Experimental Researches for Manufacturing the Nickel Powder

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Products made from sintered powder with uses of the most diverse in top areas such as engineering or medicine have a precise and uniform composition, being characterized by a great deal of consistency. Nickel powders used in the production of porous permeable product must meet a set of physical characteristics (shape, size of particle density, specific surface, etc.) are rigorously controlled by the technological process and conditions of manufacture. These characteristics in turn make both technological properties such as flow or flow velocity in sintering contraction, etc., and use such as porosity product (min. 75%) and uniformity of pores, mechanical strength, toughness, and more. Experiments were carried out in the field of temperatures 200-600 °C using as the reducing agent – the hydrogen with a flow rate of 30 L/h in conditions: directly from the hydrogen storage container, passed through a drying and purification plant consisting of concentrated sulphuric acid, calcium chloride, and silica gel, hydrogen passed through liquid nitrogen.

Keywords: powder, nickel oxide, hydrogen, reduction, sintering, porosity, mathematical model

Obtaining the products from sintered powder with uses in the most varied peak areas of current technique is an alternative to the classical processes having the following main advantages [1, 2]:

- realizing small parts with complex geometry in economic conditions and with high dimensional precision;
- realizing the parts which by the nature of the operation must have a porous structure (filters, diaphragms pitted electrodes, etc.);
- obtaining pure metal and hard material alloys, fuses the melting and the casting are difficult to achieve and lead to pollution;
-obtaining material whose components are not allies naturally (e.g. W-Ag, W-Cu, Mo-Ag, Mo-Cu, as well as metallic materials with graphitized charcoal).

Powder metal manufacturing is done by methods that determine the characteristics of powder and determines their behaviour in stages of production (pressing-sintering) the final sintered product as follows [1-3]:

- chemical methods as is precipitation from aqueous solutions, which generate very fine powders, soft, and with tendency to agglomeration;
- physico-chemical methods such as electrolysis of aqueous solutions or electrolysis of fused salts, the reduction with hydrogen at high temperatures or decomposition of metal carbonyls and metal vapour condensation resulted, which generates very pure powders with adjustable fineness and with large capacity of pressing;
- mechanical methods as it is dry and wet grinding, applicable to metals and brittle alloys, which generates great powder granulation, hardened and with less free pressing reduced capacity.

The physical characteristics of the powder, particularly the shape and dimensional characteristics of the particles makes its surface area and the physico-chemical reactivity increased of the powdery material. The role in determining the specific surface of powder reaction arises from the physical nature of the free surfaces of the arrangement of the atoms from the top layer. The rough character of free surfaces characterized by electronic non-saturation of the atoms from the superficial layer and the presence of superficial defects is the explanation of the increased reactivity area and underlies phenomena like adsorption, catalysis, corrosion, germination and growth of crystals [2].

The role of nickel powder in electric batteries is as deposit for electrochemical active substances. This role can be played at the first sight of any metallic sintered powder [4]. Research demonstrates, however, that all kinds of experienced, such as those of copper, iron and nickel, which corresponds in all respects to the aims pursued is nickel powder, very stable in alkaline solution and a good electrical conductor. Normally for the achievement of the alkaline nickel-cadmium batteries are used the powder resulting from decomposition of nickel tetra carbonyl obtained through a complex technology, determined by the operation of tetra carbonyl purification of nickel, which makes its price to be quite high compared to other processes.

The opportunity of studying the kinetics of reduction with hydrogen oxides of nickel for the production of nickel powder and subsequently, the process of optimization on the basis of mathematical models elaborated based on the grounds that sometimes, though, are possible as thermodynamic reaction, the speeds/processes can be so small as the systems are not useful from a practical standpoint [5].

Experimental part

Materials and methods

Experimental researches have pursued the establishment of key kinetic parameters as information useful in optimizing the process of nickel powder by reduction of nickel oxide [4,-7]. The reducing agent is hydrogen used as such, directly from the storage container (dew point - 22°C), hydrogen went through a drying and purification plant consisting of concentrated sulphuric acid, calcium chloride, and silica gel (dew point of - 33°C) and liquid nitrogen hydrogen passed through (dew point of- 50°C). Hydrogen flow is 30 L/h. Nickel oxide powder is placed in the free state on mounted platform, with thin layer of approx. 3 mm thick. Purging the areas in which the

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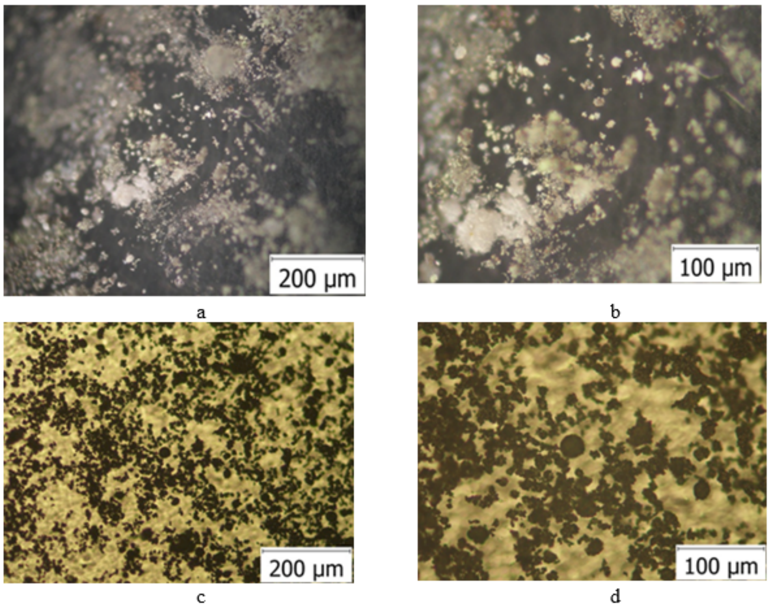


Fig. 1 Microscopic aspects of dust a - nickel oxide (X 200); b - nickel oxide (X 400); c - nickel powder (X 200); d - nickel powder (X 400)

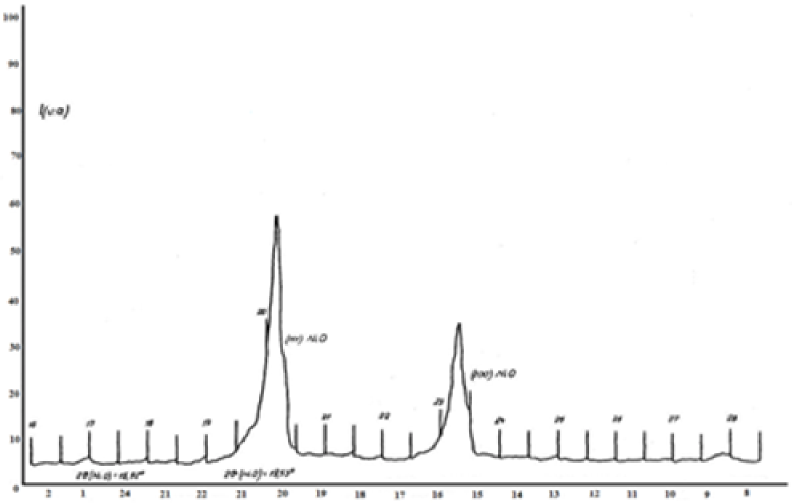


Fig. 2 Characteristic diffraction spectrum of nickel oxide (NiO)obtained by calcination of nickel hydroxide [4]

reduction was made of nickel oxide was achieved with dry argon and purified in the same way as the drying and purification of hydrogen. Experiments were carried out in the field of temperatures 200-600 ° C and nickel oxide from nickel hydroxide was used to the roasting temperature of 1050 ° C, powdery material given the apparent density of 0.51-0.8 g/cm^3 and the surface area of 1.54 m^2/g.

Results and discussions

The microscopic appearance of powders (nickel oxide and nickel powder) is rendered in figure 1, and the results of the analysis of x-ray diffraction in figure 2 and figure 3.

Controlling the degree of reduction (α) by controlling the residual oxygen content in the powder has been carried out in parallel with experiments aimed at obtaining powder in different schemes for reducing nitrogen oxide, through measurement of the sintering of powder and macroscopic evaluation of the status of the surface porous sintered plate.

In figure 4 are presented the macroscopic aspects of porous plates sintered, nickel powder produced at different stages (different discount schemes, nickel powders with a variable oxygen content). For a correct assessment of the capacity of sintering of powders obtained by reducing oxides of nickel, it has worked in parallel with two types of Carbonyl nickel powder (powder type 287, labelled B and powder type 255 labelled C) produced by the INCO Company, Canada.

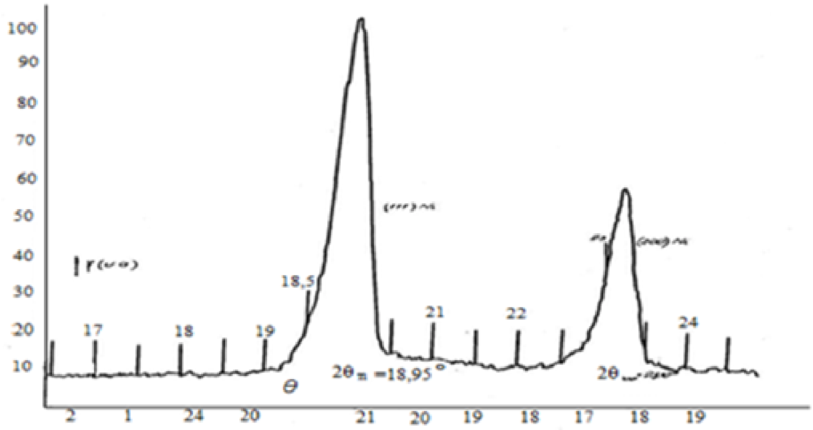


Fig. 3. Diffraction spectrum characteristic of nickel powder achieved by reducing the nickel oxide with hydrogen in optimal regime established through the technology under study [4]

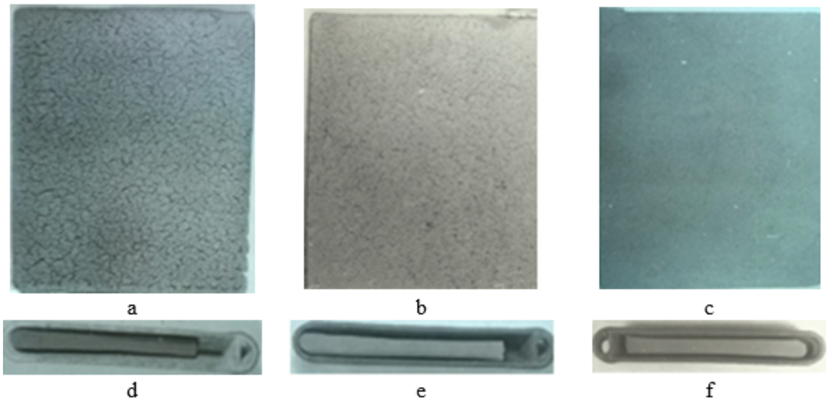


Fig. 4. Sintered porous plate appearance from nickel powders with a residual oxygen content greater than 0.10% (defect type cracks) **(a, b)** and the residual oxygen content lower than 0.10% (no faults) **(c),** in conjunction with a large contraction in sintering of powder in elevated controlling **(d, e)** and small shrinkage at sintering **(f)** [4, 6-8]

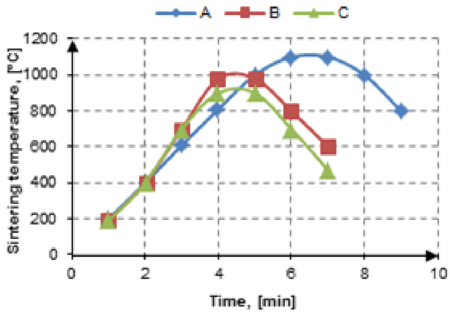


Fig. 5 Sintering process parameters for nickel powders obtained by different methods (B, C - Carbonyl method and A-reducing soda oxides) [4]

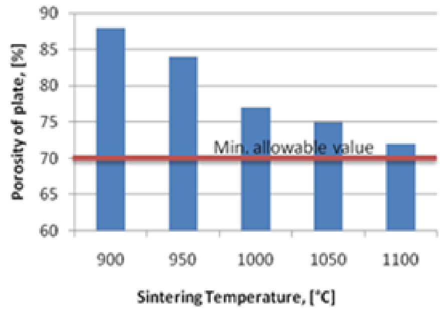
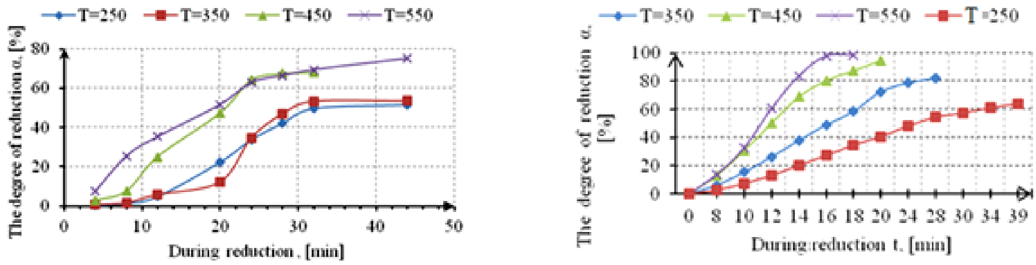


Fig. 6. The influence of sintering temperature on the porosity of porous Ni plate



a b

Fig. 7. The influence of reduction process parameters (temperature and duration) on the degree of reduction of nickel oxide (NiO) to: **a**-dew point of reducing atmosphere (-22°C), **b**-dew point of reducing atmosphere (-33°C)

The study of nickel oxide reduction kinetics in original installations designed for this purpose allowed the calculation of kinetic parameters of main and the formulation of conclusions concerning the obtaining of nickel powder for high porosity of porous plates. The reaction order n has been calculated, the values of constants, the activation energy, and the pre-exponential factor on the interval of temperatures between 250 and 550°C. Calculation of kinetic parameters by means of integral methods was verified and supported by more accurate differential methods.

On the basis of measurements regarding the decrease in mass over time at various temperatures reduction was calculated on the degree of reduction α using the relationship:

$$\alpha = \frac{m_0 - m_t}{m_0 \frac{\%NiO}{100} \cdot \frac{M_{O_2}}{M_{NiO}}} \cdot 100, [\%] \qquad (1)$$

where:

m_0- initial mass of the sample;

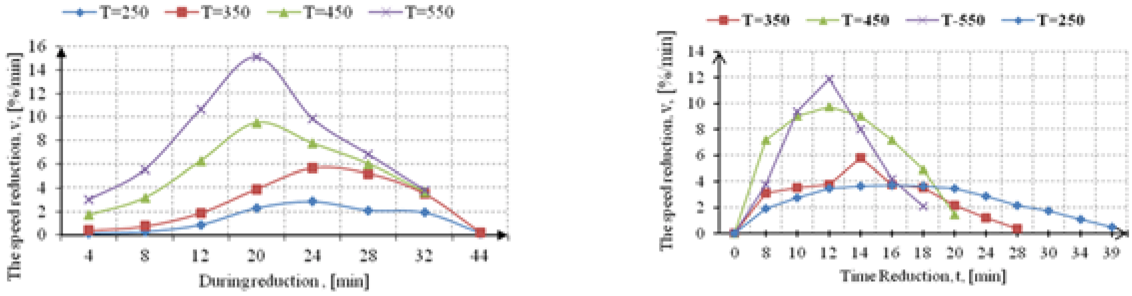
m_t -specimen at time t;

M_{O2}- molecular mass of oxygen;

M_{NiO} -molecular mass of Ni oxide.

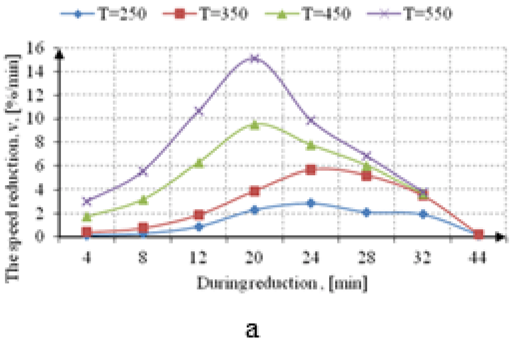
In figure 7 are presented the experimental results concerning the reduction in α, whereas reduction at different temperatures and atmospheric characteristics of the reduction.

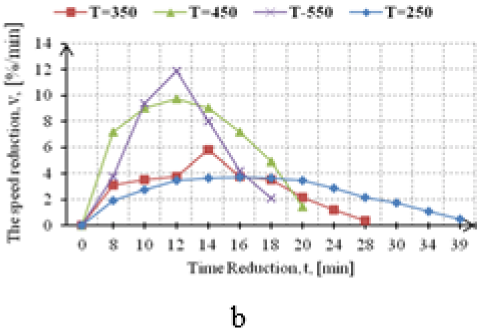
Speed reduction of nickel oxide is obtained through the differentiation degree of reduction in α as a function of time. The results appear in figure 8.



a b

Fig. 8. The influence of reduction process parameters (temperature and duration reduction) on speed reduction of nickel oxide (NiO) to: a - dew point of reducing atmosphere (-22°C), b - dew point of reducing atmosphere (-33°C)





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Conclusions

The paper presents a part of the research results from an experimental program concerning the study of the process of hydrogen reduction of nickel oxides for obtaining nickel powder with physical characteristics of the chemical and technological processes of manufacture of porous tiles imposed with high porosity (over 75%) values, such as porous support for electric batteries.

The study on the reduction process kinetics of nickel oxide (from nickel hydroxide by calcination) provided information concerning the main kinetic parameters, and the moulding process by the method of the experiment process led up to the scheduled demonstration link relationships between the main parameters (temperature and time reduction, reducing agent purity) and the performance of the process (the degree of reduction, speed reduction), with an important role in getting the product imposed features.

References

1. S. GADEA, M. Petrescu, Metalurgie fizicã si Studiul metalelor, EDP, Bucuresti, 1981, p.241-259.
2. T. SURDEANU, M. PERNES, Piese sinterizate din pulberi metalice, Ed. Tehnica, Bucuresti 1984
3. I.V. SIMITI, I. MAGYAROSY, Materiale poroase permeabile sinterizate, ISBN 973-95641-0-0, ICTCM, Bucuresti, 1992, p.153
4. E. VASILESCU, Studii si cercetãri privind procesul de reducere al oxizilor de nichel cu hidrogen pentru obtinerea pulberii de nichel destinatã fabricrii acumulatorilor alcalini Ni-Cd, teza dedoctorat, Galati 1996
5. STERNBERG, S., LANDAUER, O. Chimie fizicã, E.D.P., 1981, partea a VII-a, Cinetica chimica
6. CICIC, D-T., RONTESCU, C., C. GH. AMZA, CHIVU, O., (2015), The Combined Effect of Chemical Elements on the Propertiesof a Layer Deposited by Welding, Rev. Chim.. (Bucharest), **66**, no. 9, 2015, p.1299
7. CHIVU, O., RONTESCU, C., CICIC, D-T., Research On The Quality Of Heterogeneous Welded Joints Between Copper And Stainless, Rev. Chim. (Bucharest), **66**, no.11, 2015, p. 1752
8. GHIBAN A., GHIBAN B, BORTUN C.M., BUZATU M., Structural Investigations in CoCrMo(Ti) Welded Dental Alloys, Rev. Chim.(Bucharest), **65**, no. 11, 2014, p. 1314

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