

# Sintering of cobalt-doped nickel oxide

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The influence of Co additions on the sintering of nickel oxide was studied. On the basis of the density, specific surface area and  $Me^{3+}$  ion concentration changes, in the  $Co_yNi_{1-y}O$  samples, having 0, 1, 5 and 10 cation % of Co, a positive effect of Co ions on the densification was assumed, during sintering at 500 to 900°C in an argon atmosphere. Using special heat-treatment, the differences in specific surface area of the investigated powders were eliminated. The differences in green densities were excluded as well and from the results, it was possible to show that dissolved Co ions enhance nickel oxide densification process.

## 1. Introduction

The effect of additives on the sintering of basic oxides is a complex problem, especially when by doping, considerable changes in physical properties of powders are produced. This fact makes a study of the effect of additions only, on the densification of basic oxides impossible, because changes of the sample characteristics during sintering are not unambiguously determined by different dopant concentration, but also by the different physical properties of the starting powders and green pellets [1]. In that case, the discussion of the results should take into account all important effects which are produced by the process of additive introduction. After the synthesis of  $Co_yNi_{1-y}O$  solid solutions with different Co concentrations [2], produced under essentially the same conditions, it was found that the powders with 0, 1, 5 and 10 cat. % Co, possessed considerably different physical properties; for example, the specific surface area was 29, 30, 40 and 94  $m^2 g^{-1}$  respectively. Green pellets, obtained from synthesized powders, possessed obviously different densities. It was not unexpected that the densities achieved after sintering were due to both the structural factors, i.e. composition, non-stoichiometry, and geometrical ones, i.e. different physico-chemical properties of powders [1].

In this paper, the influence of dissolved Co ions, from 0 to 10 cat. %, on the sintering of nickel oxide was investigated. The discussion of the results is based on both the Co ions present

in solid solution, i.e. their role in the densification process, and on the contribution of starting powder and green pellet properties to the densification process. On the other hand, by subsequent heat-treatment of starting powders, a new series of powders was obtained which showed almost no difference in specific surface area values. By pressing pressure variation, green pellets of different composition having the same per cent of theoretical density were made. After sintering these samples, results were obtained on the basis of which the influence of solute  $Co_{Ni}$  only, on the densification during sintering of CoO-NiO, could be discussed. In that way, the positive effect of the presence, as well as of the increasing concentration of Co ions, on the mass transport mechanisms during sintering, were unambiguously stated.

## 2. Experimental work

$Co_yNi_{1-y}O$  powders, with various cationic contents of Co ( $y = 0.01, 0.05$  and  $0.1$ ) were obtained by simultaneous precipitation of cobalt and nickel carbonates, and by subsequent decomposition of mixed salts, at 450°C in an  $N_2$  atmosphere. A description of this procedure and a detailed characterization of the powders are given in a previous paper [2]. The powder properties are summarized in Table I.

Experiments performed initially involved the pressing of these powders under a pressure of 98.1  $MN m^{-2}$ , and sintering in an argon atmosphere in the temperature range 500 to 900°C, for 1 h. Sample densities before and after sintering,

TABLE I Characteristics of synthesized CoO–NiO powders

Sample	Me <sup>3+</sup> (cationic %)	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	Lattice parameter (Å)	Theoretical density (g cm <sup>-3</sup> )
A NiO	1.405	29.4	4.176 <sub>6</sub>	6.808
A1 Co <sub>0.01</sub> Ni <sub>0.99</sub> O	1.468	30.8	4.176 <sub>8</sub>	6.800
A2 Co <sub>0.05</sub> Ni <sub>0.95</sub> O	2.604	40.2	4.178 <sub>4</sub>	6.791
A3 Co <sub>0.10</sub> Ni <sub>0.90</sub> O	3.746	94.6	4.183 <sub>3</sub>	6.780

determined from weight and dimension measurements, are shown in Fig. 1. The concentration of Me<sup>3+</sup> ions, determined according to Chervinko [3] (Fig. 2) as well as specific surface area (Fig. 3), were determined before and after sintering under identical conditions. In Fig. 4, the change in linear dimensions of the investigated samples during sintering, is shown.

### 3. Discussion of results

From the density values of the powders, after sintering at 500 to 900°C, given in Fig. 1, it can be seen that at each temperature, samples having

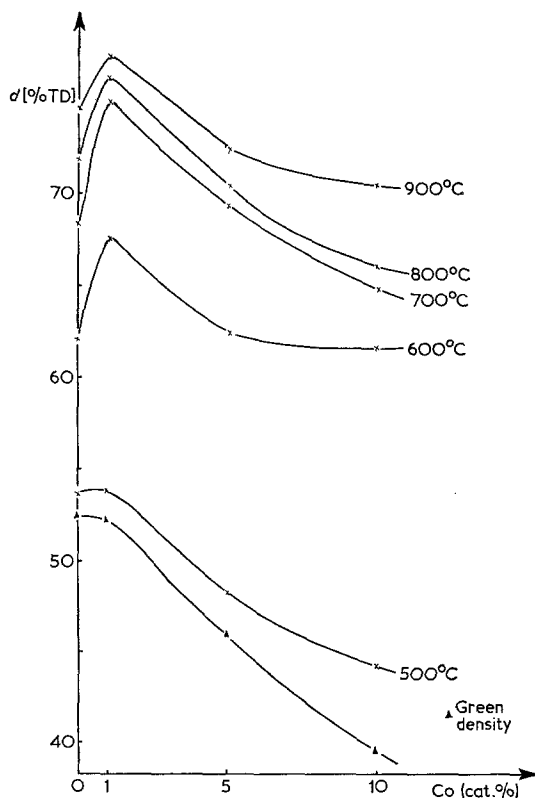


Figure 1 Isothermal density change as a function of Co content.

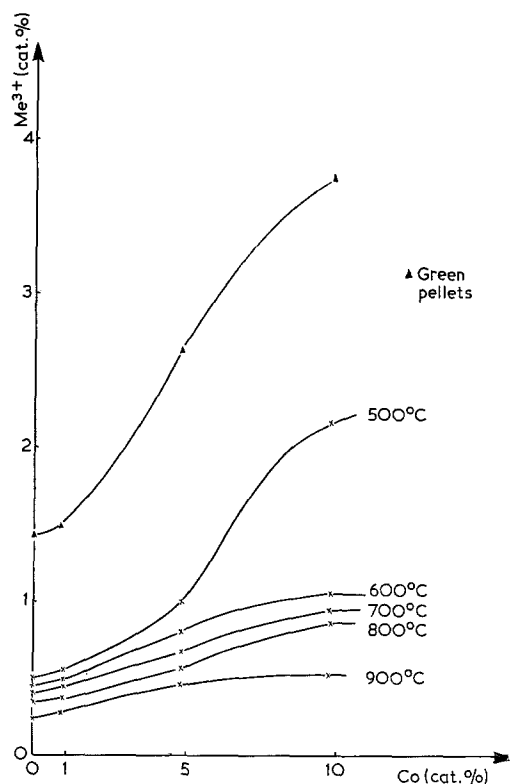


Figure 2 Me<sup>3+</sup> ion concentration as a function of sintering temperature and Co content.

1 cat.% of Co, show higher densities compared to those of pure NiO. At the same time, the densities of specimens containing higher Co concentrations are lower, the higher the Co content. It may also be noted that green density, given in per cent of the theoretical, for different solid solutions, varies inside 12%. This latter information suggests that even at the beginning, samples of different states exist, so it is quite natural that the final states after sintering are in some degree the result of this fact.

Specific surface area (Fig. 3) during sintering, in the conditions mentioned above, changes more considerably with increasing Co content in the samples and is greatest for sample A3. The

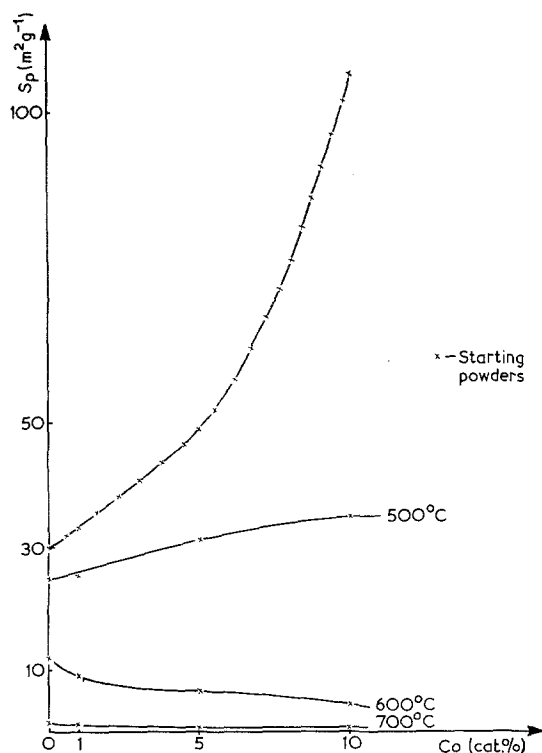


Figure 3 Specific surface area change during sintering as a function of sintering temperature and Co ion content.

same is valid for the change in  $Me^{3+}$  ion concentration (Fig. 2). Green and sintered densities results, shown in Fig. 1, as well as the data for linear dimension changes during sintering (Fig. 4), indicate a more pronounced densification during sintering, with increasing Co concentration.

It was mentioned earlier [4] that during the first stage of intense shrinkage of  $Ni_{1-x}O$ , an important role was played by structural factors (stoichiometry). Owing to these factors, the driving force for mass transport by volume diffusion increases because of the setting up of the oxygen chemical potential gradient, which is the consequence of gas-solid interaction (non-stoichiometric oxide- $O_2$  from the atmosphere). Specific surface area, as shown for  $Ni_{1-x}O$ , [4] did not greatly influence the shrinkage kinetics, and its role as a geometrical factor was not of importance. Much more important was its role in the gas-solid interaction.

Taking into account the density change during sintering (Fig. 5), it was found that this change was greater the higher the Co ion concentration in CoO-NiO. From these data a positive effect

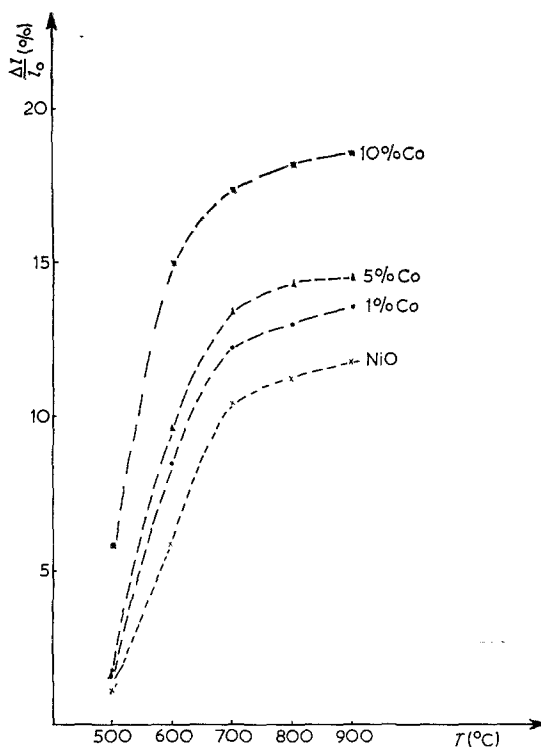


Figure 4 Temperature dependence of linear shrinkage.

of dissolved Co ions on the densification could, however, be stated only in the case of sample A1 because the starting properties of powders and green pellets of NiO and  $Co_{0.1}Ni_{0.99}O$  (Fig. 1, Table I) are almost the same.

Density change, i.e. increase during sintering, of samples A2 and A3, could be due to the different Co contents, and also to the different starting properties of powders and green pellets. By presenting the results in the form of a Lenel parameter (Fig. 6), one can see that the densification degree of Co-doped samples is higher as compared to the pure NiO, but at the same time, is greatest in the case of sample A1, and less for samples A2 and A3. Although the Lenel parameter transforms the results to the percentage of achieved densification degree as a fraction of theoretical, it cannot exclude the influence of different powder activities, contact area and particle packing inside the green pellets. Not even these results are a reliable base from which the effect of Co ions, present in solid solution in concentrations higher than 1 cat.%, on the NiO densification, could be deduced and conclusions given.

A greater decrease of specific surface area

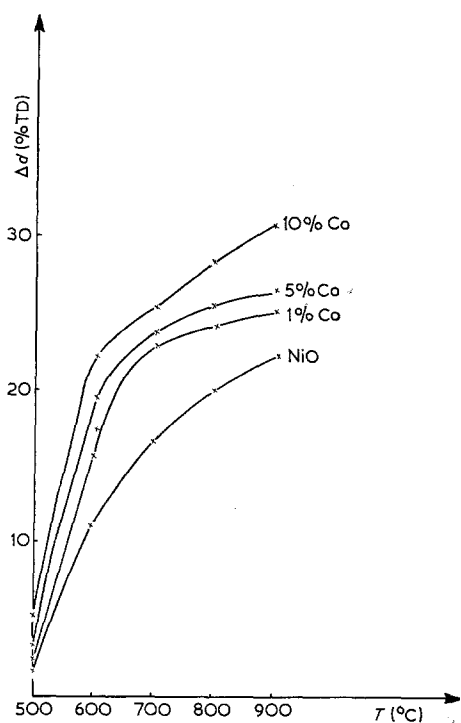


Figure 5 Density change ( $d_s-d_i$ ) as a function of sintering temperature.

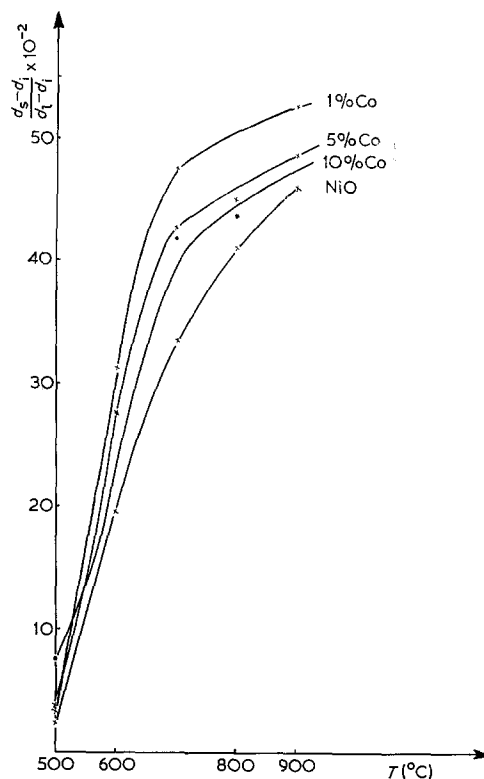


Figure 6 Lenel parameter as a function of sintering temperature and Co content.

during sintering, with increasing Co content (Fig. 3), indicates that during this process, in the samples having a higher Co concentration, the rounding and welding of the particles were intensified. There is no doubt that a decrease of specific surface area during sintering results from both processes. As mentioned earlier, dimensional changes during sintering were greater with samples having a higher Co content. In relation to this, it could be said that the increasing Co ion concentration enhances the rate of approach of two particle centres, according to the sphere-sphere model. On the other hand, on the basis of specific surface area change in different atmospheres [1], it could be said that the contribution of a particle rounding process to the lowering of specific surface decreases with increasing Co concentration in the samples, while simultaneously the surface diffusion coefficient increases. This means that the retardation effect of surface diffusion [5] on the driving force for volume diffusion slows with increasing Co content. This conclusion is in accordance with Kröger's theory [6] of surface diffusion, which takes into account the fact that

subsurface layer thickness narrows with increasing defect concentration in the bulk.

A higher densification rate, with increasing Co concentration could be expected on the basis of the results given by Stiglich *et al.* [7] as well, according to which chemical diffusion in CoO–NiO solid solutions is promoted by raising the Co content.

In order to prove the positive effect of dissolved Co ions on the densification of the specimens investigated, some differences in the starting properties of powders and green pellets, which could mask the Co additive effect, were eliminated by chosen treatments. By annealing the powders A NiO and A1 at 500°C for 1 h in argon, and sample A2 in oxygen, a new series of powders was obtained, with almost no differences in specific surface area (specific surface was 21, 22 and 24 m<sup>2</sup> g<sup>-1</sup> respectively). These powders were pressed under pressure of 98.1 MN m<sup>-2</sup>, and then sintered in a range of temperature, 600 to 900°C, for 1 h in argon. The densities of these samples are given in Fig. 7. The results show that the sintering process

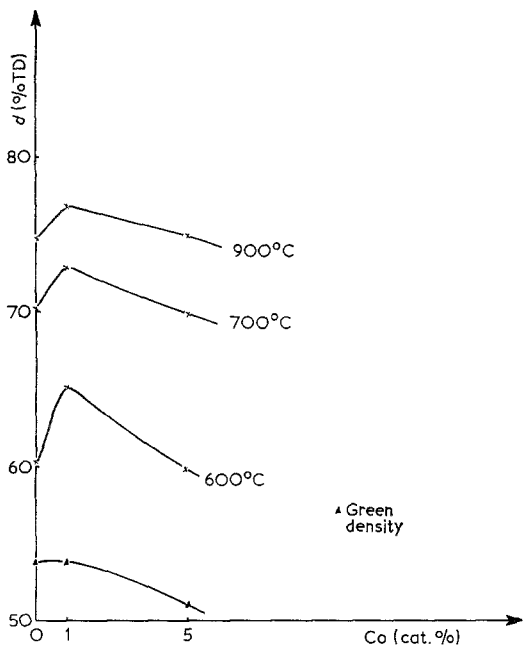


Figure 7 Isothermal density change of the treated samples, having the same specific surface area, as a function of Co content.

course is unchanged, and similar to the case of untreated powders. They show also that the specific surface area differences do not cause a

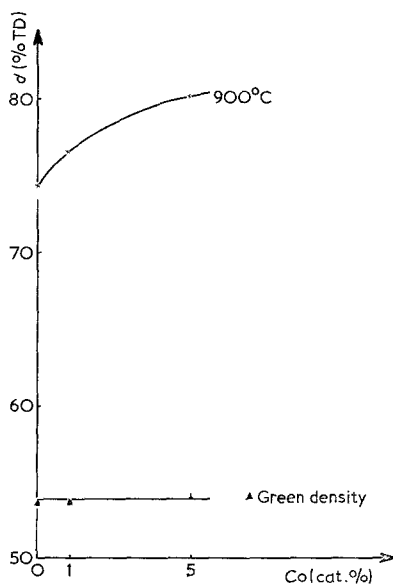


Figure 8 Sintered pellet densities of the treated samples, having the same specific surface area and the same green density, as a function of Co content.

variation in sintering kinetics appreciably as was also stated earlier for  $Ni_{1-x}O$  [4]. The specific surface area decreased due to the annealing of powders caused slight lowering of densification degree only, as compared to the untreated powders.

In the next step, treated powders with similar specific surface area, were pressed to the same green density (% TD), and thereafter sintered at 900°C. The results shown in Fig. 8 make possible proof that dissolved Co ions affect NiO densification.

By pressing untreated powders to the same green density, and sintering at 900°C, results are obtained (Fig. 9) which indicate that the density increases during sintering, with samples having a higher Co content. In this case, the density increase is somewhat greater than in the former one (Fig. 8) as would be expected.

The results obtained in the latter two cases indicate that factors taking into account particle packing are of great importance. They also show that the influence of impurities dissolved in NiO, on the atomic diffusion mechanisms, is considerably masked by them. At the same time, it may be noted that specific surface area does not mask this influence substantially, although its role in sintering is obvious. Namely, as mentioned above, samples having the same green density only (Fig. 9), but not the same specific surface

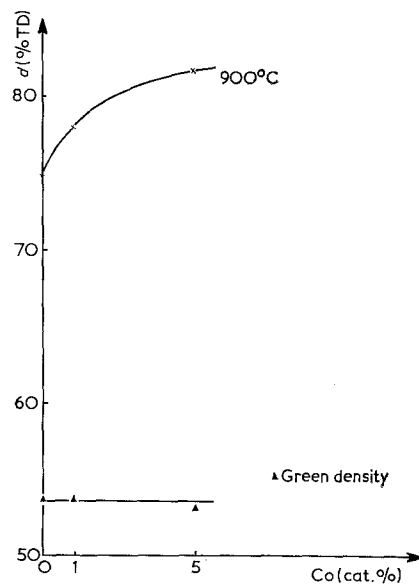


Figure 9 Sintered density of untreated samples, having the same green densities, as a function of Co ion concentration.

area, achieved higher densities after sintering under the same conditions than those which have both the same specific surface area and green density (Fig. 8). The role of specific surface area, as a geometrical factor, is obviously of less importance, but its role in gas-solid interaction is very significant. This can be understood if one notes that the defect concentration during treating of powders decreases. With the treated powders, the process of approaching stoichiometry, which brings about the formation of additional driving force for sintering [8] (oxygen chemical potential gradient), becomes less intense. This is the consequence both of the state reached after treatment (i.e. closer to the stoichiometrical one), and of the specific surface area (which enables the change of stoichiometrical composition) being lower.

$\text{Me}^{3+}$  ion concentration, i.e. deviation from stoichiometry, with the samples of different composition (different  $y$  in  $\text{Co}_y\text{Ni}_{1-y}\text{O}$ ), both treated and untreated powders, was different but in both cases higher with the samples having a higher Co content. After the treating procedure, the deviation from stoichiometry was less as compared to the untreated state; however, the  $\text{Me}^{3+}$  ion concentration, which represents the direct measure of this state, remained higher in specimens containing higher concentrations of Co ions. In treated samples A NiO, A1 and A2 it reached 0.47, 0.53 and 0.98 cat.%  $\text{Me}^{3+}$ , respectively. Therefore, in this case, it is the different rates of approaching stoichiometry that determines the different values of oxygen chemical potential gradient, i.e. the driving force for material transfer by volume diffusion. No doubt the gradient was the highest with sample A2, which reached the highest densities after sintering.

It has been mentioned already that increased Co ion concentration in CoO–NiO solid solutions brings about the increase in chemical diffusion coefficient [6]. It follows that higher densification rates with the solid solutions possessing increasing concentrations of Co, as is the case here, should be expected. Higher densities, i.e. densification degree, with the samples containing an increased Co content, is the consequence of enhancement both of the chemical diffusion coefficient and the additional driving force, due to local changes of stoichiometrical composition. However, one must bear

in mind that these two factors are not completely independent.

#### 4. Conclusion

The influence of dissolved Co ions in the concentration range 0 to 10 cat.%, on the sintering of nickel oxide was examined. The  $\text{Co}_y\text{Ni}_{1-y}\text{O}$  powders, of different cobalt content, obtained under identical conditions, possessed different physico-chemical characteristics. The density change of the pellets, obtained under the same pressing pressure, and also the densification degree, although proportional to the Co ion content, could not give absolute proof of the positive effect of Co ions, on the atomic diffusion mechanisms, which determine mass transport during sintering. Taking into account that the initial states of the samples with different Co contents differed in activity, densities achieved after sintering were influenced both by the starting composition and states of the solid solution powders. By excluding some differences in the starting characteristics (specific surface area, green density), data are obtained which show:

- (i) the presence and increasing concentration of Co ions in solid solutions CoO–NiO in the nickel oxide rich region, enhances the densification process;
- (ii) specific surface area also exhibits a positive effect on the process;
- (iii) the effect of particle packing in green pellets, that determines the densification to a high degree and also considerably masks the influence of Co ions.

Enhancement of the densification process of nickel oxide by the present Co addition, can be explained as:

- (a) setting up a higher additional driving force for mass transport due to local fluctuations in stoichiometry, i.e. due to the formation of a higher oxygen chemical potential gradient with samples having a higher Co content;
- (b) a higher chemical diffusion coefficient in the CoO–NiO [7] system, with increasing Co concentration;
- (c) a decreasing contribution of surface diffusion to the deactivation of powders having increasing Co contents, during sintering.

The last conclusion is based on the results obtained by measuring the change in specific surface area in different atmospheres [1], and is in accordance with Kröger's theory [6]. This indicates that although the rate of mass trans-

port on the surface of metal deficient oxides increases with increasing deviation from stoichiometry, the total surface mass flux can be less, due to a narrowing of the sub-surface layer.

### Acknowledgements

The authors wish to thank Dr Šandor Kiss for reviewing the paper, and for useful suggestions.

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Received 22 May and accepted 21 June 1974.