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Sintering of nickel oxide powders of different stoichiometric composition

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The sintering process of non-stoichiometric oxide of Me_{1-x} type, with different "x" values, was examined. Sintering was performed in air at temperatures up to 1400°C. In the analysis of the results obtained, special attention was paid on the role of steric factors (the geometric conditions in the powder compact, and the space arrangement of the particles in it), and structural factors (lattice defects of non-stoichiometric origin), in the sintering process of the non-stoichiometric nickel oxide.

1. Introduction

The sintering of non-stoichiometric materials is a special problem owing to the possibility of continuous change in the chemical composition of these materials during the sintering process. In other words, the chemical composition of non-stoichiometric oxide materials, changes according to the sintering temperature, the oxygen partial pressure in the surrounding atmosphere, and the initial state of the material. Interaction with the atmosphere, which results in a local change of the chemical composition, consequently leads to the formation of, or a change in, the oxygen chemical potential gradient between the surface and interior of the particle. The existence of a gradient of the chemical potential of oxygen is an additional driving force in the sintering process [1], i.e. of the mass transport by volume diffusion. Therefore, when we speak of the sintering of non-stoichiometric compounds we must take account of the contribution of this flux of the mass to the total flux of the material by the mechanism of volume diffusion.

In addition, non-stoichiometric oxide materials are characterized by all the properties possessed by other ceramic materials. This means that in the sintering process both structural and steric factors play a part. In the paper by Bošković and Živanović [2] a contribution is made to knowledge concerning the part played by structural and steric factors in the sintering of nickel oxide. The authors are of the opinion that the influence of structural factors is of greater significance in the sintering of this material.

This paper deals with the sintering of nickel oxide powders of different initial chemical compositions where special attention is paid on the influence of structural factors (of the non-stoichiometric type), i.e. to the contribution of the gradient of the chemical potential of oxygen, and to the influence of steric factors, i.e. to the contribution of the gradient of "elastic potential" [1], during the sintering of real nickel oxide powder.

TABLE I Characteristics of initial NiO powders

Property	NiO-1	NiO-2	NiO-3
$S_p(m^2g^{-1})$	0.22	38.4	24.8
Ni^{3+} cation %	0.04	1.695	1.660
D (10^{-10}m) crystallite size	—	198	205

2. Experimental work

For the experimental work, three powders of nickel oxide were used, designated NiO-1, NiO-2 and NiO-3. The characteristics of these powders are given in Table I.

The NiO-3 powder was obtained by the thermal treatment of the NiO-2 powder in specially chosen conditions of time, temperature and atmosphere, in order to yield a definite change in the specific surface of the material but not in the Ni^{3+} ion concentration [3].

The powders were pressed at pressures of 49 and 294.3 MN m^{-2}. Sintering was carried out in a dilatometer at an annealing rate of 10° min^{-1}. in air. The curves of linear shrinkage are given in Fig. 1.

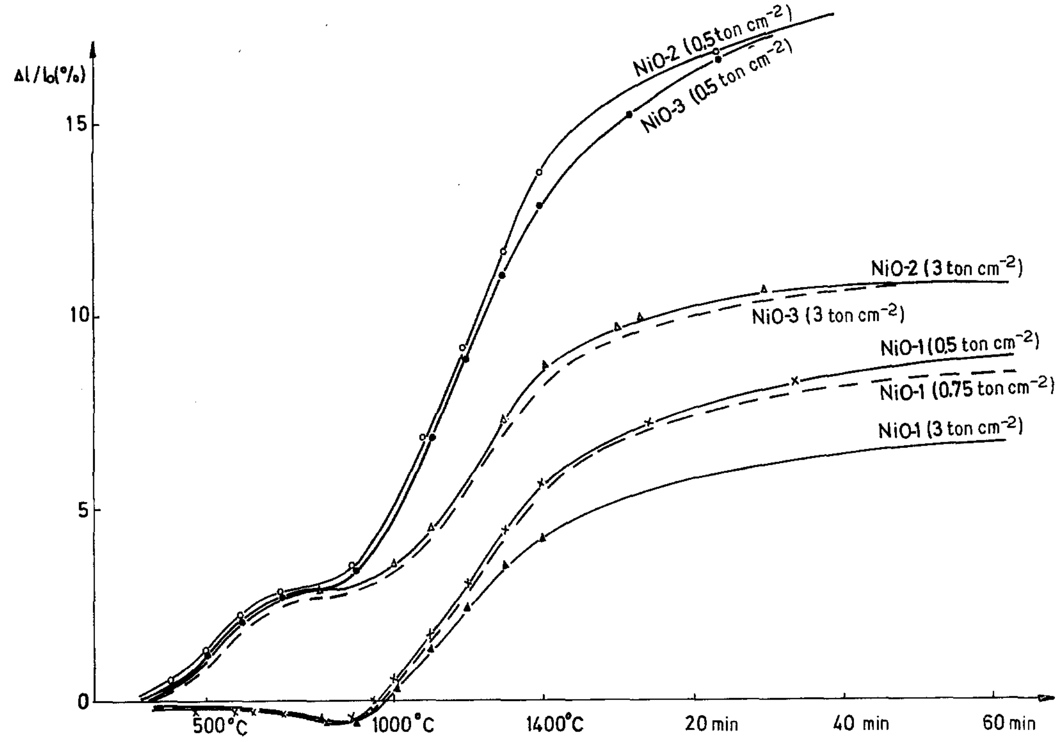

Figure 1 Linear shrinkage of NiO-1, NiO-2 and NiO-3 powders.

3. Discussion and results

Active nickel oxide powders have two phases of intense shrinkage. This has been confirmed earlier [2 3, 4], but these results make it obvious (Fig. 1). The first stage of intense shrinkage occurs between 400 and 800° C, and the second between 900 and 1300° C. In our earlier studies [3], we noticed that during the first period of intense shrinkage of "active" powders of nickel oxide such as NiO-2 and NiO-3, great changes occur in the specific surface and in the concentration of Ni^{3+} ions, i.e. a deviation from the stoichiometric composition. Detailed conclusion regarding the influence of these two factors can be drawn from the data given in Fig. 1. Thus, the powders NiO-2 and NiO-3 have the same concentration of nickel vacancies, but a different specific surface. This difference in specific surface is reflected only in the shift in maximum shrinkage rate in NiO-3, during the first stage of intense shrinkage (Fig. 2), towards higher temperature by about 50° C. However, as has been stated previously [2], the influence of the specific surface cannot be considered in the light of the part it plays as a steric factor, as it is much more complex. In fact, its contribution is very significant also in the gas-solid interaction. In agreement with this, we obtained different separation rates of oxygen in NiO-2 and NiO-3 according to the reaction

$$2Ni^{3+} + O^{2-} + V_{Ni} \rightarrow 2Ni^{2+} + 1/2\,O_2 \qquad (1)$$

as shown in Fig. 3. These results are quite in accordance with the fact that a powder with a more developed surface (NiO-2) reacts more intensely with the surrounding gaseous atmosphere. In our opinion, this is reflected in the shift in maximum shrinkage rate in the first phase of intense shrinkage. In fact, on the basis of our results up to now [2, 3, 5, 6], it can be said that the reaction with the atmosphere controls the sintering of nickel oxide, especially in the first stage. To support this, the following results can be introduced. The powders NiO-2 and NiO-3, pressed at different pressing pressures (49 and 294.3 MN m^{-2}) have different steric conditions in their initial pressings. It could be expected that this factor might have an influence on the course of the shrinkage curve. However, if we compare this result with those shown in Figs. 2 and 4, we may conclude that the shrinkage

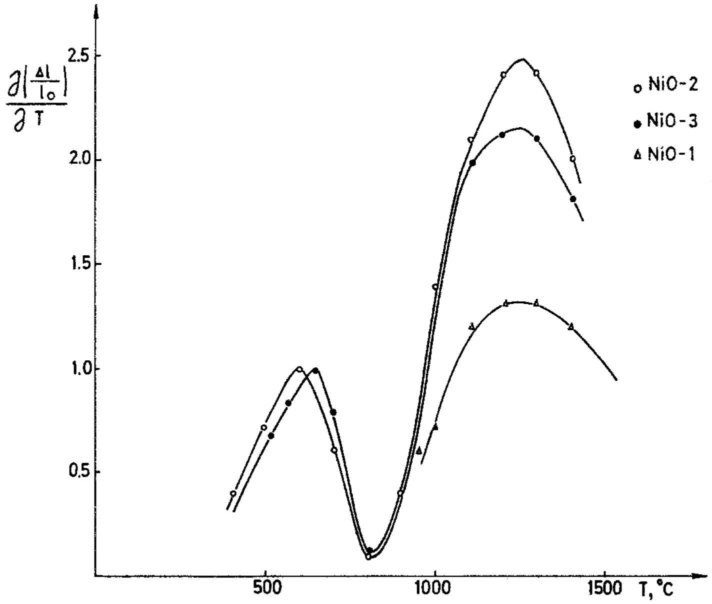

Figure 2 Shrinkage rate of NiO-1, NiO-2 and NiO-3 compacts obtained under 49 MN m^{-2} pressure.

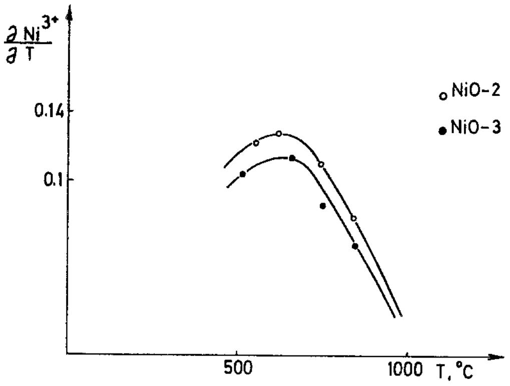

Figure 3 Rate of decrease in Ni^{+3} ion concentration in NiO-2 and NiO-3 samples.

rate in the first phase of intense shrinkage hardly changes as the pressing pressure increases. The influence of the pressing pressure is reflected in the second phase of intense shrinkage where the shrinkage rate of the pressings falls as the pressing pressure increases. Fig. 1 reveals one other fact. Namely, if we look at the differences between the course of shrinkage in the powders NiO-2 and NiO-3 on the one hand, and NiO-1 on the other, it may be noticed that now NiO-1, whose composition is very similar to a stoichiometric one, has no first phase of intense shrinkage. In our opinion, the reason for this may be that, in this case, the interaction with the atmosphere does not occur to the degree that would, in our experimental conditions, reflect the action of the flux of mass caused by a local difference in the chemical composition. However, it must not be concluded that this did not happen at all, rather that if it did, it was not in such a degree as to be reflected in the sintering of the NiO-1 powder. Therefore, when referring to the sintering of this powder, the driving force resulting from a local difference in the chemical composition does not exist in a sufficient degree to produce the flux of the mass which is, therefore, missing. In other words, the first member on the right side of Equation 2 [1]

$$J_{\text{tot.}} = J_{\text{ch}} + J\text{e}, \qquad (2)$$

where $J_{\text{tot.}}$ = total flux of mass caused by volume diffusion; J_{ch} = flux of mass following the gradient of the chemical potential of oxygen excess; J_{e} = flux of mass as a result of a gradient of elastic potential (owing to different curvatures of the neck and particle surface), is insignificant in this case for tests carried out in the range of the temperature examined, and in air. This also contributes to our opinion that Reaction 1 controls the sintering during its first stage.

The shrinkage of NiO-1 powder is first noticed about 900 to 1000° C, at precisely the point where the powders NiO-2 and NiO-3 begin their second phase of intense shrinkage. In the temperature

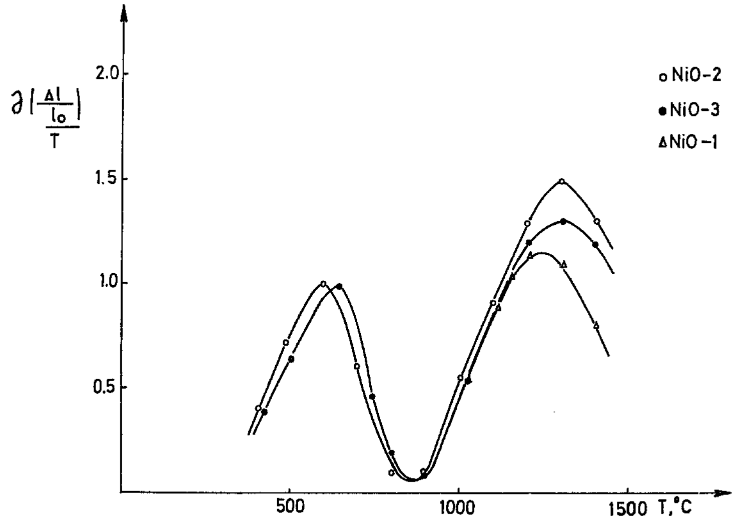

Figure 4 Shrinkage rate of NiO compacts obtained under 294.3 MN m^{-2} pressure.

range above 900° C, the influence of the pressing pressure on shrinkage can be observed, as mentioned earlier. As the pressing pressure rises there is a decrease in the shrinkage rate of all the powders examined, where the temperature of maximum shrinkage rate remains unchanged.

In our earlier paper [3], we stated that, on the basis of microstructural analysis, the sintering process occurs within the framework of agglomerates of the nickel oxide powder. This was confirmed by measurements of the specific surface area of sintered samples as well as of loose powder having the same values. In the second phase of intense shrinkage, the sintering process occurred between the agglomerates. This indicates that in all probability the geometry inside the specimens (if agglomerates are concerned) has remained whole right up to the second phase of intense shrinkage when the influence of the pressing pressure is clearly noticed. This would mean that the second member of the right-hand side of Equation 2, i.e. the gradient of elastic chemical potential, now plays a more important part.

4. Conclusions

1. The first phase of intense shrinkage in active powders of nickel oxide is the result of the existence of a gradient of the chemical potential of oxygen which acts as the driving force of the mass transport by volume diffusion. This is in relation to the compounds which are stable in the same conditions, an additional driving force in sintering, which appears as a result of a local fluctuation in the chemical composition of the material.
2. The part played by the specific surface in the process of sintering of nickel oxide cannot be examined separately from the part it plays in the interaction of gas-solid which controls the sintering of nickel oxide.
3. The pressing pressure has no influence on the first phase of intense shrinkage of nickel oxide and, consequently, greater importance should be attributed to the structural factor in sintering in this area. The influence of the pressing pressure is reflected in the second phase of intense shrinkage which leads us to the conclusion that the part played by the steric factor here is much more visible.

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