

Equilibrium relationships in the system NiO-CoO-O₂

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As part of a programme to investigate the possibility of using conducting oxide electrodes in the fused carbonate fuel cell, equilibrium relationships in the system NiO-CoO-O₂ were investigated using a thermobalance. An isobaric ternary diagram of the system was constructed and it is shown that the variation in the temperature of the boundary between the single phase (NiO-CoO solid solution) and the two phase (Co₃O₄ + NiO-CoO solid solution) fields, with cationic composition, is consistent with approximately ideal behaviour. A mechanism based on the established phase relationships is also suggested to explain the observation that loss of oxygen from two-phase mixtures on heating results in the formation of NiO-CoO solid solution in the interior of the Co₃O₄ grains. Results are also presented to show the effects of composition and heat-treatment on the electrical conductivities at high temperatures of selected mixtures.

1. Introduction

The work was undertaken to explore the possibility of using conducting oxide electrodes in the fused carbonate fuel cell. The cathode in this cell is required to resist corrosion in an oxidizing atmosphere at 600°C and to retain an adequate surface area (porosity) while resisting disintegration in the fused alkali carbonate. Noble metals have been used as cathodes with some success in experimental fuel cells but their high cost, difficulty of fabrication and inadequate corrosion resistance has encouraged research into the use of conducting oxides as cathode materials.

Although several studies of this system have been reported, the phase relationships have not been clearly determined and in particular, there is uncertainty as to the stability of a spinel phase, NiCo₂O₄. Knop *et al.* [1] and Andrushkevich *et al.* [2] obtained this spinel by firing the mixed nitrates at low temperatures in air, and reported that it decomposed on heating to higher temperatures. However, the authors differed on their identification of the decomposition products.

Robin [3] examined the system in air using X-ray diffraction of quenched samples and established the position of the boundary

between the single-phase NiO-CoO solid solution field and the two-phase region in which Co₃O₄ was also present.

2. Starting materials

2.1. Nickel oxide

The nickel oxide was prepared from Analar nickel nitrate, Ni(NO₃)₂ · 6H₂O, by heating over a bunsen flame until nitrous fumes were no longer evolved, followed by calcining at 1200°C for 3 h. The oxide was then pale green in colour and was crushed to pass a 300 mesh B.S. sieve.

2.2. Cobalt oxide

Co₃O₄ was used and was prepared from Analar Co(NO₃)₂ · 6H₂O. As above, the nitrate was heated over a bunsen flame prior to calcination at 1200°C in air for 3 h. CoO was formed by this procedure, so to convert it to Co₃O₄, the oxide was held at 800°C for 4 h. The black powder was then crushed to pass a 300 mesh B.S. sieve.

3. Experimental procedure

In a preliminary series of experiments, a mixture (mixture 1) of the hydrated nitrates of cobalt and nickel, in proportions corresponding to the stoichiometry of the spinel NiCo₂O₄, was

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heated at 240°C for 12 h in air until no more nitrous fumes were evolved. The reaction product was identified by X-ray analysis as the spinel NiCo_2O_4 with a lattice parameter of 8.116 Å.

To investigate the stability of this spinel in air, further mixtures of the nitrates to the same composition as above, were heated at 600°C for 1½ h in air, followed by various heat-treatments prior to X-ray analysis of the products. Mixture 2, which was quenched from 600°C with no further heat-treatment, was found to consist of the spinel NiCo_2O_4 and a NiO-CoO solid-solution (lattice parameter 4.196 Å), while mixture 3, which was heated to 800°C for 14 h prior to quenching, consisted of Co_3O_4 and a Co-rich NiO-CoO solid solution (lattice parameter 4.222 Å). An identical sample (mixture 4) which was given the same firing treatment as mixture 3, and subsequently cooled and held at 600°C for 70 h before quenching, was found to consist of Co_3O_4 and a Ni-rich NiO-CoO solid solution (lattice parameter 4.181 Å), no NiCo_2O_4 being observed, i.e. the latter phase had not been reformed on holding at the lower temperature. This can probably be attributed to the fact that the temperature at which NiCo_2O_4 becomes unstable on heating in air is too low for the reverse reaction to occur on cooling (see Fig. 3 below).

To investigate further the equilibrium between the spinel and the NiO-CoO phases in air, the thermobalance was used to follow weight changes in prereacted mixtures of NiO and Co_3O_4 at equilibrium as a function of temperature.

4. The isobaric ternary diagram NiO-CoO-O₂ in air

In the first instance, the isothermal transition temperature for the reaction $\text{Co}_3\text{O}_4 \rightleftharpoons 3\text{CoO} + \frac{1}{2}\text{O}_2$ in air at 1 atm pressure, was established using the thermobalance. A small hysteresis of 3°C was observed between the transition temperatures obtained on heating Co_3O_4 and on cooling CoO. Since this hysteresis appeared to result simply from the low velocity of the reaction in the immediate vicinity of the equilibrium transition temperature, the average value of the two isotherms, 918.5°C, was taken.

Selected mixtures of NiO and Co_3O_4 were then fired at 1300°C in air in the thermobalance until they had reached constant weight showing that equilibrium with the atmosphere had been

reached. Each mixture was then brought to equilibrium at progressively lower temperatures by holding it at these temperatures until its weight had become constant. (At temperatures below 800°C, the oxidation reaction became so slow that several weeks were required for the equilibrium weights to be reached.)

Because supercooling of the NiO-CoO phase occurred on initial cooling of the mixtures, the equilibrium weights during the initial stages of oxidation were established by next bringing each sample to equilibrium at progressively increasing temperatures until a temperature was reached at which no further weight loss occurred. In each case this occurred when the atomic ratio O/(Ni + Co) had reached unity; indicating that the mixture consisted only of the NiO-CoO solid-solution phase.

The results obtained are shown in Fig. 1, the at. % of oxygen being plotted against temperature. (The amounts of nickel and cobalt in the mixtures were calculated by assuming that the

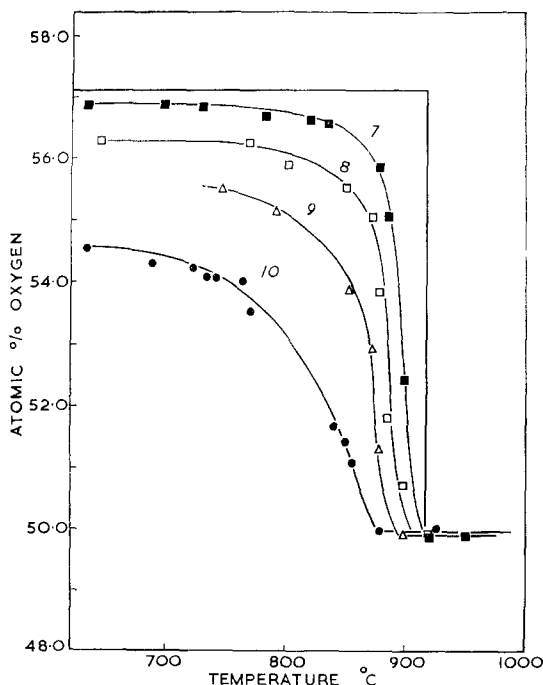


Figure 1 Curves showing variation of oxygen content with temperature at equilibrium in cobalt-nickel oxide compositions in air. The cation compositions of the mixtures in at. % were (7) 95.25 Co + 4.75 Ni; (8) 90.0 Co + 10.0 Ni; (9) 80.0 Co + 20.0 Ni; (10) 66.67 Co + 33.3 Ni. The curve for cobalt oxide is also shown.

starting materials were stoichiometric NiO and Co₃O₄.)

The equilibrium curve for cobalt oxide alone is included in the diagram for comparison. In the latter sample the transformation from Co₃O₄ to CoO occurred at constant temperature as required by the phase rule, and thus appears as a vertical step in the curve. In the mixtures of cobalt and nickel oxides, however, the oxidation on cooling (and oxygen loss on heating) occur over a range of temperatures as would again be expected from the phase rule if the transformation still involved only two condensed phases.

The isobaric diagram of the system at one atm pressure in air is shown in Fig. 2. The diagram was constructed from the dissociation curves in Fig. 1, the compositions being expressed as mol % of the components CoO, NiO and $\frac{1}{2}$ O₂. The dashed straight lines represent the reaction paths along which the composition of the experimental mixtures would change with change in oxygen content. The plotted points on the reaction paths represent compositions reached at various temperatures on the dissociation curves. The isotherms (continuous lines with temperatures alongside) were constructed by joining the compositions reached at the temperatures indicated except for the 600°C isotherm which was constructed by joining the composition of the NiO-CoO solid solution determined by X-ray analysis of mixture 4 (which

had been quenched from this temperature – see above) to the composition Co₃O₄.

These isotherms lie in an area where two condensed phases co-exist and so are tie lines joining the compositions of the two phases in equilibrium with each other and with the gas phase at the particular temperature. It will be seen that while, in the presence of NiO, the composition of the spinel phase remains constant, approximating to Co₃O₄ over the temperature range covered, the NiO/CoO ratio in the NiO-CoO solid solution phase increases progressively with decreasing temperature as Co₃O₄ is formed by oxidation of CoO in the solid solution.

The relationships shown in Fig. 2 provide a probable explanation for the fact that NiCo₂O₄ has only been formed from the low temperature decomposition of the mixed nitrates, since they suggest that the NiCo₂O₄ phase, which would lie on the join Co₃O₄-Ni₃O₄, should only become thermodynamically stable in air at temperatures well below 600°C.

A temperature-composition diagram of the system, plotted after the manner of Robin [3], has been derived from Fig. 2 by plotting the temperatures at which Co₃O₄ would first separate from the NiO-CoO solid solutions, against the composition of the latter, as obtained from the intersections of the various isotherms in Fig. 2 with the NiO-CoO join. The resultant diagram is shown in Fig. 3. The continuous line

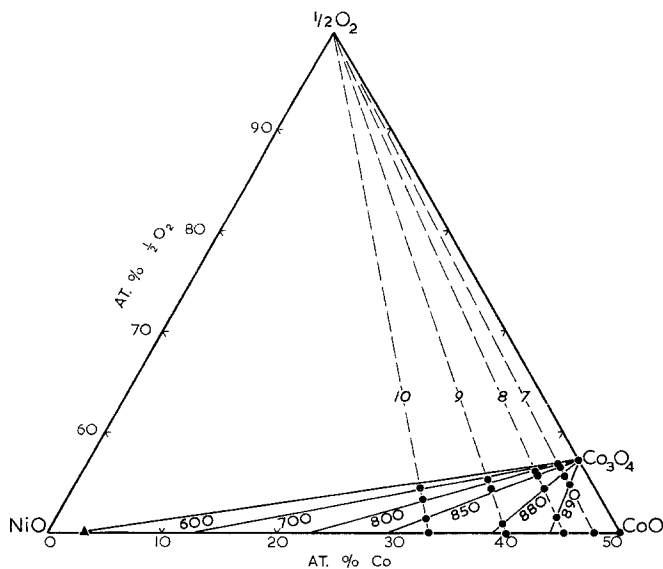
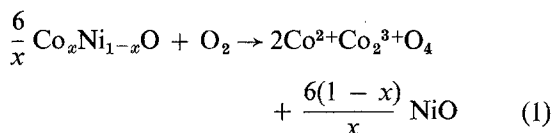


Figure 2 Isobaric ternary diagram of the NiO-CoO- $\frac{1}{2}$ O₂ system in air at 1 atm pressure. (See text for explanation.)

represents the phase boundary between the single phase (NiO-CoO solid solution) and the two phase ($\text{Co}_3\text{O}_4 + \text{NiO} - \text{CoO}$ solid solution) field as established in this way.

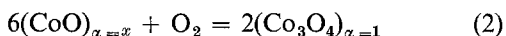
5. Thermodynamic considerations

Since from Fig. 2, the spinel can be regarded as approximating to pure Co_3O_4 , the equilibrium existing along the boundary of Fig. 3 can be written,



where the NiO is retained in the NiO-CoO solid solution.

Consider the situation when the temperature of an NiO-CoO solid solution has been lowered to that at which the first traces of spinel separate from the solution so that the activity of the NiO in the latter can be regarded as unchanged. Then if the solution of NiO in CoO is ideal, the equilibrium can be written,



where α denotes chemical activities and is unity in the case of the spinel and equal to x in the case of the CoO. This follows since, with a common anion, the solution of NiO in CoO involves only the mixing of the cations on the cation lattice so that [4],

$$\alpha_{\text{CoO}} = \frac{n_{\text{Co}}}{n_{\text{Ni}} + n_{\text{Co}}} = \frac{n_{\text{CoO}}}{n_{\text{NiO}} + n_{\text{CoO}}} = x$$

where n denotes the quantity moles.

Using the function $\Delta G^\circ = -RT \ln K_T$ and applying the law of mass action, the free energy change associated with Equation 2 may be written (since $\alpha_{\text{Co}_3\text{O}_4} = 1$)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = RT(6 \ln \alpha_{\text{CoO}} + \ln P_{\text{O}_2}). \quad (3)$$

Hence solving for T ,

$$T = \frac{\Delta H^\circ}{R(6 \ln \alpha_{\text{CoO}} + \ln P_{\text{O}_2}) + \Delta S^\circ} \quad (4)$$

$$= \frac{\Delta H^\circ}{R(6 \ln x + \ln P_{\text{O}_2}) + \Delta S^\circ} \quad (5)$$

which defines the relationship between composition and temperature along the phase boundary of Fig. 3. For the reaction,



in the absence of NiO, Kubaschewski and Evans [5] give

$$\Delta G^\circ = -87600 + 70.8T \quad (7)$$

so that ΔH° and ΔS° in Equation 5 have the values -87.6 kcal and -70.8 cal K^{-1} respectively.

The phase boundary for the reaction in air at 1 atm pressure was calculated from Equation 5 and is shown by the dashed line in Fig. 3. It can

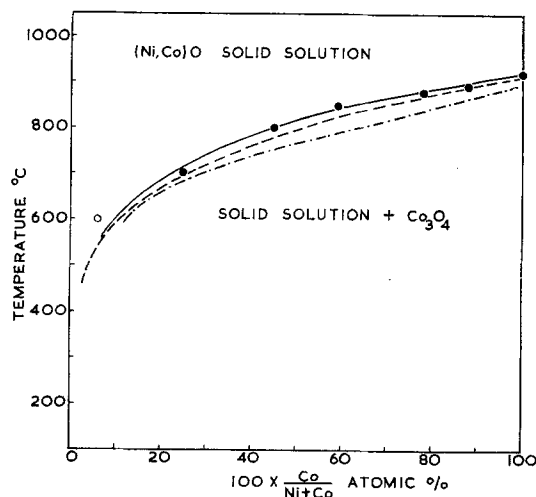


Figure 3 Temperature-composition diagram of the system NiO-CoO-O₂ in air showing the phase boundary between the single-phase (NiO-CoO solid solution) and the two-phase ($\text{Co}_3\text{O}_4 + \text{NiO-CoO}$ solid solution) fields plotted against the cationic composition of the NiO-CoO solid solutions. (Dashed line is the boundary calculated from Equation 5. Robin's boundary indicated by dots and dashes.)

be seen that this boundary is similar in shape to the boundary established from the experimental results but lies slightly below it. One reason for this is that the temperature of the Co_3O_4 -CoO equilibrium in air predicted by Equation 8 is 912.4°C , while the experimental temperature was 918.5°C . In addition, the calculated boundary is slightly steeper than the experimental one suggesting that the NiO-CoO solutions are not strictly ideal. Calculations based on the assumption that these solutions are regular show that the slope of the experimental line can be reproduced with a positive interaction parameter of the order of 500 cal mol^{-1} .

6. Microstructural changes

The topological relationship between the spinel and RO phases in incompletely transformed samples containing NiO was found to differ from that in samples containing only cobalt oxides. This difference is illustrated in Figs. 4 and 5.

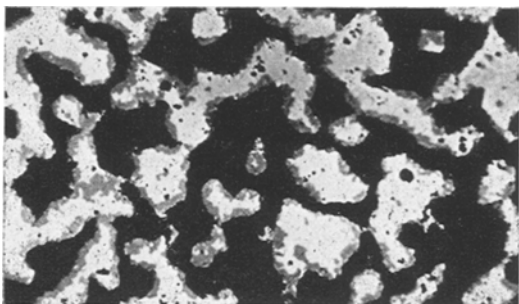


Figure 4 Micrograph of a pellet of Co₃O₄ after heating at 920 to 930°C in air to convert it partially to CoO. Light phase is Co₃O₄; dark phase CoO. (Reflected light × 610.)

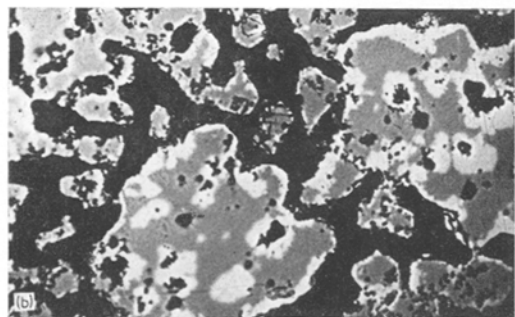
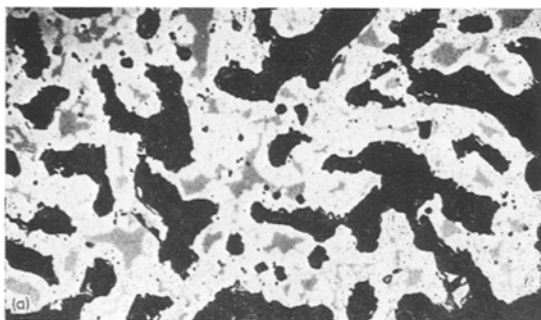


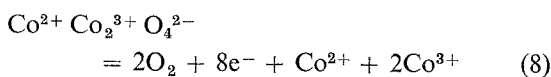
Figure 5 Micrographs of mixture 8 of Fig. 1 after firing at 1500°C in air to convert it to NiO-CoO solid solution and (a) heating at 800°C in air to convert it partially to Co₃O₄, (b) heating at 800°C as above and then at 900°C in air to increase the proportion of NiO-CoO solid solution. Light phase is Co₃O₄; dark phase NiO-CoO solid solution. (Reflected light × 610.)

Fig. 4 shows the microstructure of a pellet of cobalt oxide which was air-quenched after densifying (and converting to CoO) at 1500°C, then held at 870°C in air until it consisted entirely of Co₃O₄, and finally held at 920 to 930°C for about 30 min to convert it partially to CoO again. It will be seen that the CoO (dark phase) has formed at the surfaces of the Co₃O₄ grains. Similarly, when a pellet which had been converted entirely to CoO was held at 870°C in air, Co₃O₄ was found to have formed at the surfaces of the CoO grains.

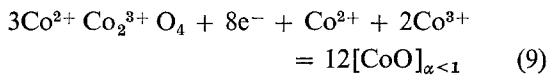
Figs. 5a and b are micrographs of pellets containing both cobalt and nickel oxides (mixture 8 of Fig. 1), both of which were also initially densified and converted to the NiO-CoO solid solution phase by firing at 1500°C. Pellet a was then brought to equilibrium at 800°C and quenched, while pellet b was brought to equilibrium at 800°C and then held at 900°C for 30 min before quenching to increase the proportion of the NiO-CoO solid solution present. In both samples the dark NiO-CoO phase occurs in the interior of the grains surrounded by the lighter spinel. Consequently, growth of the former in b at 900°C has occurred by displacement outwards of the RO-spinel interface.

This behaviour can be explained in terms of the compatibility relationships indicated by Fig. 2, which show that, in air, dissociation of Co₃O₄ to CoO according to Equation 2, can only occur at temperatures below 918.5°C when the CoO formed has its activity lowered by solution of NiO. Hence, since transport of nickel ions through the spinel phase is likely to be slow because of the low solubility of nickel oxide in it, the most probable site for the formation of CoO at temperatures below 918.5°C will be at the RO-spinel interface. A possible mechanism is as follows:

If diffusion of O²⁻ through the spinel is negligible, loss of oxygen on heating must occur at the spinel-air interface and since the loss of four O²⁻ ions is accompanied by the destruction of one tetrahedral and two octahedral cation sites there will then be an excess of one Co²⁺ and two Co³⁺ at the surface, i.e.



These excess Co ions and the electrons will diffuse to the RO-spinel interface where the reaction



will occur, the CoO being diluted by NiO from the existing RO solution. On cooling, the reverse reaction will occur, oxygen being picked-up at the spinel-air interface, while spinel is formed at the RO-spinel interface.

With gross overheating, as for example during the initial firing of the pellets at 1500°C, the restriction that oxygen can only be lost from the spinel-air interface might no longer apply since the oxygen pressure corresponding to reaction (2) might become sufficient to generate internal blow-holes. Evidence that such blow-holes were in fact formed during the initial firing can be seen in Figs. 4 and 5.

7. Electrical conductivity measurements

The electrical resistance of fired pellets was measured at progressively lower temperatures between 1150 and 20°C in air using a potential probe technique in which the potential drop between two platinum probes was measured by a null current potentiometer with direct current passing through the specimen. Prior to testing, all the pellets were fired at 800°C for 2 h in air in order to produce bodies of comparable

porosity (approximately 40%). Before each measurement was made the temperature was held constant for 12 h.

Fig. 6 shows the plot of log conductivity against $1/T$ K for a pellet which contained only nickel oxide. It consists of three approximately linear portions of different slope, the breaks occurring at 730 and at 320°C. The first of these apparently corresponds to the "knee" found by Mitoff [6] to occur on the plot for NiO single crystals and attributed to freezing-in of the defects responsible for conduction. Mitoff showed that above the knee the crystal was in equilibrium with the atmosphere and the activation energy for conduction included both the energy to form defects and the activation energy for motion of the positive holes. Below the knee, since the concentration of positive holes is constant, only the activation energy for movement of these is involved. From Fig. 6, the indicated energy for conduction below the knee is 0.21 eV which is in reasonable agreement with published values for single crystals (about 0.24 eV [6]) but the indicated value above the knee, 0.47 eV, is low relative to published values (about 1.0 eV [6, 7]).

Similar increases in slope to that occurring at 320°C have been reported in the literature, and

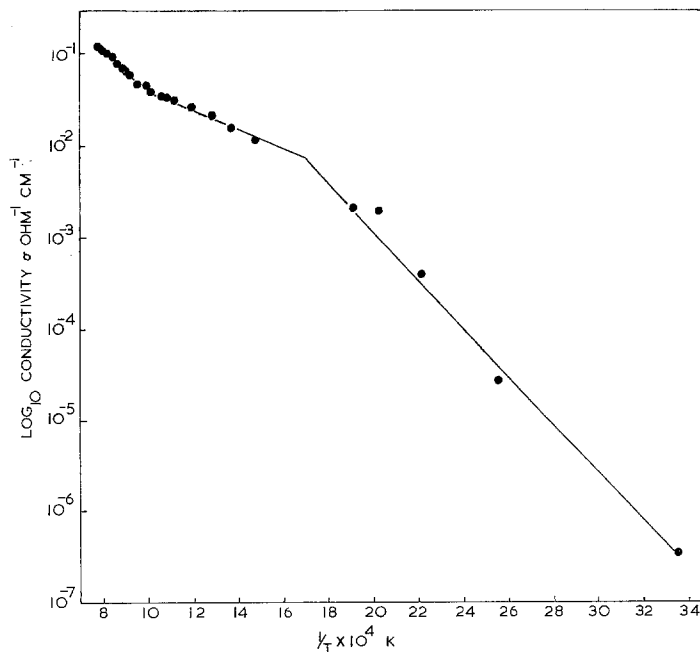


Figure 6 Log conductivity ($\Omega^{-1} \text{ cm}^{-1}$) versus reciprocal temperature curve for pellet of NiO cooled in air.

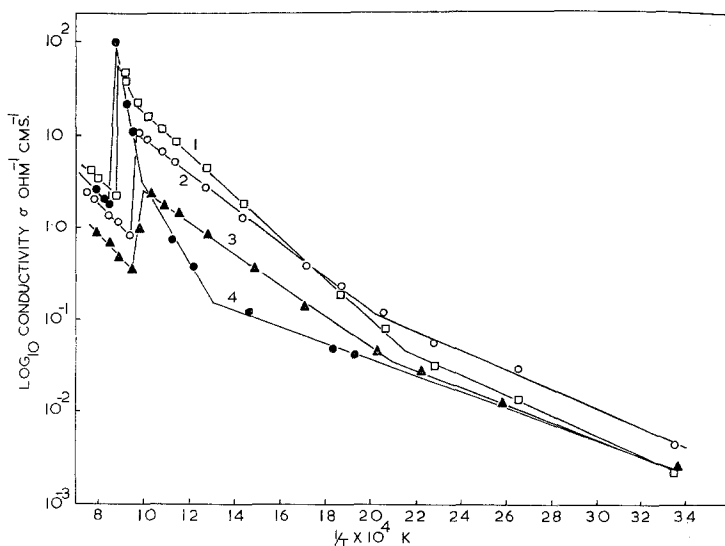


Figure 7 Log conductivity ($\Omega^{-1} \text{ cm}^{-1}$) versus reciprocal temperature curves for pellets cooled in air. Cation compositions were as follows: (1) 100% Co, (2) 90% Co:10% NiO, (3) 66.7% Co:33.3% NiO, (4) 50% Co:50% NiO.

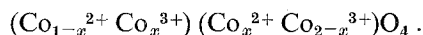
it has been suggested that they may be associated with the Néel temperature [8], although it is not known why the magnetic transition should have such an effect.

Fig. 7 shows similar plots for pellets consisting of cobalt oxide and of three different nickel oxide-cobalt oxide mixtures. On all four, oxidation on cooling of the divalent-oxide phase to spinel, which would form the continuous phase (see Fig. 5), is accompanied by a sharp rise of conductivity to a maximum, which decreases as the NiO content increases and hence as the maximum quantity of spinel that would be formed, decreases. (This follows from Fig. 2 which also indicates that separation of spinel on cooling began at temperatures rather lower than the equilibrium temperatures, apparently due to supercooling.)

On cooling from the peak temperature, the conductivity of the cobalt oxide fell rapidly (decreasing about 1000 times between 840 and 490°C) and those of the mixtures less steeply. The effect of NiO addition was, therefore, to increase the conductivity in this temperature range, although, as will be seen from the curves, the conductivity of the mixtures decreased with increasing NiO content over the range of compositions covered.

The reason for this behaviour has not been

established. Crystal field theory predicts that Co_3O_4 should have the normal spinel structure at low temperatures [9] with the enthalpy of cation interchange positive up to $x = 0.67$, where x is the disorder parameter [10] in the formula



Some degree of disordering would, therefore, be expected to occur on heating, and re-ordering on cooling, which would probably tend to increase the steepness of the log conductivity plot.

On the other hand, since the Ni^{2+} ion has high octahedral site preference, its presence in the spinel would prevent reversion to the ordered structure on cooling and decrease the steepness of the plot. According to Fig. 2, the NiO content of the spinel in equilibrium with the NiO-CoO phase in air at high temperatures appears to be low but it might be enough to produce the observed effect on the temperature dependence of the conductivity. Further, the spinel phase, which was formed by oxidizing the NiO-CoO phase by cooling, might have been super-saturated with NiO to some degree.

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