JOURNAL OF MATERIALS SCIENCE 7 (1972) 1369–1372

Studies of solid solutions of chromic oxide in nickel oxide

J. SŁOCZYŃSKI, Z. KOWALSKI, T. WÓJCIKIEWICZ
Institute of Materials Engineering, School of Mining and Metallurgy, Cracow, Poland

A method of preparation of solid solutions of Cr_2O_3 in nickel oxide has been described. The homogeneity of the solid solutions obtained was controlled by determining the nickel and chromium content polarographically in the course of the zone dissolution of the samples. The presence of chromium-nickel spinel was detected by the X-ray analysis. The limiting concentration of Cr_2O_3 in the solid solution in equilibrium with the spinel has been determined.

1. Introduction

Classical works by Verwey on the changes of the electrical conductivity of nickel oxide caused by the incorporation of lithium oxide into its lattice have initiated extensive studies on physicochemical properties of solid solutions of metal oxides in which the metals have different valencies. Numerous papers on this subject appeared after 1950 owing to the rapid development of electronic theories of point defects and of chemisorption and catalysis. It is held that chemisorptive and catalytic properties of semiconducting oxides depend on the Fermi level position and hence can be modified by the formation of dilute solid solutions with metal oxides of different valencies (doping). One of the model systems frequently studied is nickel oxide and solid solutions of Li_2O and Cr_2O_3 in NiO [1-4].

There exist, however, some doubts as to whether the conditions of preparation of the doped nickel oxide samples used so far, do ensure the formation of homogeneous solid solutions. Fensham was the first to draw attention to the fact that even extensive annealing at 1100° C may not be sufficient for the preparation of the solid solution of Li_2O in NiO [5]. The method of preparation of the solid solutions of lithium oxide in nickel oxide has been a subject of studies by Bielański and co-workers [6] and more recently by Tseung and Bevan [7].

In the case of the Cr_2O_3-NiO system, the formation of the solid solution may be even more complex owing to the following facts. In the first place Cr_2O_3 may not be completely incorporated (Cr^{+3} ions may not be distributed uniformly in the bulk of nickel oxide phase), and secondly one may expect the formation of the chromium-nickel spinel, $NiCr_2O_4$ at higher amounts of chromium oxide introduced.

The aim of the present work is to propose the conditions for preparation of solid solutions of chromium oxide in NiO and to investigate analytical methods which may be applied in studies of this system.

2. Preparation of the samples

The solid solutions of Cr_2O_3 in NiO were obtained by annealing at high temperatures coprecipitated nickel and chromium hydroxides. The dried hydroxides were calcined at 500° C in a stream of pure oxygen for 1 h and then one portion of the preparation was annealed for 3 h at 1000° C and another one for 10 h at 1100° C. The preparations contained from 0.02 to about 10 at. % Cr. The preparation containing 66 at. % Cr of the composition corresponding to nickel-chromium spinel, and pure nickel and chromium oxides were also made.

The decomposition of the precipitates was followed by DTG and DTA analysis. All the precipitates with the exception of that containing 66 at. % Cr lost the water in a one-stage process at 340° C.

The precursor of the spinel phase shows a different pattern of decomposition: up to 350° C the dehydration is a continuous process, at 350° C the preparation loses one molecule of water and the last molecule of H_2O is removed at 510° C.

3. X-ray studies of the decomposition products

The studies comprised determination of the elementary cell parameters of the nickel oxide phase and analysis of the samples for the presence of the spinel and Cr_2O_3.

The parameter of the elementary cell, a_0, was determined with the powder method using Cu $K\alpha$ radiation with a Ni filter. The NaCl standard was added to the analysed samples. The measurements of the distance between the diffraction lines were made with the accuracy of ± 0.05°. From the *hkl* values obtained the parameter a_0 was then calculated, and a correction was introduced from the position of the diffraction lines of the standard NaCl. The final value of a_0 reported here is a mean value.

The semi-quantitative phase analysis was performed with the aid of a Tur M 1 diffractometer in the angle range 19 to 23° using Cu radiation. In the experimental (optimal) conditions used, the detectability of the $NiCr_2O_4$ phase was about 1 to 2% and that of Cr_2O_3 about 1%. The results obtained are given in Table I.

TABLE I

Total content of Cr (at. %)	Lattice parameter (Å)	Content of $NiCr_2O_4$ phase	Content of Cr_2O_3 phase
0	4.178 ± 0.003	–	–
0.55	4.176 ± 0.003	–	–
1.3	4.175 ± 0.002	–	–
3.75	4.178 ± 0.002	+	–
4.55	4.176 ± 0.003	+	–
6.7	4.178 ± 0.002	++	–
10.46	4.177 ± 0.002	+++	–

As seen from Table I, the values of lattice parameter of the preparations under study may be taken as constant within the limits of experimental error. The reasons why the lattice parameter of NiO is not affected by the introduction into its lattice of Cr^{3+} ions will be considered below. In the first place, it is possible that the ionic radii of nickel and chromium are practically identical. Although the earlier data on ionic radii give different values for these two ions (0.78 and 0.64 Å respectively for Ni^{2+} and Cr^{3+} according to Goldschmidt, and 0.69 and 0.63 Å according to Ahrrens), the more recent calculations by Smith [8] of 1963 indicate that the two radii are identical with a value of 0.69 Å. On the other hand, even assuming different values for the ionic radii of chromium and nickel, one should not expect large changes in the value of the lattice parameter owing to the relatively low solubility limit of Cr_2O_3 in NiO. This latter point will be considered in more detail in the next sections. It follows also from Table I that none of the preparations contained Cr_2O_3, and that beginning from the chromium content of 3.75 at. %, a systematic increase in the content of the spinel phase is observed.

4. Chemical analysis

The fractional (zone) dissolution method was used in the analysis, the chromium and nickel content being determined in successive fractions which were dissolved. The preparations annealed at 1000°C for 3 h were dissolved in 1N HCl; in the case of samples annealed at 1100°C, 4N HCl was used. The procedure was as follows: 0.1 g of the sample was introduced into 100 ml of boiling HCl and the solution was boiled under reflux conditions for a determined period of time. The solution was then separated from the undissolved part and the filtrate was analysed for the chromium and nickel content using a.c. and d.c. polarography methods described in detail elsewhere [9]. In additional experiments it was found that both nickel-chromium spinel and Cr_2O_3 prepared in the same conditions as the samples under study were practically insoluble in the studied solutions of hydrochloric acid; hence chromium detected in the filtrate came solely from the solid solutions which underwent dissolution. Table II presents the results of the zone analysis of the preparation containing about 3 at. % of Cr annealed at 1000°C for 3 h.

TABLE II

Fraction of the sample dissolved (wt %)	Concentration of Cr in dissolved fraction (at. %)
0– 9.5	2.5
9.5– 26.3	1.7
26.3– 53.9	1.25
53.9–100	0.4

It follows from the data given in Table II that the distribution of chromium in the bulk of the sample is not uniform and that there exists a gradient of its concentration directed from the surface towards the bulk of the crystallites. Such behaviour may be due to the insufficiently high temperature and insufficiently long time of the annealing. The analogous results for the series of preparations annealed at 1100°C for 10 h are listed in Table III.

TABLE III

Total amount of Cr (at. %)	Fraction of the sample dissolved (wt %)	Concentration of Cr in the dissolved fraction (at. %)	Mean concentration of Cr in the dissolved fraction (at. %)
1.3	0 - 19.2	1.00	1.00
	19.2- 52.0	0.89	
	52.0-100	1.10	
2.3	0 - 3.6	1.78	2.00
	3.6- 15.8	2.04	
	15.8- 28.9	1.97	
	28.9- 63.6	1.97	
	63.6- 79.3	2.06	
	79.3-100	2.04	

As seen from the data of Table III in the case of the samples containing 1.3 and 2.3 at. % Cr, the concentration of chromium in the bulk of the sample is constant within the limits of experimental error, which proves that in these cases we are dealing with homogeneous solid solutions. The samples of the higher chromium content beginning from 3.75 at. % Cr on the other hand show a different behaviour during the zone analysis. These samples are not dissolved completely even after the several-hour boiling in 4N HCl. The ratio of chromium to nickel in the dissolved fraction of these samples is practically constant and corresponds to a Cr content of about 1 at. %. At the same time, with the increase of the total amount of chromium the amount of the sample undissolved also increases; these results are illustrated in Fig. 1.

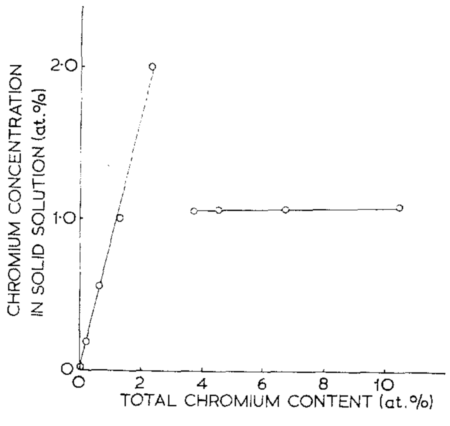

Figure 1 The dependence of the chromium concentration in the solid solution on the total chromium content in the sample. The samples were annealed at 1100°C.

It appears that the facts given above can be interpreted in the simplest way as follows. Above the chromium content of 3.75 at. % the spinel phase $NiCr_2O$ (practically insoluble in hydrochloric acid) is formed. In equilibrium with this phase, there is present a solid solution of Cr_2O_3 in nickel oxide, the concentration of which is at a given temperature, constant and independent of the amount of the spinel formed. This interpretation is fully confirmed by the results of the X-ray studies described previously.

A separate problem involved in the preparation of the solid solution under study is provided by the volatility of Cr_2O_3. In order to evaluate the losses of chromium caused by evaporation of Cr_2O_3 at the annealing temperature, a mass balance with respect to chromium was made for the preparation with total chromium content of 10.46 at. %. The calculations were done assuming that the total amount of nickel which had not been dissolved had reacted with the formation of the spinel. The volatility of NiO, which at 1100°C is negligible, was not taken into account in these calculations. The data obtained indicate that about 76% of the total amount of chromium in the sample reacted with the formation of the spinel, 9 % is present in the solid solution and about 15% evaporated owing to the volatility of Cr_2O_3.

5. Discussion

In the light of the results presented above it appears that the method of zone analysis can be successfully applied to studies of the solid solutions of chromium oxide in NiO. This method enables not only detection of the presence of small amounts of the spinel phase but also provides the possibility of accurate determination of the chromium oxide distribution in the bulk of the nickel oxide phase. The authors believe that this method may be successfully applied to the studies of other oxide systems.

The results obtained for the samples annealed at 1100°C made it possible to determine the chromium concentration in the solid solution in equilibrium with the spinel phase. This concentration is about 1 at. % Cr (which corresponds to 0.5 mol % Cr_2O_3). This result is in good agreement with the values of Greskovich

[10] obtained in the studies on rate of diffusion of chromium in NiO. Different results were obtained by Mehandjiev *et al* [11], who found that solid solutions of Cr_2O_3 prepared at 1000°C show different concentrations of Cr depending on the total amount of Cr_2O_3 in the preparation. The limiting concentration of chromium obtained in the solid solution was about 10 at. % Cr. According to the above authors also the spinel phase shows variable chromium content. It appears that these discrepancies may be due to the fact that the preparations studied by Mehandjiev *et al* were not in thermodynamic equilibrium with the spinel phase. This is highly probable as both the annealing temperature was comparatively low (1000°C) and the time of annealing was rather short (3 h).

It follows from the data of Fig. 1 that at 1100°C in equilibrium with the spinel phase, there exists a solid solution containing about 1 at. % Cr. In view of this fact the solution obtained in the present studies and containing 2 at. % Cr should be regarded as a supersaturated solution. From Fig. 1 one may estimate the limiting supersaturation at which the crystallization of the spinel begins as being equal to about 3 at. % Cr.

References

1. G. PARRAVANO, *J. Amer. Chem. Soc.* **75** (1953) 1452.
2. G. M. SCHWAB and J. BLOCK, *Z. Physik Chem.* **1** (1954) 42.
3. S. Z. ROGINSKI, N. P. KEJER, and I. S. SAZONOWA, *Doklady Akad. Nauk. SSSR* **106** (1956) 859.
4. M. E. DRY and F. S. STONE, *Discuss. Faraday Soc.* **28** (1959) 192.
5. P. FENSHAM, *J. Amer. Chem. Soc.* **76** (1954) 969.
6. A. BIELAŃSKI, J. DEREŃ, J. HABER, and J. SŁOCZYŃSKI, *Trans. Faraday Soc.* **58** (1962) 166.
7. A. C. C. TSEUNG and H. L. BEVAN, *J. Mater. Sci.* **5** (1970) 604.
8. F. G. SMITH, "Physical Geochemistry" (Wesley Publishing Inc, New York, 1963).
9. Z. KOWALSKI, J. SŁOCZYŃSKI, and T. WÓJCIKIEWICZ, *Chem. Analit.* in press.
10. C. GRESKOVICH, *J. Amer. Chem. Soc.* **53** (1970) 498.
11. D. MEHANDJIEV, I. TSOLOVSKI, and B. PIPEROV, *Bulg. Acad. of Sciences, Comm. of Department of Chemistry* **2** (1969) 181.

Received 2 February and accepted 12 May 1972.