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Structural changes during pressing of fine nickel powders

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Structural changes that take place during pressing of carbonyl powder of nickel are discussed. Particular attention has been paid both to the formation and state of the oxide powder surface during this process.

1. Introduction

The influence of pressing pressure on metal powders consolidation has been most frequently investigated from a phenomenological point of view [1]. A mathematical relationship that describes this process from macrokinetical point of view was sought [2]. However, in our previous paper we have focused our attention on the mechanism of consolidation when we established that at the macrolevel consolidation is the process that results from elementary processes occurring in a dispersed system under the influence of pressure [3].

In this paper we investigated the influence of the pressing pressure on consolidation of nickel powder that was obtained by carbonyl process.

2. Experimental procedure

Carbonyl powder of nickel, with particle size of 1–4 μm (Fig. 1) was pressed under pressures of 100, 400 and 700 MPa. In order to provide a better packing oleic acid was used as a lubricant. The density and porosity of samples obtained are presented in Table I.

The microstructure of obtained samples was studied by light microscopy. It is evident that the increment of the pressing pressure is followed by better packing of the nickel powder particles as well as by reduction of size and quantity of pores (Fig. 2).

With the aim to determine the influence of pressing on secondary changes during this process, Auger electron spectroscopic and X-ray photoelectron analyses of powder pellets were performed.

Apart from this, determination of the oxygen content in obtained samples (Table II) was carried out using a vacuum-melting method.

3. Results and discussion

Due to the analysis of the microstructure of the nickel powder (Fig. 1) it is evident that particles are badly focused on the electron scanning microscope giving evidence of the high degree of their oxidation. It was established by X-ray diffraction that NiO lines mainly exist on diffractograms, while nickel lines are of considerably lower intensity. Oxygen content in the initial powder is 1.1% (Table II) and it is very likely in the form of an oxide on the surface of the nickel powder. This also results from stability conditions of oxide coatings [4] according to $V_{\mathrm{MeO}}/V_{\mathrm{Me}} = 1.52$, which means that NiO represents a compact layer covering the whole surface of the initial nickel particles. (V_{MeO} and V_{Me} are the volume of the metal oxide and metal, respectively.)

In order to estabish the physicochemical processes that are performed during pressing, the oxygen content was determined in samples as a function of the pressing pressure (Table II). Measured results have shown the following:

1. pressing increases oxygen content in pellets in comparison to the initial state;
2. the rise in pressing pressure decreases the oxygen content in pellets.

Such a high concentration of oxygen in the pellets of finely dispersed carbonyl powder can be explained by its presence:

1. in the air that remains in the pores during pressing;
2. in the near surface layer from oleic acid that absorbs oxygen from the air;
3. in the surface oxide layer on initial powder particles.

Analysis of the oxygen content in pellets, without application of lubricant showed no change of oxygen content in the pellet's volume during an increment of pressing pressure and was the same as in the starting powder of nickel (~ 1%). The porosity of pellets was

TABLE I Change of density (ϱ) and porosity (P) during pressing of nickel powder

p (MPa)	ϱ (g cm^{-3})	P (%)
100	4.04	54.60
400	6.13	31.10
700	6.84	23.14

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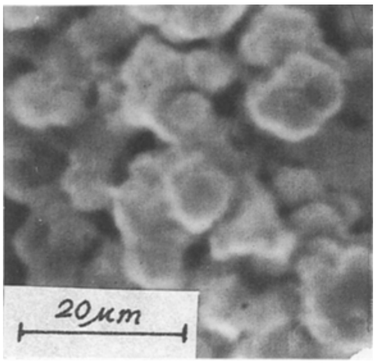


Figure 1 Microstructure of fine dispersed nickel powder.

practically the same either with lubricant or without it. Thus, the rise in oxygen content in the pellets, compared with its content in the initial nickel powder, should be attributed to oxygen that is adsorbed by the mineral oil used as a lubricant. On the other hand, reduction of oxygen content in pellets with an increment in pressing pressure explains the decrement in porosity and, in this connection, explains the weakening of the surface active influence of mineral oil in the pore volume.

Pressing of any powder, and consequently of investigated nickel powder, begins with the interaction of its particles. To establish the state of surface layers and the changes that take place in the same way, we used X-ray photoelectron (RFES) and Auger electron spectroscopic analytical methods. Selection of these methods was conditioned by the fact that surface appearances can be explained in the most rational way by different spectroscopic methods.

Results of X-ray photoelectron analysis are shown in Fig. 3. As the analysed depth was 2.5 nm then the results obtained by this method should be considered as the surface oxidation layer of nickel particles in a pellet. It is evident from experimental X-ray photoelectron spectra that the rise of the pressing pressure from 100 to 700 MPa, increased the oxygen content (Fig. 3a). This process is followed by an increment in the degree of oxidation. The rise of the NiO peak intensity on the spectrogram with an increment in the pressing pressure, favours the above mentioned process (Fig. 3b).

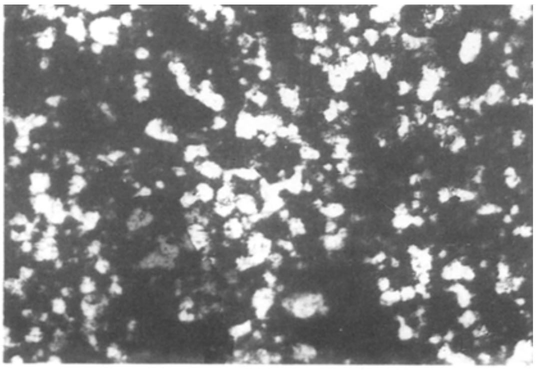
TABLE II Oxygen content in nickel powder.

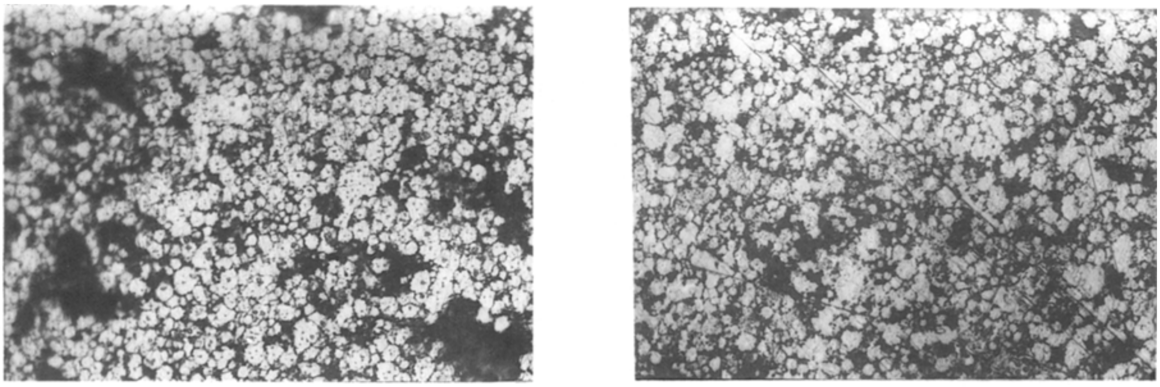
Pressure (MPa)	Oxygen content (%)
0 (powder)	1.1
100	3.7
400	1.8
700	1.5

At the very moment of particle interaction during cold forming of powders, a considerable quantity of heat, localized in a very small matter volume is released. Although the released heat rapidly expanded through particles at that moment, it first causes a local rise in temperature. This causes an increment in degree of oxidation of metal particles during cold pressing. From that point of view we explain the growth of the NiO peak intensity during the rise of the pressing pressure, as the rise in the pressing pressure increased the number of metal contacts between particles. It is very likely that the additional oxidation aggregates densification of the investigated finely dispersed nickel powder. Thus we showed [1] that additional oxidation of metal powders during pressing without the presence of a lubricant is several hundred parts of oxygen percentage for tiny powders and even tenth parts for every fine powders.

Results obtained by X-ray photoelectron analysis were confirmed by investigations by Auger spectroscopy as is given in Fig. 4. Increment in the oxygen content in the surface NiO layer (1 nm) of nickel particles with a rise in pressing pressure is evident even during etching of layers by ionic bombardment of the surface to the depth of 70 nm (ionic etching for 5 min).

It is known that a free surface in a crystal represents a source and sink of vacancies as well as of other point


(a)


(b)

(c)

Figure 2 Microstructure of nickel powder pellets (× 1000). (a) p = 100 MPa; (b) p = 400 MPa; (c) p = 700 MPa.

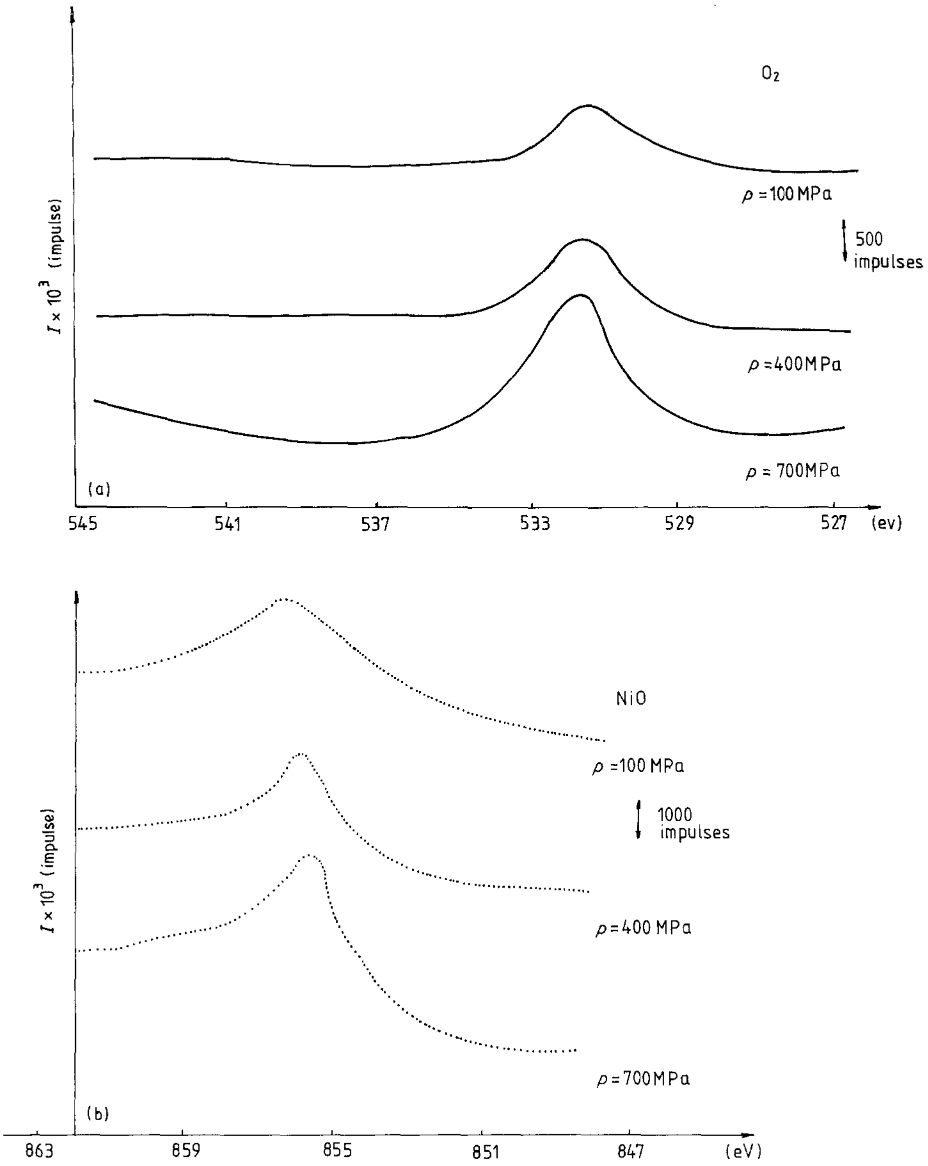


Figure 3 RFE – spectra of nickel powder pellets, (a) $1s_{1/2}$ electron spectra at particle surface; (b) $2p_{3/2}$ electron spectra of NiO.

defects. Therefore the presumption prevails that in powder materials, where the participation of free surface energy in total free energy system is high (it particularly increases with an increment in degree of dispersity), the concentration of vacancies is far greater than in a compact metal. Owing to the method of annihilation spectroscopy it was discovered that during pressing under high pressures ($p = 1200$ MPa) of ultradispersed nickel powders, the particle size of which is 70 nm, the concentration of vacancies over 10^{-4} is formed which corresponds to parameters of a overheated melt [5]. Therefore, the attempt was made to estimate the concentration of vacancies in finely dispersed carbonyl nickel powder by annihilation of positrons.

The study was made difficult by the fact that different sorts of defects exist in a crystal lattice (pores, vacancies, dislocations) because of the high powder dispersity, as well as numerous division surfaces. Today, two-component decomposition of experimental spectra can be performed with high precision. Analysis of tri- or even tetra-component spectra can be carried out.

Table III gives data on the change of the mean life-time of positrons and the results of two-component decomposition of experimental spectra. The mean life-time was calculated according to the following formula:

$$\bar{\tau} = (I - J)\tau_1 + J\tau_2 \qquad (1)$$

where J is the intensity of a long-life component, τ_1 and τ_2 are short and long-life components.

The life-time $\tau_1 = 170$ psec corresponds to the life-time of positrons in NiO and is constant for all pressing pressures.

The life-time τ_2 corresponds to the life-time of positrons existing in micropores. Comparison of the obtained life-times to literature data [6] where the life-time τ_2 is determined for vacancy clusters of different size, it can be concluded that during fine pressing of dispersive nickel powder τ_2 corresponds to

TABLE III Change of annihilation parameters of positrons in pellets in nickel powder depending on the pressing pressure

p (MPa)	$\bar{\tau}$ (psec)	τ_1 (psec)	τ_2 (psec)	J
100	184	170	330	60
400	215	170	276	53
700	218	170	260	50

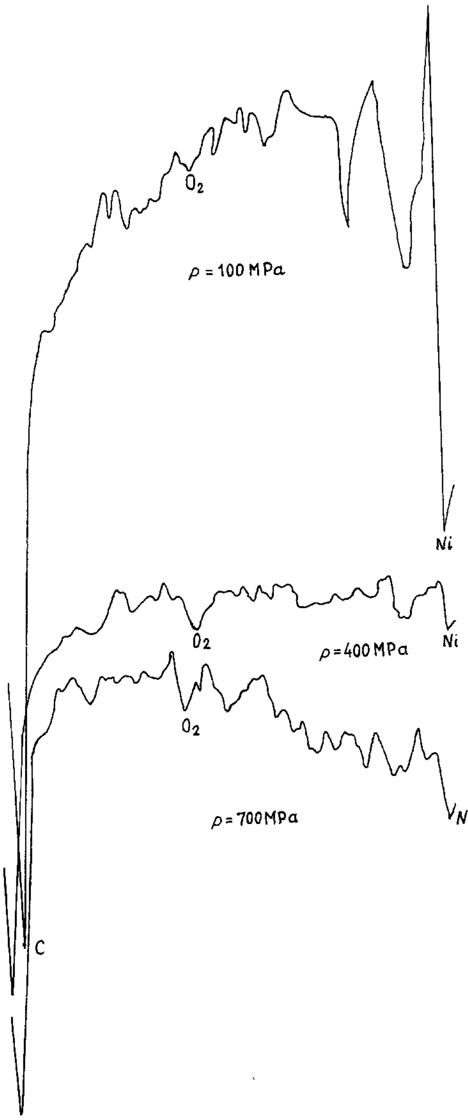


Figure 4 Auger spectra of nickel powder pellets.

the life-time of positrons in a vacancy cluster consisting of 3 to 5 vacancies. It is obvious that owing to the annihilation investigation we can determine the presence of submicropores. On the basis of analyses of obtained data on the change of intensity life of a long lasting component it can be concluded that in samples of finely dispersed carbonyl powder of nickel ($\sim 1\ \mu$m) the rise in pressing pressures caused reduction of both size and quantity of submicropores.

4. Conclusion

On the grounds of performed physicomechanical and structural investigations of carbonyl finely dispersed powder of nickel, the conclusion can be made that cold pressing of this powder with a lubricant, performed in air, is followed by reaction in a solid phase due to which the rise of the pressing pressure causes:

1. increment in degree of oxidation of the starting particles;
2. increment in O_2 content in surface oxide layer;
3. reduction of O_2 content in a whole pellet's volume because of a decrement in porosity and absorption influence of a lubricant as a surface active matter;
4. reduction of size and quantity of submicropores.

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