production of fine monodispersed metal nickel particles. An organic solvent allows higher reaction temperatures to be used at atmospheric pressure than is the case when an aqueous medium is used [5]. Previous work on similar systems using only ethylene glycol as the solvent and reducing agent has shown the feasibility of this method for the production of fine metal powders [6, 7]. In this study the effect of using hydrazine as an additional reducing agent and the concentration of the nickel ions in solution on the properties of the metallic particles formed have been investigated.

Experimental

Reactions of nickel(II) ions with hydrazine in EG were carried out in glass beakers equipped with a stirrer. A solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in EG was firstly prepared, along with a solution of hydrazine in EG. All the chemicals were p.a. quality manufactured by 'Carlo Erba Reagenti'. The anhydrous hydrazine solution was prepared by the thermal decomposition of hydrazido-carbonic acid ($\text{N}_2\text{H}_3\text{COOH}$) in EG [8]. The volume of the reaction mixture was 300 ml in all cases. The initial concentration of Ni^{2+} ions varied from 3 to 9 g l^{-1} . The solution of the nickel salt in EG was heated to 185°C , and subsequently the hydrazine solution in EG was added. After a few minutes nickel powder precipitated from the solution. The metal powder was filtered off, dispersed in ethanol, filtered again and dried in a vacuum at room temperature. The nickel powder was characterized by chemical analysis, and scanning electron microscopy (JEOL-300T). The purity of the nickel powders were determined by complexometric titration [9]. Size distribution curves of the products were determined by laser light scattering (Fritsch-Analysete 22). TG, DTG (Mettler TG-50, Thermobalance) and DSC (Mettler DSC-20, Standard Cell) methods were also used to determine the properties of the fine nickel powders. Nickel powder samples of mass 10 mg were analyzed in oxidative (O_2) and reductive (4 vol % H_2/Ar) atmospheres with a gas flow of 30 l min^{-1} . A heating rate of 4 K min^{-1} was used from 30 to 500°C .

Results and discussion

Nickel metal powders of submicrometer and micrometer dimensions were prepared by reduction/precipitation in EG with hydrazine as the reducing agent. The effect of initial metal ions concentration on the process and products was studied.

The reduction and precipitation of nickel are accompanied by the evolution of gases from the reaction mixture. The yield of the reaction as reported in Table 1 is a function of the reaction parameters and is strongly affected by the thermal instability of hydrazine and its susceptibility to catalytic decomposition. High excesses of hydrazine were therefore needed in the experiments. A decrease in the yield of the reaction could be at least partially explained by the fact that hydrazine catalytically decomposes on the nickel powder precipitated from the reaction solution [8]. Because of this the reduction of nickel ions was incomplete.

Nickel powders are obtained with a purity ranging from 98.0 to 99.9 wt%. Mode particle sizes as determined by laser light scattering range from 1.8 μm to 3.9 μm . This method actually indicates the size of the agglomerates and not of primary particles as observed by SEM analysis. As the concentration of nickel ions in solution increases the agglomerate particle diameter (d_{FRITSCH} Table 1) increases. The purity of nickel powder is seen to decrease as the nickel ion concentration increases. This increase in organic impurities could be due to solvent trapping in the

Table 1 Results of reduction-precipitation reaction in EG

Sample	Initial conc. of Ni^{2+} ions/ g l^{-1}	Yield of the reaction/ %	Purity of the product/ %	$d_{\text{FRITSCH}}^1/$	$\sigma_{\text{FRITSCH}}^2/$	$d_{\text{SEM}}^3/$
						μm
A	3	97.8	99.9	1.8	0.75	0.5
B	6	89.9	98.9	2.6	1.19	0.9
C	9	35.4	98.0	3.9	1.68	1.3

¹ Mode agglomerate size determined from frequency distribution data

² Standard deviation of frequency distribution data

³ Average particle diameter visually estimated from SEM photomicrographs

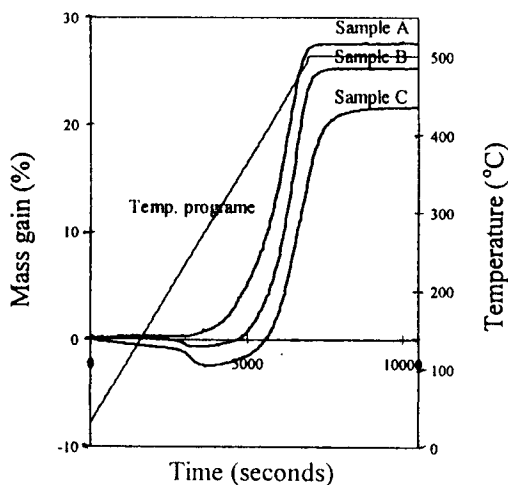


Fig. 1 TG curves of the samples A, B, C in the flow of oxygen

agglomerates or an increase in surface area with the associated surface impurities previously seen on such metal particles [7].

All three samples of the fine metal powders were first analysed by thermoanalytical methods. The nickel powders were examined by TG/DTG in dynamic oxygen atmosphere from 30 to 500°C. The samples were held at 500°C until a constant mass was reached. After oxidation, reduction in an atmosphere of H₂/Ar was carried out. The oxidation/reduction cycles were repeated four times for all the nickel powder samples. DSC measurements with only one oxidation/reduction cycle were also made under the same conditions as the TG/DTG measurements. The oxidation

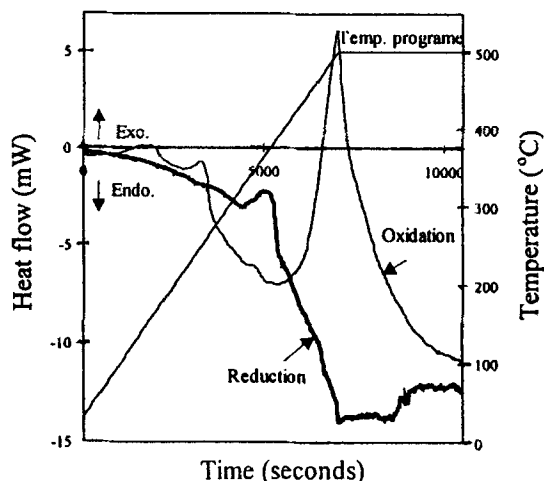


Fig. 2 DSC curves of the sample C in the flow of oxygen and hydrogen

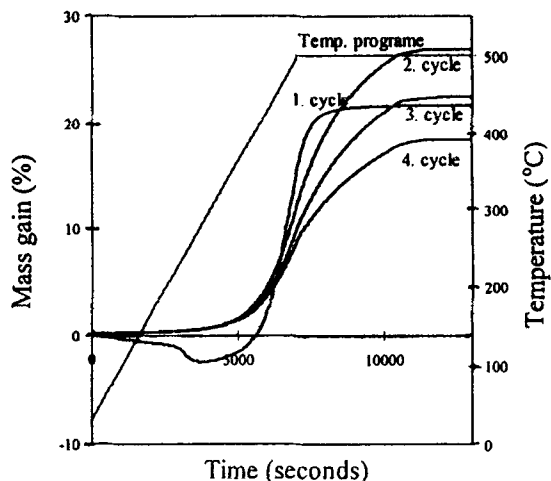


Fig. 3 TG curves of the cyclic oxidation of the sample C with a reduction step between each oxidation

reactions of all three samples were preceded by the evaporation of the last remains of the solvent (Fig. 1). The weight loss below 270°C closely corresponds to the difference in the nickel content of each sample to 100%. Before the oxidation of nickel takes place, all the solvent evaporates from the sample. This temperature is lower for purer products and for smaller agglomerates of metal powder. The end mass of the partially oxidized nickel is different for all three samples possibly as a result of the different specific surface areas and sizes of the particles that form the product. TG thermograms of all three samples show that the oxidation depends on purity and the morphological properties of the product.

Subsequent reduction of the same sample in a reductive atmosphere showed smaller decrease in the mass of the sample compared to the mass gain during the oxidation run. This is the result of the sintering of nickel during the first oxidation run (Fig. 6). A shift in the starting temperature for reduction toward higher values is a consequence of the different morphological properties and purity of each sample.

The temperatures of the evaporation of the solvent, and oxidation and reduction of the nickel powder are also evident from the DSC curves (Fig. 2). The endother-

Table 2 Results of oxidation/reduction cycles of the sample C

Number of cycles	Weight gain on oxidation/	Weight loss on reduction/
	wt. %	
1.	21.66	22.42
2.	26.92	19.97
3.	22.54	17.39
4.	18.42	14.31

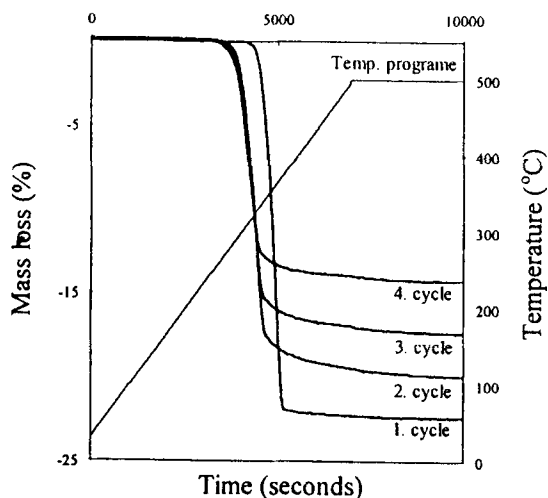


Fig. 4 TG curves of cyclic reduction of the sample C with an oxidation step before each reduction

mic DSC peak in the temperature range 30 to 350°C corresponds to the evaporation of EG. After evaporation a sharp exothermic peak of the nickel powder oxidation reaction may be seen at the temperature of 498°C. The temperature intervals from TG/DTG and DSC curves are comparable.

The cyclic oxidation and reduction of the samples was also tested in order to get an insight into behaviour of the powders under such conditions. SEM photomicrographs of the samples were made before and after oxidation/reduction treatments. In the first oxidation cycle it is evident that oxidation proceeds after the EG evaporation. When the sample is treated in oxygen the EG combustion takes place [7]. The formation of a NiO layer on the surface of the nickel powder prevents complete oxidation (Fig. 3) [4]. TG curves of the second, third and fourth oxidation cycle are, as expected, very similar, since after the first run there is no longer any solvent present in the sample. After each oxidation cycle, the amount of oxidized nickel is lower, as a result of changes in the product surface. The sintering and coalescence of the particles of the metal powder lower the surface of metal available for oxidation and hinder the diffusion of the oxygen and hydrogen molecules inside the product [4, 10].

The process of fine nickel powder sintering is also evident from the SEM photomicrographs. The first photo shows the initial particles of nickel powder after pre-

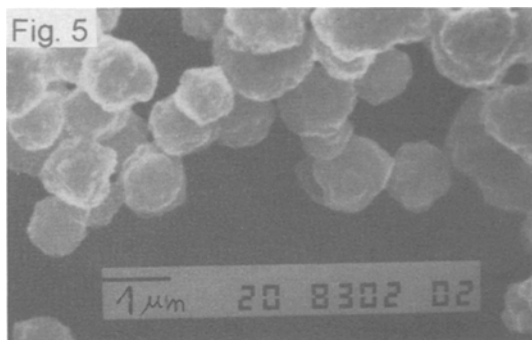


Fig. 5 Nickel powder after precipitation in EG (magnification 10.000)

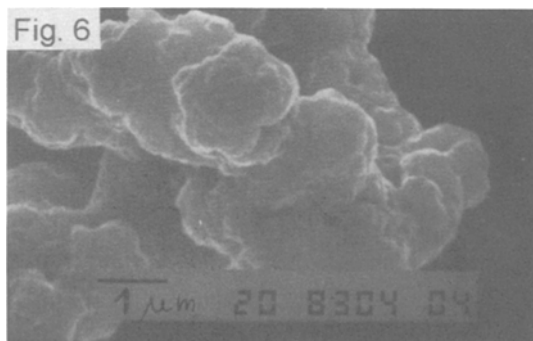


Fig. 6 Nickel powder after first oxidation cycle (magnification 10.000)

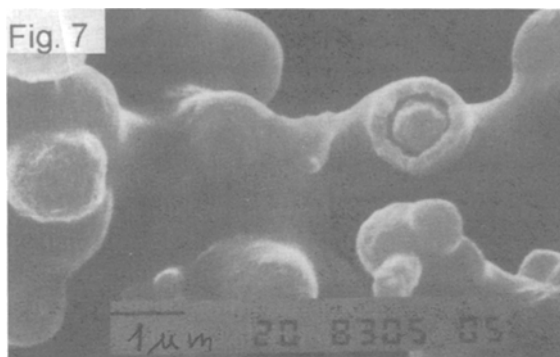


Fig. 7 Nickel powder after second oxidation cycle (magnification 10.000)

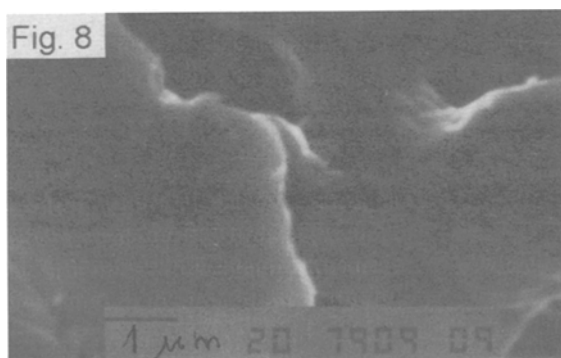


Fig. 8 Nickel powder after fourth oxidation and reduction cycle (magnification 10.000)

precipitation from ethylene glycol (Fig. 5). The average diameter of the particles is 1.3 μm . In the first oxidation cycle the nickel particles are partially sintered and necks between the initial particles are formed (Fig. 6). The voids are also visible (Fig. 7). The rise of the voids in the growing oxide is related to the compressive stresses at the oxide metal interface. Further oxidation and formation of gases (trapped in the void) on heating causes the growth of these voids [4]. After the last oxidation/reduction cycle the particles are sintered to a great extent (Fig. 8).

Conclusion

Hydrazine in an ethylene glycol medium reduces nickel solutions and fine nickel particles are precipitated. The primary particle sizes range from 0.5 to 1.3 micrometers. The morphological properties and purity of the fine nickel powders can be altered by controlling the concentration of nickel ions in the reaction mixture. TG, DTG and DSC methods provide information on the behaviour of powders exposed to heat treatment under conditions similar to those during application. The residual solvent (EG) can be removed by heat treatment. Nickel powder samples start to oxidize in the temperature around 200°C. The degree of powder oxidation

depends on the particle size and the formation of an oxide layer hinders the further oxidation of the sample. The high reactivity of the powders is also evident from the relatively low sintering temperatures.

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