[CONTRIBUTION FROM THE SIGNAL CORPS ENGINEERING LABORATORIES]

X-Ray Diffraction Studies of the Solid State Reaction in the NiO–ZnO System

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X-Ray diffraction studies of the solid state reaction between the cubic NiO and the hexagonal ZnO revealed that a solid solution of NiO and ZnO is formed which may contain up to 40% of ZnO. The cubic lattice is hereby maintained but the lattice constant of the solid solution (Ni,Zn)O increases as the amount of dissolved ZnO increases. A possible mechanism of the reaction is suggested.

Introduction

It is known that some metal oxides, when heat-treated, show a departure from stoichiometric proportion in either oxidation or reduction. As a consequence, there is an excess of one or the other constituent present in the crystal lattice. With few exceptions, the metal monoxides crystallize either in the sodium chloride or the wurzite lattice type. If the oxygen is appreciably larger than the metal ion, as for instance NiO[1] and ZnO, the oxygen lattice, arranged in closest packing, can be considered as the lattice frame. In the sodium chloride lattice this closest packing is cubic, and in the wurzite structure it is hexagonal. The interstitial spaces of these oxygen lattices are partially, but systematically, occupied by the corresponding metal ions. Since the oxygen ion is too big to fit into the lattice interstitially an excess of oxygen can be explained only by empty cation sites. Similarly, excess of cations occupy additional interstitial spaces which are equivalent to an oxygen deficiency. In order to preserve electrostatic balance in such defect lattices, the cations must be present in more than one valence state.

After heating in air, NiO, like cuprous oxide or ferrous oxide,[2] takes up excess oxygen, as a result of which cation vacancies appear by the migration of nickel ions to the surface. ZnO behaves differently when heated in air. Its non-stoichiometric composition[3] is pictured by losing oxygen from the surface by disassociation and leaving excess zinc atoms behind which diffuse into interstitial positions of the lattice.

Because of the possibility of driving off oxygen and forming interstitial cation sites in the Zn lattice on the one side and because of the possibility of observing oxygen and creating cation vacancies in the NiO lattice on the other side, it was thought that this complementary behavior of these oxides should favor the formation of solid solutions between them.

Previous investigations[4] have shown that upon heating a powder mixture of these two oxides, a solid solution actually was formed. From X-ray diffraction data it was found that the cubic lattice of NiO was maintained, while the hexagonal ZnO phase disappeared. Since there was no indication of the formation of a new compound, or superlattice, it was assumed that a solid solution of the substitutional type was formed by a random replacement of Ni ions by Zn ions in the lattice. This solid solution can be described by a chemical formula

$$(1 - x)\mathrm{NiO} + x\mathrm{ZnO} \longrightarrow (\mathrm{Ni}_{1-x}\mathrm{Zn}_x)\mathrm{O}$$

where x is the mole % ZnO dissolved.

In order to study the mechanism and the kinetics of this reaction, an extended X-ray diffraction investigation, applying a quantitative X-ray method was undertaken.

Solid Solution of NiO and ZnO.—Mixtures of different mole ratios of NiO/ZnO (30:70; 50:50; 60:40; 70:30) fine powders of C.P. quality were pressed into pellets at a pressure of 10,000 p.s.i. From electron micrographs, the particle size of the NiO and the ZnO powder was measured and found to be about 0.01 and 0.1 μ, respectively. These pellets were fired in air at different temperatures up to 1250° for about five hours. Powder diffraction patterns were recorded with the North American high angle spectrometer using filtered Cu radiation. The change of lattice constant of the cubic phase in each mixture was determined as a function of firing temperature by measuring the shifts of a number of diffraction peaks in the high angle region relative to the peak positions of the unfired NiO. In the case of a cubic lattice the relation between the shift of lines as measured in Δd and the change in lattice constant Δa_0 is given by the simple relation

$$\Delta a_0 = \Delta d_{hkl}\sqrt{h^2 + k^2 + l^2} \qquad (1)$$

where h, k, l, are Miller's indices of the corresponding diffraction peak. Δa_0 was determined from the average shift of the last five lines in the pattern. The results are shown in Fig. 1 where the lattice constant of the cubic (Ni, Zn)O phase is plotted against the reaction temperature for different mole ratios NiO/ZnO of the initial mixtures. Preliminary studies on the completion of the reaction have shown that at low reaction temperatures equilibrium is reached after about a five-hour heating period, whereas at higher reaction temperatures about a three-hour heating period is sufficient. Therefore, a uniform reaction period of five hours was chosen for the equilibrium reaction studies at all temperatures. The solid state reaction, as may be seen, starts at about 600° as indicated by an increase of the lattice constant. Before the lattice constant begins to increase, however, a contraction is observed. A similar effect is reported by Brownlee and Mitchell[5] on heat-treated NiO. According to the hypothesis of the lattice defect in NiO cations

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[1] H. P. Rookby, *Acta Cryst.*, **1**, 226 (1948), showed as indicated by the splitting of X-ray diffraction lines that NiO at temperatures up to 275° is slightly rhombohedral distorted. Above 275° NiO is cubic. A distortion of the lattice at room temperature could not be observed from our diffraction pattern taken with Cu radiation.

[2] H. Dunwald and C. Wagner, *Z. physik. Chem.*, **22B**, 212 (1933).

[3] H. Baumbach and C. Wagner, *ibid.*, **22B**, 199 (1933).

[4] H. Kedesdy and G. Katz, *Cer. Age*, **62**, 29 (1953).

[5] L. D. Brownlee and E. W. I. Mitchell, *Proc. Phys. Soc.*, **LXV**, 710 (1952).

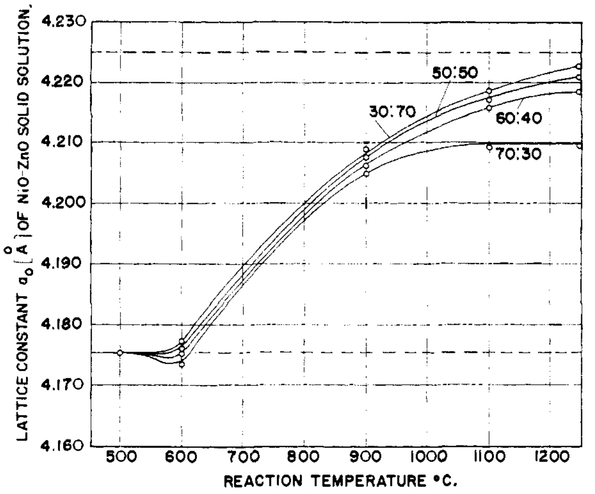
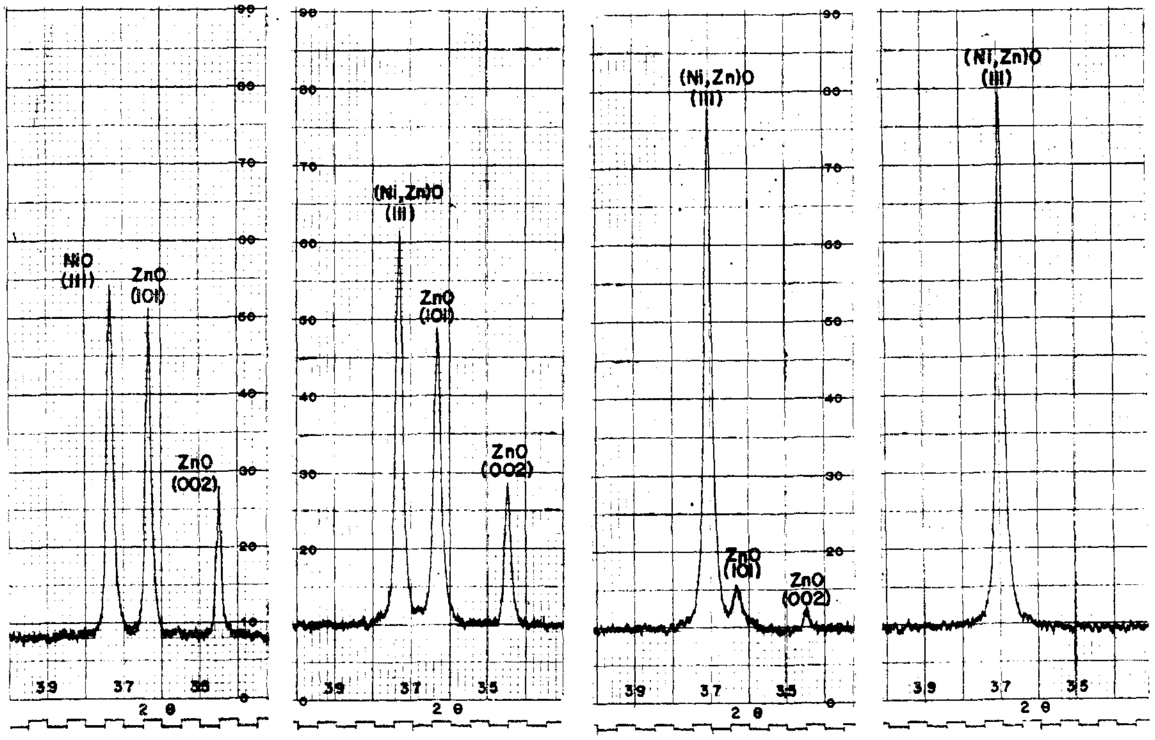


Fig. 1.—Lattice constant of (Ni, Zn)O solid solution at equilibrium obtained from NiO–ZnO powder mixtures of different mole ratios as a function of firing temperature. Heating time at the reaction temperatures was five hours.

vacancies and Ni^{3+}-sites are created when oxygen from the air is adsorbed on the crystal surfaces during the heat treatment. Since the ionic radius of Ni^{3+} is somewhat smaller than that of Ni^{2+}, the lattice contracts. During the reaction of NiO with ZnO, the larger Zn ions occupy cation sites in the NiO lattice which results in an increase of the cubic lattice constant as the reaction proceeds. The maximum increase in lattice constant at the highest reaction temperature used (1250°) is about 0.05 Å. above the value a_0 = 4.1762 Å. for the unfired NiO.

A direct analysis of the amount of unreacted ZnO may be made from measurements of the progressive reduction of diffraction line intensities of the residual ZnO component, which may, in turn, be compared with a calibration curve prepared from unheated mixtures of NiO and ZnO of different mole ratios. For this purpose several carefully selected diffraction peaks of the ZnO pattern using different NiO/ZnO mixtures were automatically recorded with the X-ray diffractometer mentioned previously. By this method it was possible to determine the unreacted ZnO to within a probable error of 10%. Figure 2 shows an example of a portion of a diffractometer chart of the 70:30 NiO/ZnO powder mixture and of the solid solution formed from it when heated at different temperatures. One can see how at increasing reaction temperatures the intensities of the (101) and (002) diffraction peaks of ZnO fall off as the ZnO disappears whereas the intensity of the (111)-diffraction peak of the solid solution (Ni, Zn)O increases. A shift toward a smaller diffraction angle 2*θ* indicates an increase in lattice constant. The results of the evaluation of such diffractometer records, *i.e.*, the determination of the integrated intensity of the ZnO diffraction peaks and using the calibration curve is shown in Fig. 3 for fired NiO/ZnO powder mixtures of varying mole ratios. In this figure the amount of unreacted ZnO is plotted as a function of reaction temperature. From the curves obtained it can be seen that a complete solid solution from a 70:30 mole ratio mixture has been formed at about



UNHEATED. 600°C. 900°C. 1100°C.

Fig. 2.—Portion of the diffractometer recording of the 70:30 NiO/ZnO mixture and of the solid solutions formed when heated at different temperatures for five hours.

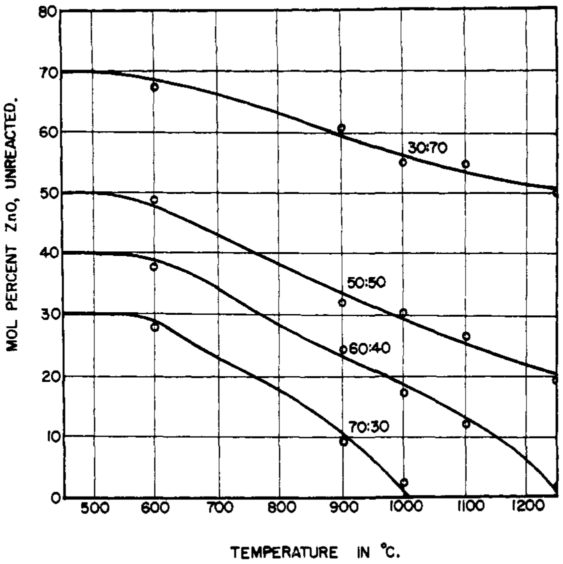


Fig. 3.—Mole % of unreacted ZnO for different mole ratios of the initial NiO/ZnO mixtures as a function of firing temperature. Heating time at the firing temperatures was five hours.

1000° and for a 60:40 mole ratio mixture at about 1250°. From the differences of the amount of ZnO present at the beginning and at the end of the reaction period, *i.e.*, where the ZnO is completely dissolved or where no more ZnO can be dissolved, the mole % of ZnO in solid solution with the NiO can be calculated. Table I gives the data obtained. The values of the amount of reacted ZnO for the 50:50 and 30:70 mole ratio initial mixtures are determined by extrapolation of the corresponding curves to higher reaction temperatures until they reach a constant value of unreacted ZnO.

TABLE I

CALCULATION OF THE MAXIMAL MOLE % ZnO POSSIBLE IN THE (Ni, Zn)O SOLID SOLUTION AS DETERMINED FROM THE AMOUNT OF UNREACTED ZnO (SEE FIG. 3) FROM EQUILIBRIUM REACTION STUDIES OF NiO/ZnO POWDER MIXTURES OF DIFFERENT MOLE RATIOS HEATED AT HIGH TEMPERATURES FOR FIVE HOURS

Mole ratio of initial NiO/ZnO mixture	Mole % of ZnO left unreacted	Mole % of ZnO reacted	Mole % of ZnO, in (Ni, Zn)O
70:30	0	30	30
60:40	0	40	40
50:50	Approx. 34	34	40
30:70	Approx. 20	20	40

It is apparent from the data of the table that a maximum of approximately 40 mole % of ZnO can be dissolved into NiO. Hence, the chemical formula representing the solid solution can be written as

$$(Ni_{1 \rightarrow 0.6}Zn_{0 \rightarrow 0.4})O$$

Combining the results of Figs. 1 and 3 by taking for each temperature the corresponding values of a_0 and the amount of ZnO reacted, the change in lattice constant of (Ni, Zn)O as a function of dissolved ZnO can be obtained. Choosing, for example, the 30:70 mixture fired at 800°, one finds from Fig. 1 the lattice constant of the solid solution at this reaction temperature to be $a_0 = 4.200$ Å. From Fig. 3, the amount of ZnO that reacted of the initial 70 mole %, can be found as 70 − 63.3 = 6.7 mole %, which in the solid solution amounts to $6.7/(30 + 6.7) \times 100 = 18.7$ mole % ZnO. The complete evaluation of Fig. 1 and Fig. 2 leads then to Fig. 4 which shows clearly that a continuous series of solid solutions between the reactants NiO and ZnO can be formed.

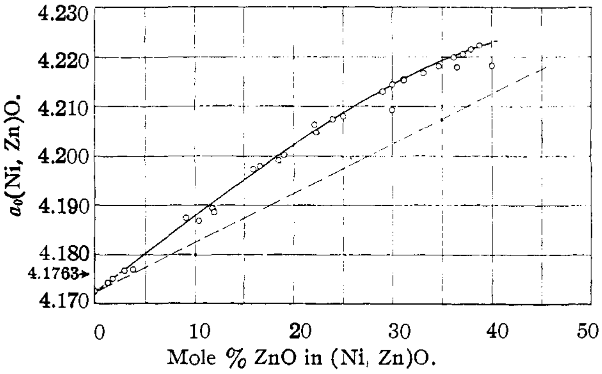


Fig. 4.—Lattice constant of the (Ni, Zn)O solid solution as a function of the amount of ZnO in mole % present. The data were obtained from the equilibrium data taken from Figs. 1 and 3 for different reaction temperatures. The dashed line represents the change in lattice constant on the basis of the ionic radii of Ni^{2+} and Zn^{2+} using Vegard's law.

Extrapolations of the experimental data to zero amount ZnO reacted shows here, as in Fig. 1, a contraction of the heated NiO lattice before the reaction with ZnO begins. From Fig. 4 the decreases of the lattice constant can be determined to be about 0.004 Å.

Expressing the increase in lattice constant of the cubic (Ni, Zn)O phase with increasing amounts of dissolved ZnO by Vegard's law on the basis of the ionic radii one obtains

$$\Delta a_0 = 2\Delta r x \qquad (2)$$

where Δr is the difference in ionic radii between Ni^{2+} and Zn^{2+} and x is the mole % of ZnO dissolved. Using the revised ionic radii after Ahrens[6] for $Ni^{2+} = 0.69$ Å. and $Zn^{2+} = 0.74$ Å. (octahedral coördinations), $\Delta r = 0.05$ Å., equation 2 becomes

$$\Delta a_0 = 0.1x \qquad (3)$$

This equation is represented in Fig. 4 by the dashed line. The deviation of the experimental curve from Vegard's law is probably due to a repulsion between neighboring cations of different elements (Zn and Ni).

Time Dependent Solid State Reaction Studies.—In order to determine the reaction rate and the activation energy of the reaction between NiO and ZnO, time dependent reaction studies, at various temperatures, using a 50:50 mole % mixture, were made. After the firing periods the samples were air-quenched to room temperature to stop the reaction. The rates of reaction between the two oxides were determined in the same way as in the reaction

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(6) L. W. Ahrens, *Geochim. Cosmochim Acta*, **2**, 155 (1952).

studies under equilibrium conditions, that is, by determining the amount of residual ZnO after the reaction period from intensity measurements of the ZnO diffraction peaks.[7] The result of this investigation is shown in Fig. 5 where the amount of ZnO reacted, expressed in percentage of the amount of ZnO in the initial mixture, is plotted as a function of reaction time for different firing temperatures. From the oxide mixture fired at 800° it can be seen that, at this temperature, the reaction velocity is very slow; the end of the reaction is not reached even after a three-hour firing period. Using higher reaction temperatures, the reaction is completed in about two hours. Finally, a constant value of ZnO reacted is reached, depending upon the firing temperature.

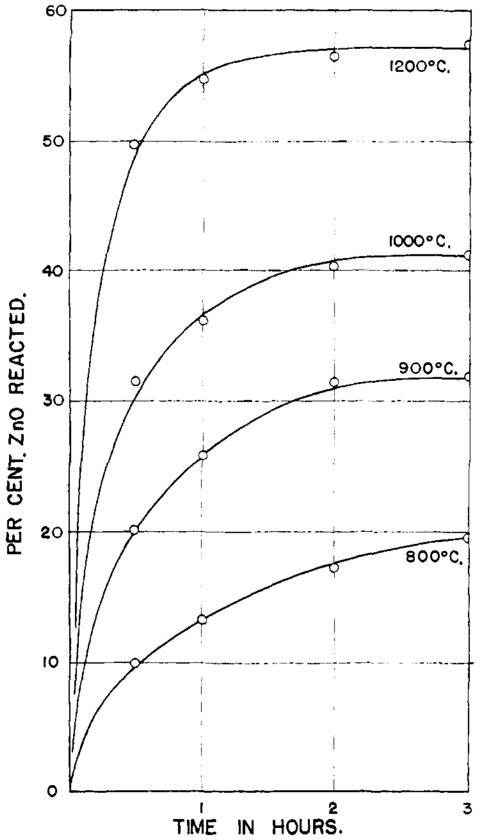

Fig. 5.—Time dependent reaction curves of a 50:50 mole % NiO/ZnO mixture for different reaction temperatures.

In a mixture of particles the solid state reaction is initiated between two particles which are in direct contact. Considering the case where a solid solution between NiO and ZnO is formed by a diffusion process, the rate of reaction that takes place is governed by the rate of diffusion. If diffusion determines the reaction rate, it can be assumed that the number of migrating atoms is proportional to the thickness y of a reaction layer which is formed at the boundary between contacting NiO and ZnO particles. The increase of this layer toward the center of the ZnO particle with time t can be expressed by the parabolic law

$$y^2 = 2Dt \qquad (4)$$

provided that $y = 0$ when $t = 0$. Assuming a semi-stationary state for the concentration gradient between the reactants, then D, the diffusion coefficient can be considered as a constant. Jander[8] and others, assuming the reacting particles are spheres, have derived an expression for the reaction layer thickness y

$$y = (1 - \sqrt[3]{1 - z})r \qquad (5)$$

where r is the mean radius of the reacting particles and z is the fraction of completion of the diffusion process. Combining equation 4 with equation 5 gives

$$K = \frac{2D}{r^2} = (1 - \sqrt[3]{1 - z})^2/t \qquad (6)$$

K, which is proportional to the diffusion coefficient is called the reaction rate constant. Furthermore, K is related to temperature by the usual relationship

$$K = C\exp(-E/RT) \qquad (7)$$

where C is a constant depending upon the physical properties of the reactants, T is the absolute temperature, E the activation energy and R is the gas constant.

From the curves in Fig. 5, the fraction of completion z can be determined for each temperature and the reaction rate constant K can be calculated from equation 6. The result is shown in Table II. The values of K obtained from z for different reaction times, at a given reaction temperature are shown to be constant indicating that the diffusion equation used describes this reaction process very well. The temperature dependence of K is shown in Fig. 6, where log K is plotted against $1/T$ and a straight line is drawn through the experimental points. From the slope of this line the activation energy of the reaction is found to be E = 17,200 cal./mole = 0.75 e.v. The constant C found from the intercept of the straight line is C = 0.63/sec. The equation of the straight line in Fig. 6 then becomes

$$K = 0.63\exp\left(-\frac{8650}{T}\right) \qquad (8)$$

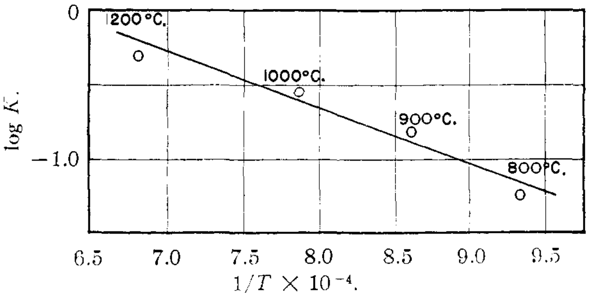

Fig. 6.—Diffusion rate constant as a function of reaction time for different reaction temperatures.

This calculated activation energy is of the order of magnitude of activation energies determined for

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[7] Determination of the amount of ZnO reacted from the change in lattice constant failed because the intense reaction in the first firing period caused an additional increase of the lattice constant of the (Ni, Zn)O phase due to lattice distortion. In the equilibrium studies this distortion was not observed because the samples were kept at the reaction temperatures for five hours, leaving sufficient time for recrystallization.

[8] W. Jander, *Z. anorg. Chem.*, **163**, 1 (1927).

TABLE II

CALCULATION OF THE REACTION RATE CONSTANT K FROM THE TIME DEPENDENT REACTION STUDIES

The fraction of completion z of the diffusion process as a function of reaction time is determined for different temperatures (see Fig. 5) and K is calculated using equation 6.

	800°		900°		1000°		1200°	
t, hr.	z	$K \times 10^2$	z	$K \times 10$	z	$K \times 10$	z	$K \times 10$
0.167	0.26	5.40	0.42	1.65	0.51	2.68	0.62	4.85
.333	.36	5.55	.55	1.64	.66	2.74	.78	4.80
.50	.42	5.50	.64	1.67	.75	2.75	.87	4.75
.667	.47	5.46	.70	1.64	.82	2.74	.92	4.85
.835	.52	5.65	.75	1.64	.86	2.76	.95	4.80
1.00	.57	5.85	.79	1.56	.89	2.72	.97	4.75
Av. K =		5.57×10^{-2}		1.64×10^{-1}		2.73×10^{-1}		4.80×10^{-1}
log K =		−1.25		−0.79		−0.56		−0.31

the diffusion of cations in ionic lattices[9] and agrees very well with the activation energy of ZnO, as determined from electrical conductivity measurements[10] for the formation of interstitial lattice sites.

Atomistic Interpretation of the Solid State Reaction between NiO and ZnO.—Because the reaction rate is more or less structure-sensitive it cannot be employed directly to establish the reaction mechanism. Therefore, based on the non-stoichiometric conditions of the two reacting oxides at elevated temperatures, the following picture of the solid state reaction, illustrated in Fig. 7, is proposed: In a NiO–ZnO particle mixture, if heated to the reaction temperature (about 600°), oxygen from the ZnO crystals will be released and adsorbed by the NiO crystal in contact (A). The gaseous oxygen takes up electrons from the NiO lattice by the removal of electrons from Ni^{2+} ions and enters normal anion sites (B). The electron donating Ni^{2+} ions change to Ni^{3+} ions. More crystalline NiO is then formed by the diffusion of equivalent numbers of Ni^{2+} ions from cation lattice sites to the surface, leaving cation vacancies behind. For each adsorbed oxygen atom two Ni^{3+} lattice sites and Ni^{2+} vacancies are formed. This may be written in the form of the following two equations

$$2Ni^{2+} \longrightarrow 2Ni^{3+} + 2e \quad (9)$$

$${}^1/{}_2O_2 + 2e + Ni^{2+} \longrightarrow NiO + 1Ni^{2+}\text{ vacancy} \quad (10)$$

The excess of Zn, created by the release of oxygen from the ZnO, moves first into interstitial positions in the ZnO lattice where it will be ionized to Zn ions and loosely bound electrons, as assured from electrical conductivity measurements. When the cation vacancies in the NiO lattice are formed, the Zn ions with their electrons move away from the interstitial sites into the NiO lattice, filling the vacant cation sites as Zn^{2+} ions (C,D). The two electrons, as given off to the trivalent Ni-ions, convert them back to Ni^{2+}. This may be represented by an equation

$$2Ni^{3+} + 1Ni^{2+}\text{ vacancy} + Zn^{2+} + 2e \longrightarrow 2Ni^{2+} + Zn^{2+} \quad (11)$$

Continuation of this process, represented by equations, 10 and 11, results in a growth of the cubic (Ni, Zn)O phase, and a simultaneous disappearance of ZnO phase in the initial powder mixture. This disappearance of ZnO can be explained by the diffusion of anion and cation sites in equal numbers into NiO.

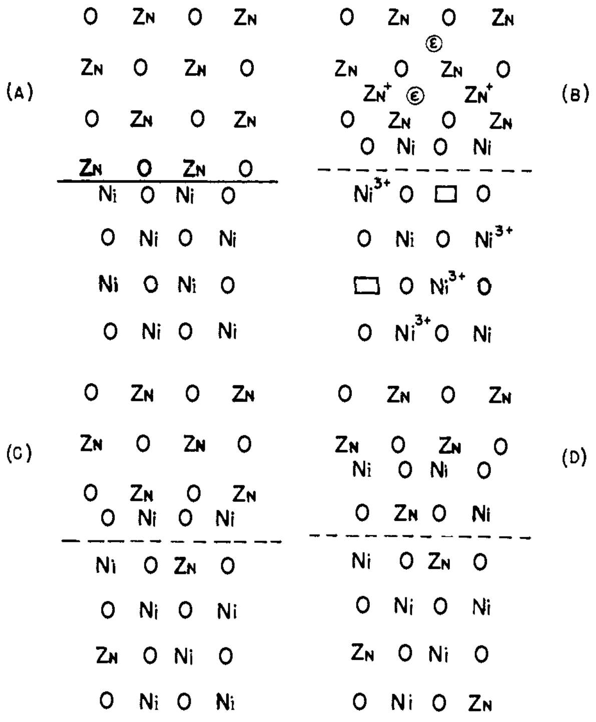

Fig. 7.—Schematic representation of the solid state reaction mechanism between NiO and ZnO leading to the solid solution (Ni, Zn)O.

The decrease of the reaction velocity and finally the end of the reaction between NiO and ZnO at the temperatures above 1000° may be explained by the increasing concentration of the Zn ions in the cubic (Ni, Zn)O lattice. As the concentration increases the Zn ions (as a cation member of the lattice) can form cation vacancies as well and can move to the surface. If this is the case, then the Zn ions can react either with the adsorbed oxygen from which a recombination of ZnO would result, or it would diffuse back into the ZnO lattice, occupying interstitial lattice sites.

Conclusion

The formation of solid solutions between NiO and ZnO by solid state reaction was studied by quantitative X-ray analysis employing a Geiger counter-spectrometer. The following results were

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(9) R. M. Barrer, "Diffusion In and Through Solids," Cambridge University Press, London, Chap. VI, 1951.

(10) C. A. Hogarth, *Proc. Phys. Soc.*, **64**, 691 (1951).

obtained. As much as approximately 40 mole % ZnO can be dissolved in NiO forming a solid solution of (Ni, Zn)O whereby the cubic NiO lattice is maintained. As the reaction proceeds, the lattice constant increases due to the larger Zn ion. The maximum increase in lattice constant for a 40 mole % dissolution of ZnO is about 0.05 Å. The parabolic law of diffusion expressed the behavior of the reaction and from time dependent reaction studies the activation energy of this reaction has been determined to be E = 17,200 cal./mole = 0.75 e.v. The mechanism of the reaction is explained on the basis of defect structure formation in the NiO and ZnO lattice at elevated temperatures.

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The Mechanism of the Precipitation of Magnesium Oxalate from Supersaturated Solutions

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The precipitation of magnesium oxalate from supersaturated solution, after the formation of nuclei, is first order with respect to the concentration of magnesium oxalate. The reaction leading to the formation of nuclei is third order. Also, the conductivity and the pH of the solution do not change during the formation of embryos and the precipitation. The following mechanism is therefore proposed: $Mg^{2+} + C_2O_4^{2-} = MgC_2O_4$ rapid, $MgC_2O_4 + MgC_2O_4 = (MgC_2O_4)_2$ rapid and complete, $(MgC_2O_4)_2 + MgC_2O_4 \rightarrow (MgC_2O_4)_3$ slow, $(MgC_2O_4)_3 + MgC_2O_4$ = individual crystals. The composition of the critical nuclei corresponds to $(MgC_2O_4)_2$.

Introduction

The comparatively slow rate of precipitation of magnesium oxalate from its supersaturated solutions has long been used as the basis of the separation of calcium ions from magnesium ions in analytical chemistry. Several studies of the characteristics of supersaturated solutions of magnesium oxalate have been made[2] but none deal with the mechanism of the reaction involved. An investigation of the kinetics of the precipitation of magnesium oxalate has therefore been undertaken.

From an analysis of the data on the solubility of magnesium oxalate in salt solutions and the conductivity of magnesium oxalate solutions, Pedersen[3] has concluded that magnesium and oxalate ions are in equilibrium with undissociated magnesium oxalate. Since crystallization ultimately occurs from the association of ions or molecules, we postulated the following general mechanism: magnesium and oxalate ions combine to form undissociated magnesium oxalate. Magnesium oxalate then associates stepwise to form the critical nuclei, each of which adds one more molecule of magnesium oxalate and become nuclei. Precipitation then occurs on each nucleus producing individual crystals. This mechanism also embodies the views of Reiss and LaMer[4] on the theory of nucleation and the production of homogeneous colloidal systems. Conductivity and pH measurements as a function of time were therefore made to determine the rate controlling step. The time lag, the period between the initial mixing of reactants and initial appearance of crystals, were measured to determine the order of the reaction leading to the formation of nuclei. The concentration of oxalate in solution was measured as a function of time to determine the order of the precipitation reaction.

Experimental

Stock Solutions.—All materials used were of reagent grade. Magnesium chloride was standardized by the Fajans method for chloride using dichlorofluorescein indicator. Ceric solution, prepared from ceric ammonium sulfate, was standardized against primary standard sodium oxalate, using excess ceric solution, warming to 50°, back titrating with ferrous sulfate to a slight excess, and then titrating the ferrous with the ceric solution in the presence of ferroin indicator.[5] The ceric–ferrous titer was determined each day the ferrous solution, prepared from ferrous ammonium sulfate, was used.

Potassium oxalate was standardized with the ceric solution. Buffer solution was prepared by titrating 244.7 g. of sodium acetate dissolved in water with concentrated acetic acid to pH 5.50, determined with pH meter, and then diluting to one liter.

Procedures.—Aliquot portions of standardized magnesium chloride and potassium oxalate solutions were mixed and diluted. pH and resistance measurements were then made prior to and during precipitation. Leeds and Northrup number 7662 pH meter and Industrial Instruments conductivity bridge model RC–BC were used for these measurements.

For the kinetic measurements, the aliquot portions were mixed with 5.0 ml. of standardized buffer solution, a weighed quantity of sodium sulfate, and water to a total volume of 205 ml. The sodium sulfate was added to maintain a constant ionic strength of 0.94; pH was constant at 5.70 ± 0.05; for all measurements, temperature was maintained at 25.00 ± 0.07°. At various time intervals, aliquot (10.00 ml.) portions of solution were filtered through a medium sintered glass filter, acidified and titrated with standardized ceric solution.

The duration from initial mixing to initial appearance of crystals was determined from a plot of the log of the concentration of magnesium oxalate against the time. The slope is zero initially since, during the formation of nuclei, the concentration of magnesium oxalate in the solution is not altered. When crystallization starts, the slope decreases.

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[1] Department of Chemistry, Columbia University. This work was carried out while a senior student at the City College.

(2) Z. Karaglanov, *Z. anorg. Chem.*, **124**, 92 (1942); E. Pozner and K. A. Samov, *J. Phys. Chem., U.S.S.R.*, **13**, 889 (1939); W. M. Fischer, *Z. anorg. allgem. Chem.*, **153**, 62 (1926).

(3) K. Pedersen, *Trans. Faraday Soc.*, **35**, 277 (1939).

(4) H. Reiss, *Trans. N. Y. Acad. of Sci.*, [II] **11**, 236 (1949); H. Reiss and V. K. LaMer, *J. Chem. Phys.*, **18**, 1 (1950); H. Reiss, *ibid.*, **18**, 840 (1950).

(5) G. Walden, L. Hammett and R. Chapman, THIS JOURNAL, **55**, 2649 (1933).