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SELF-DIFFUSION OF Co^{60} IN SINGLE CRYSTALS OF Co_{1-x}O

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Ph. D. Thesis Submitted to Iowa State University

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Self-diffusion of Co^{60} in single crystals of Co_{1-x}O

by

Syed Fakhrur Rahman

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TABLE OF CONTENTS

Abstract	Page vi
GENERAL INTRODUCTION	1
PART I: ARC-TRANSFER METHOD OF CRYSTAL GROWTH	2
INTRODUCTION	3
EXPERIMENTAL PROCEDURE	8
Arc-Transfer Method of Crystal Growth	8
Characterization of Single Crystals	11
RESULTS AND DISCUSSION	13
Growth Parameters	13
Characterization of Single Crystals	17
PART II: TRACER SELF-DIFFUSION MEASUREMENTS IN Co_{1-x}O	32
INTRODUCTION	33
LITERATURE SURVEY: DEFECTS AND TRANSPORT PHENOMENA IN Co_{1-x}O	35
THEORETICAL CONSIDERATIONS	47
Phenomenological Description of Diffusion	47
Diffusion Mechanisms	48
Atomic Theory of Diffusion	53
Defects in Oxides	55
Pure stoichiometric oxides	56
Pure nonstoichiometric oxide	58
Defects in Co_{1-x}O	60
Tracer Self-Diffusion Measurements	62
EXPERIMENTAL PROCEDURES	70
RESULTS AND DISCUSSION	85
Constant x-Variable Temperature Experiment	85
Constant Temperature — Variable x Experiment	101

	Page
CONCLUSIONS	109
REFERENCES	111
ACKNOWLEDGEMENTS	115
APPENDIX A: PENETRATION PLOTS FOR Co^{60} DIFFUSION IN SINGLE CRYSTALS OF Co_{1-x}O	116
APPENDIX B: ANALYSIS OF PRE-DIFFUSION ANNEALING TREATMENTS	127

Self-diffusion of Co^{60} in single crystals of $\text{Co}_{1-x}\text{O}^*$

Syed Fakhrur Rahman

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Tracer self-diffusion coefficients in single crystals of Co_{1-x}O were measured as a function of temperature for a constant deviation from stoichiometry, and as a function of deviation from stoichiometry for a constant temperature. High purity single crystals of Co_{1-x}O were grown by the arc-transfer technique and a tracer sectioning technique was employed to measure the diffusion coefficients.

The arc-transfer technique of crystal growth was found to produce crystal of Co_{1-x}O of essentially the same purity as the starting Co rod. The quality of the crystals was comparable to that of commercially available crystals grown by Verneuil process.

Results of measurements at constant deviation from stoichiometry of $x = 0.005$ in Co_{1-x}O showed the Co tracer self-diffusion coefficient to vary with temperature according to

$$D = (3.88 \pm 4.95 \atop - 2.18) \times 10^{-4} \exp \left(\frac{-31600 \pm 2400}{RT} \right) \text{ cm}^2/\text{sec}$$

between 1037-1350°C. This activation energy is in direct agreement with published results for measurements made in air, provided that proper compensation is made for the effect of variation in stoichiometry in the

* USERDA Report IS-T-691. This work was performed in the facilities of Ames Laboratory under Contract W-7405-eng-82 with the ERDA.

latter. The limits represent a 95% confidence interval.

Results of measurements of Co tracer self-diffusion coefficient for crystals having deviations from stoichiometry between 0.002-0.008 at 1150°C showed the diffusion coefficient to depend on p_{O_2} as

$$D = (9.74 \pm 1.11) \times 10^{-9} p_{O_2}^{1/(3.59 \pm 0.47)} \text{ cm}^2/\text{sec}$$

where p_{O_2} varied between $10^{-2.5}$ - $10^{-0.25}$ atm. Comparison of these results with published data from thermogravimetric and electrical conductivity measurements confirms that the defects responsible for Co diffusion in the range of temperature and p_{O_2} of this investigation are singly ionized cobalt vacancies.

The Co tracer self-diffusion coefficients measured in single crystals in this study are nearly identical to those measured in polycrystalline $Co_{1-x}O$ under the same conditions of temperature and p_{O_2} by other investigators.

GENERAL INTRODUCTION

Atomic transport properties in materials are strongly dependent on the concentration of point defects. In CoO , the concentration of defects is most readily influenced by controlling departure from stoichiometry. For this reason, Birchenall (1) has classified CoO among those materials having transport properties reasonably independent of impurities at low concentration.

Several methods are known by which high purity single crystals of this oxide can be grown in the laboratory. These methods are reviewed in Part I of this dissertation. In particular, crystal growth by the arc-transfer method is attractive in the sense that this technique produces high purity crystals of CoO using relatively inexpensive equipment and simple procedures.

The purpose of this investigation was two-fold: first, to investigate the arc-transfer method as a means of growing single crystals of CoO , and second, to use these crystals to study cation self-diffusion as a function of temperature and deviation from stoichiometry. Consequently, this dissertation is presented in two parts. Part I contains the details of the arc-transfer crystal growth method. A brief review of crystal growing of high melting point oxides is also presented. In Part II, a self-diffusion study using Co^{60} tracer is described. Literature on the topics of defects and transport phenomena in CoO are also reviewed. Finally, the entire investigation is summarized and conclusions are made.

PART I: ARC-TRANSFER METHOD OF CRYSTAL GROWTH

INTRODUCTION

Cobaltous oxide, CoO , is a cubic rock salt type structure (2). It exists over a wide range of compositions. Fig. 1 (2) describes in detail the field of its existence along with the Co and spinel (Co_3O_4) phases. It is a nonstoichiometric oxide, and is believed to be metal deficient (3, p. 238). This is usually shown by the formula Co_{1-x}O , where x is a measure of deviation from stoichiometry or mole fraction of the vacant Co sites.

Like Co_{1-x}O , all 3-d transition metal oxides have high melting points and show deviations from stoichiometry. As with all high melting point materials, a major problem in growing crystals of these oxides is to find a suitable container for the melt. Since the oxidation states and the stoichiometry are influenced by the prevailing partial pressure of oxygen, an independent control of atmosphere during growth is also of great importance. Moreover, some of the oxide compositions in these systems melt incongruently and thus present additional problems because of the phase change which occurs below the melting point.

During the past thirty years, there has been considerable research in developing methods to overcome these difficulties. Some of the methods, developed by the late fifties, have been reviewed in detail by Harrison (4). These are: Verneuil or flame fusion method, Bridgman-Stockbarger method, flux method, and grain growth method. Some methods of minor importance are the hydrothermal and induction heating methods for growing ferrites, and the method of depositing single crystals of FeO , NiO , and CoO as thin films on cleaved surfaces of MgO single crystals. Among these

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Figure 1. The stable phase field of cobaltous oxide

Symbols ● and ■ represent values from two different investigators as discussed in Reference 2.

the Verneuil method is the most economical and has been successfully used for producing large single crystals of high melting point oxides, aluminates, ferrites, and mullite (4). Most commercial Co_{1-x}O single crystals are produced by this method. However, the method is not simple and requires complicated heating and cooling systems and often yields strained crystals because of a steep temperature gradient along the crystal boule. The Bridgman-Stockbarger method has the advantage of producing more mechanically sound crystals compared to the Verneuil crystals, but does not produce crystals of constant stoichiometry (5). The lead oxide flux method is most promising in view of the low growth temperature, but is very time consuming (approximately two weeks) and very critical temperature control is required throughout the experiment (4). Flux methods may also introduce impurities.

Another method, based on the principle of zone refining, has been used during the past fifteen years for the growth of high melting point oxides by several investigators (5, 6). The conventional rf heating is usually replaced by some more efficient power source. This technique is commonly referred to as the floating zone or zone melting method. Kooy and Couwenberg (5) used heating from an arc image furnace to produce NiO , TiO_2 , and various Mn-ferrites. Gerthsen (6) has zone melted a number of refractory oxides by using a transverse arc to establish the molten region.

The zone melting method produces crystals which do not show marked deviation from stoichiometric composition (5). On the other hand, Bridgman-Stockbarger and lead flux methods produce crystals with a gradual change in the chemical composition during growth (5). Zone melting also

has an advantage over the flame fusion method, as no special preparation is required for the starting materials (5). However, like the Verneuil process, the prevailing temperature gradient may give rise to cracks in the crystal (5).

A very simple and novel method employing direct heating by a dc arc struck between two electrodes was introduced by Drabble and Palmer at the University of Exeter, England (7). A molten cap is formed on the anode which grows at the expense of the cathode. This technique has been known as "arc-transfer." Oxides of Co, Fe, Ni, Ti, and V were grown by using sintered cathode rods of these oxides (7). Smith and Austin (8) extended the arc-transfer technique to produce pure or Li-doped crystals of NiO, CoO, Fe_3O_4 , and Mn_3O_4 . Drabble (9) also attempted to grow pure and doped crystals of other than transition metal oxides and has described them in detail. Smith and Austin (8) tried in vain to determine the mechanism of transfer of material from cathode to anode. However, they have been able to correlate such parameters as rate of growth and ingot diameter to the arc current. Theirs is a good review on the arc-transfer method up to the present time. Most of the crystals are reported to grow in [100] direction (7-9). Smith and Austin (8) have described the quality of crystals grown by the arc-transfer method. No such description is available on crystals grown by Drabble and Palmer (7) and Drabble (9).

The goal of this experiment was to optimize the experimental conditions for the arc-transfer method so as to produce high quality single crystals of Co_{1-x}O of about 1 cm diameter suitable for Co tracer self-diffusion studies.

EXPERIMENTAL PROCEDURE

Arc-Transfer Method of Crystal Growth

Cobalt metal rods of 99.999% purity, 5 mm in diameter and 15 cm long, were purchased from United Mineral & Chemical Corp.¹ A quantitative analysis report supplied by the manufacturer is given in Table 2 in the next section.

Single crystals of Co_{1-x}O were grown from these rods by arc transfer with the arc operating in air. This method of crystal growth is based on the principle of transfer of material across the gap of a dc arc discharge. Figure 2 shows a schematic diagram of the process. The cathode, which acts as a feed rod, is the high-purity Co rod. The anode or the base rod is made of a lower purity Co rod of diameter larger than the boule to be grown. One of the electrodes is capable of moving in three dimensions so that the electrodes can be mounted with their axes parallel and vertical. Depending on the mode of growth this could be either anode or cathode. In the present illustration for upward growth, this is the anode. The whole assembly is designed such that one of the electrodes can be moved up or down relative to the other fixed electrode. Molten caps are formed on the end of the electrodes with the arc striking across the narrowest part of the gap. Material transfer takes place across the gap from the feed electrode to the boule-growing electrode. During the run, adjustments are made so that the current and the arc gap are maintained constant. Finally when the growing is completed, the current is reduced in steps

¹United Mineral & Chemical Corp., New York. The rods were produced by Johnson Matthey Chemicals Ltd., London, England.

Figure 2. Schematic illustration of arc-transfer method for upward growth

and the electrodes are brought closer and closer and finally fused together.

Preliminary crystal growth experiments were done with various constant currents and arc gaps. These results are reported in the next section.

The procedure adopted after the initial experiments for preparing crystals is as follows: In each experiment, the tips of the electrodes were cleaned on a SiC wheel. They were mounted in the apparatus and checked that their axes were vertical and were held a few mm apart. A small direct current was passed and the electrodes were heated by a propane torch. When the tips were hot enough, the two electrodes were touched momentarily and separated to about 1 mm. The current was adjusted to about 3 A which was usually sufficient for the arc to remain established. This current was passed for about 15-20 minutes. Both the current and the arc gap had to be adjusted frequently for several minutes in the beginning. This was necessary because the arc kept wandering until the system was thermally stabilized. After the arc had stabilized, the current was gradually increased to constant values. The current and the arc gap were kept constant throughout the experiment by adjusting the electrode assembly at an interval of 5-10 minutes or whenever necessary depending on the growth rate. Experiments were done with constant currents between 4-10 A and arc gaps between 1-3 mm. Crystals for the diffusion experimental work were grown at currents of 6-7 A and an arc gap in the neighborhood of 1-2 mm.

The procedure adopted for terminating the growth was first to reduce the current to a lower value of 4-5 A in fast steps and then slowly to a

minimum value, usually 2 A. At the same time the arc gap was reduced. In about 30 minutes from the starting time of termination, the two electrodes were fused together and the minimum current was allowed to pass for an additional 10-15 minutes after which the power was shut off. After it was completely cooled, the crystal was easily removed from the assembly by a slight twist.

Characterization of Single Crystals

The as-grown crystals were characterized by determining:

- 1) whether the specimens were single crystals,
- 2) the orientation of the growth plane,
- 3) the presence of polygonized structure, and
- 4) the quality of the crystals.

The characterizations of the first three parameters were done by the back-reflection Laue method of X-ray analysis. The apparatus consisted of a General Electric X-ray diffraction unit (XRD-5), a Cu X-ray tube, a goniometer, and a Polaroid film cassette.

Parallel sections (perpendicular to the growth axis) were cut from the boule by a low speed diamond saw. The section was then slightly polished on 600 grit paper to remove any abrasion left from cutting and, finally, was polished with Linde A. It was X-rayed at 35 KV and 15 mA for 5 minutes. A Greignier chart was used to find the location of the closest cubic plane. Diffraction patterns are shown in the next section.

The quality of the crystals was characterized in terms of the level of impurities in the as-grown boule as compared to the impurities present in the starting metal rod, the presence of macro and micro defects such

as cavities, and the presence and mode of distribution of second phase.

The impurity analysis was done spectrographically by the emission spectroscopy method. A comparison of the concentration of impurities in the as-grown crystals and the as-received metal rods is presented in Table 2 in the next section. A Leitz Orthoplan microscope with 4x5" Large Format Camera¹ was used to determine the presence of growth defects. The samples used for this purpose were polished with Linde B to remove scratches. No etchant was necessary in order to reveal the presence of cavities and second phase. The micrographs are shown in Figure 7 in the next section.

Confirmation of the presence and a qualitative detection of the composition of the second phase was done by electron microprobe analysis.² Microprobe analysis was also done to check for the impurities attached to cavities. Electron micrographs are shown in Figures 8-10 in the next section.

¹Ernst Leitz GMBH Wetzlen, Germany.

²XMA-S Electron Microprobe Analyzer, Hitachi Ltd., Tokyo, Japan.

RESULTS AND DISCUSSION

Growth Parameters

Table 1 summarizes the results on the growth parameters of some of the typical single crystals of Co_{1-x}O grown by the arc-transfer method. Figure 3 illustrates graphically the relationships between arc current and ingot diameter (d) or linear growth rate ($\frac{\Delta x}{\Delta t}$).

For a constant arc gap, the diameter of the growing boule increases with current. This is in agreement with the investigation of Smith and Austin (8) on Co_{1-x}O . However, unlike the latter, no break in the curve was found for currents between 6-8 A. Considering the experimental error involved in the manual control of the arc gap, the dependency of the diameter on the current (for the entire range of the current and an arc gap of 1-2 mm) can be given by

$$d^2 \propto I \quad (1)$$

where I is the current.

No specific relationship between the linear growth rate and the current can be deduced. The value $\frac{\Delta x}{\Delta t}$ varied between 3 mm/hr to 4 mm/hr for currents varying between 6-8 A and an arc gap of 1-2 mm. With the exception of boule #3, the data of Table 1 can be used to calculate a mean linear growth rate of 3.5 mm/hr which is independent of current. Smith and Austin (8) reported a linear growth rate of 2 mm/hr for currents in the range of 2-5 A. Above 5 A, they found that the $\frac{\Delta x}{\Delta t}$ value increased with current. No reason was given for this behavior. A linear growth rate, independent of the current, is also predicted by Drabble (9) on the

Table 1. Growth parameters of arc-transfer grown crystals

Boule #	Current (I) A	Arc gap mm	Time hr	Length cm	Diameter (d) cm	Growth rate $(\frac{\Delta x}{\Delta t})$ mm/hr
1	6.0	2	7.25	2.3	0.82	3.2
2	6.0	1	7.0	2.5	0.80	3.6
3	6.0	3	7.0	1.1	0.90	1.6
4	7.0	1	7.33	3.2	0.92	4.4
5	7.0	1	5.25	2.2	0.91	4.2
6	7.5	1	7.5	2.4	0.99	3.2
7	7.5	2	6.75	2.2	0.98	3.3
8	8.0	2	6.0	2.2	1.06	3.7
9	6.5	1	6.0	2.2	0.89	3.7
11	7.0	1	5.0	1.5	0.95	3.0
12	6.0	1	5.5	1.7	0.85	3.1
13	6.0	1	6.9	2.0	0.85	2.9

assumption that the mass freeze-out rate is approximately proportional to the current under the condition that the square of diameter is proportional to the current. A similar result was obtained for NiO (8) with a linear growth rate of 3 mm/hr for currents up to 5 A. However, these values are all significantly smaller than the typical values of 5 cm/hr obtained in pulling methods, and 3.5 cm/hr in the zone melting of oxides (8).

The limit to which the arc gap can be varied is dependent on the magnitude of the current and the diameter of the cathode. Smaller arc gaps, and correspondingly low currents, produce crystals of small ingot diameter but good quality. However, a gap smaller than 1 mm is difficult to maintain as it often results in fusion of the electrode to the growing anode. Larger arc gaps, though yielding large ingot diameters,

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Figure 3. Comparison of data on growth parameters of Co_{1-x}O single crystals grown from Co electrodes in air by upward growth

drastically cut the linear growth rate. A detailed description of this phenomenon in Fe_2O_3 given by Kippling was reported by Drabble (9, p. 806). The rate at which material left the cathode first decreased with an increase in the arc gap. Above 2.5 mm width of the gap, the rate increased rapidly. However, the corresponding rate of mass transfer to the anode showed a continuous decrease. This leads to the conclusions that the rate of mass loss from the arc increases with increase of the arc gap. His results are shown in Figure 4.

In this investigation, preliminary crystal growth experiments were done with various values of the current (4-10 A) and the arc gap (1-3 mm). With Co electrodes of 5 mm diameter, a current of 6-7 A with arc gaps in the neighborhood of 1-2 mm produced crystals of good quality and desired diameter. In the method of upward growth, the length of the boule was only a function of time.

No specific conclusion can be deduced about the mechanism of mass transport. Smith and Austin (8) and Drabble (9) have reported that 80-90% of the material lost from the cathode appears in the growing anode with the higher transport efficiency being observed with the smaller gap.

Characterization of Single Crystals

Figure 5 shows the diffraction pattern obtained by the back-reflection Laue method of X-ray analysis of a Co_{1-x}O single crystal grown by the arc-transfer method. The X-ray beam was parallel to the growth axis.

Several investigators (7-9) have reported that spontaneous growth in Co_{1-x}O occurs along the [100] axis. The results of the Laue diffraction patterns in the present work showed that the growth axis usually deviated

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Figure 4. Experimental variation of mass transfer rates with arc gap for Fe electrodes in air from Drabble (9, p. 806)

Open points: upward growth; solid points: downward growth; circles: rate of mass leaving the cathode; triangles: rate of mass transferred from cathode to anode; squares: rate of mass loss from the arc.

from [100]. In most cases this deviation was within 20 degrees. However, in some crystals large deviation occurred and the growth axis was more nearly perpendicular to some other set of planes as shown in Figure 6. One of the reasons for this may be the misalignment of the two electrodes. Because of the manual adjustment, the axes of the electrodes may not have been exactly perpendicular to one another. In such cases, the arc will not be parallel to the axes of the electrodes. A seed may thus nucleate with (100) face inclined to the axis of the anode. For these reasons, the alignment of the electrodes may be important in the beginning when the seed is growing.

In the absence of any more sophisticated analysis of the crystal, the Laue diffraction pattern can be taken as an indicator of the character of the crystal in terms of crystallinity, substructure, and the presence of strain. For instance, the Laue diffraction pattern in single crystals of MgO usually shows well-defined diffraction spots indicating a situation of negligible strain or substructure (10). In single crystals of Ni_{1-x}O and Co_{1-x}O grown from low purity metal rods, Brosnan (10) reported doublets in the diffraction patterns indicating the presence of a polygonized structure. This was confirmed by etching. As indicated by Figures 5 and 6, the diffraction patterns obtained in the present work show reasonably well defined spots without any doublets. This indicates that the boules are single crystals and are free from any significant strain or substructures. Occasionally, the boules grew as bi-crystals and were not used in the investigation.

A comparison of the concentration of impurities present in the starting metal rods and single crystals grown by the arc-transfer method is

Figure 5. Back-reflection Laue pattern of Co_{1-x}O single crystals displaying a (100) symmetry

Figure 6. Back-reflection Laue pattern of Co_{1-x}O single crystal with X-ray beam at 90° to the growth face

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given in Table 2. The as-grown crystal does not show any significant increase in the impurity concentrations as compared to the rod. This indicates that the method does not introduce any external impurities.

Figure 7 shows the microstructure of a typical crystal as viewed with an optical microscope. Figures 7a and 7b are typical of many crystals grown in this work. The microstructure in most cases did not show any gross internal imperfections except for the randomly distributed inclusions appearing as white specks. Occasionally, blowholes or pits appeared in the microstructure as shown in Figure 7c. Both the inclusions and the pits were analyzed by electron microprobe analysis to find their compositions. Two typical sites of pits and a large inclusion were

Table 2. Impurity analysis of metal and single crystal

Impurity	Co-metal ^b ppm	CoO single crystals ^a		
		As-grown Spectrographic	As-annealed	
			Spectrographic	Wet chem ppm
Al	1	-	T, VW	29
Ni	1	T	T	
Si	1	-	T	30
Ca	Less than 1	-	-	
Cr	"	-	-	
Cu	"	-	T	2
Fe	"	TX	TX	
Mg	"	T	T	5
Ag	"	-	-	

^aBoth spectrographic (emission spectroscopy) and wet chemical analysis done by the Analytical Service Group of Ames Laboratory of Iowa State University. Symbols used: T, traces; X, interference; VW, very weak; -, element not detected; blanks are those not investigated.

^bAnalysis supplied by the producer. Exact method of analysis is not known.

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Figure 7. Microstructures of Co_{1-x}O single crystals

- (a) Crystal showing very small second phase precipitates uniformly distributed throughout
- (b) Crystal showing mixed sized precipitates
- (c) Crystal showing pits indicated by arrows

A

B

C

analyzed as shown in the electron-micrographs of Figures 8-10. The large regular shaped pit in Figure 8a did not show any significant difference in Co concentration within the pit as compared to the outside area. The white lines around the edges are due to Al_2O_3 left from polishing. Identical results were obtained in Figure 9 where an irregular shaped pit with rough surface was analyzed. The result of the microprobe analysis of the inclusion, shown in Figure 10, indicated a lower concentration of Co. This indicates that the second phase is probably Co_3O_4 .

Both the presence of Co_3O_4 inclusions and blowholes have been reported by several investigators (8, 11). In commercial boules, grown by the flame fusion technique, Clauer *et al.* (11) reported large amounts of Co_3O_4 precipitate in the as-received specimens. The presence of Co_3O_4 precipitate may be due to the slow cooling of the crystal. As is evident from Figure 1, this phase is stable below 920°C in air. This is further confirmed by Figure 11 which shows that large precipitates are found in the bottom of the boule and smaller precipitates are found in the top. This implies that Co_3O_4 nucleated on solidification and the temperature of the boule may have been high enough for these nuclei to grow with time. On the termination of the arc, the crystal boule cooled faster and the precipitates in the upper zone of the boule could not grow to larger sizes. Annealing in controlled atmosphere of oxygen pressures did not eliminate second phase in cooled specimens. Further discussion of the effect of annealing is given in Appendix B.

In Co_{1-x}O boules grown by the arc-transfer method, Smith and Austin (8) reported blowholes (cavities) in pure oxide boules while no such blowholes were found in Li doped boules. In the present work such blowholes

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Figure 8. Electron microprobe analysis of a regular-shaped pit in Co_{1-x}O (1330X)

(a) Backscattered electron image

(b) Al $K\alpha$ X-ray image

Figure 9. Electron microprobe analysis of an irregularly-shaped pit in Co_{1-x}O (1330X)

(a) Backscattered electron image

(b) Al $K\alpha$ X-ray image

Figure 10. Backscattered electron image of Co_3O_4 inclusion in Co_{1-x}O (1330X)

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Figure 11. Microstructure of Co_{1-x}O single crystals
grown in air

(a) Top of the boule

(b) Bottom of the boule

A

B

have been found to be more prominent in crystals grown at higher currents. Currents below 6 A usually produced crystals in which these defects were either not present or were not significant.

PART II: TRACER SELF-DIFFUSION MEASUREMENTS IN Co_{1-x}O

INTRODUCTION

Mass transport plays an important role in solid state processes such as chemical reaction, ionic conductivity, sintering, creep, and oxidation. In elucidating such processes, a study of diffusion in solids is of great technical importance. For this reason, considerable research has been done on diffusion, primarily in metals and alkali halides.

In recent years, due primarily to their technical potentialities, there has been an increasing interest in diffusion and other transport properties in oxides. Investigations have been done in a number of oxide systems, and the development has to a large extent followed in the footsteps of such studies in various halides. Numerous discrepancies exist in the data reported on transport properties in oxides, and this problem has been reviewed by Kofstad (3, pp. vii and viii) and also by Nowick et al. in a discussion found in Wachtman and Franklin (12, pp. 207-217). A lack of precise knowledge of the impurity content and distribution, and the stoichiometry are some of the factors responsible for the reported discrepancies.

There is considerable interest in diffusion studies in oxides of the group to which Co_{1-x}O belongs. Oxides such as MnO , FeO , CoO , and NiO , like MgO , all have the NaCl structure, which is relatively easy to evaluate theoretically (2). All of them except MgO are nonstoichiometric, with composition being a function of both temperature and partial pressure of oxygen (2). Since the transport properties are predominantly dependent on the number and type of defects present, a knowledge of the defect states in the solid can lead to a better understanding of the transport

phenomena.

The goals of this study of Co self-diffusion in Co_{1-x}O were two-fold. First, to study the phenomenon in single crystals varying both temperature and stoichiometry and thereby correlate results with probable defect structure. Second, to obtain data from arc-transfer grown crystals for comparison with those taken by other investigators using polycrystalline specimens and crystals grown by flame fusion.

LITERATURE SURVEY: DEFECTS AND TRANSPORT PHENOMENA IN Co_{1-x}O

Co_{1-x}O is a metal-deficient, nonstoichiometric oxide having the NaCl structure. Its lattice parameter is 4.26 Å and ionic radii are 0.74 Å for Co^{2+} and 1.4 Å for O^{2-} (13). It exhibits p-type semiconductivity (14).

Wagner and Koch (15) were the first to investigate the transport properties of Co_{1-x}O as a function of p_{O_2} . They found that the electrical conductivity of polycrystalline samples between 800 and 1000°C increased with increasing p_{O_2} . They also showed that at 1000°C the conductivity varied as $p_{\text{O}_2}^{1/4}$ for oxygen pressures near 1 atm, and as $p_{\text{O}_2}^{1/5}$ for oxygen pressures established by CO/CO₂ mixtures ($\sim 10^{-12}$ - 10^{-5} atm). Duquesnoy and Marion (16) investigated Co_{1-x}O formed by the oxidation of Co wire. For temperatures between 900-1200°C and over a wide range of p_{O_2} , their results showed conductivity to be proportional to $p_{\text{O}_2}^{0.25-0.27}$. Shelyky et al. (17) measured electrical conductivity of single crystals of Co_{1-x}O between 1027-1227°C. They found conductivity to be proportional to $p_{\text{O}_2}^{1/3.4 - 1/4}$ for p_{O_2} above 10^{-5} atm.

As will be discussed later, electrical conductivity dependency on $p_{\text{O}_2}^{1/4}$ in these results suggests that the reaction establishing the non-stoichiometry in Co_{1-x}O at higher p_{O_2} may be represented by

Carter and Richardson (18) have determined the O/Co ratio at 1000, 1150, and 1350°C at p_{O_2} of 1 and 5×10^{-3} atm. The ratio was determined by an oxidation and reduction method. The results showed that the concentration of excess oxygen, x , in CoO_{1+x} to be proportional to $p_{\text{O}_2}^{0.26 \pm 0.1}$.

Error and Wagner (13), using these data, determined ΔH_f° (enthalpy for cobalt vacancy formation, based on Equation 2), and showed that the average value of the p_{O_2} dependence of the cobalt vacancy concentration for the three temperatures was $p_{O_2}^{0.27}$. Error and Wagner (13) also made their own electrical conductivity and thermogravimetric measurements on single crystals of $Co_{1-x}O$. Their results showed that both electronic and atomic defect concentrations were a function of $p_{O_2}^{1/4}$ over 900-1200°C and $1-10^{-4}$ atm p_{O_2} , suggesting singly-ionized cobalt vacancies as the predominant defect.

Fisher and Tannhauser (19) made extensive electrical conductivity and thermogravimetric measurements on polycrystalline $Co_{1-x}O$ which covered a range of temperature between 900-1450°C and p_{O_2} from 1 to 10^{-12} atm. Their results for the conductivity as a function of p_{O_2} gave two distinct regions and is shown in Figure 12. In region A, which is essentially the experimental conditions of most of the above cited investigators, the conductivity varies as $p_{O_2}^{1/4}$. This suggests that V_{Co}' is the most dominant defect at higher p_{O_2} . In region B, where the p_{O_2} has been established by CO/CO_2 mixtures ($\sim 10^{-12}$ - 10^{-5} atm), conductivity is proportional to $p_{O_2}^{1/6}$. As will be discussed later, this represents the predominance of doubly ionized cobalt vacancies. Their plot of data relating conductivity to x , the deviation from stoichiometry, is reproduced in Figure 13, and again shows a region A in which $x \propto \text{conductivity} \propto p_{O_2}^{1/4}$. This result is in agreement with Carter and Richardson (18) showing $x \propto p_{O_2}^{0.26 \pm 0.1}$. However, at low p_{O_2} the slope of the curve could not be evaluated. The curves in region A show a departure from linearity for values of x corresponding to $p_{O_2} = 1$ atm. This has been reasoned by Fisher and Tannhauser

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Figure 12. Conductance of Co_{1-x}O as a function of temperature and p_{O_2} (Ref. 19)

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Figure 13. Conductance of Co_{1-x}O as a function of temperature and stoichiometry (Ref. 19)

Regions A and B correspond to the same regions in

Figure 12. O: 1347°C , ●: 1285°C , Δ : 1191°C ,

+: 1129°C , X: 1094°C , ●: 1035°C , ▲: 986°C .

(19) to be due to neutral Co vacancies which may be present at p_{O_2} above 1 atm. Based on combined measurements of conductivity and thermogravimetry, Fisher and Tannhauser (19) also have been able to plot the lines of constant stoichiometry as a function of temperature and p_{O_2} as illustrated in Figure 14. The regions A and B here indicate the two regions where defect concentration and conductivity are proportional to $p_{O_2}^{1/4}$ and $p_{O_2}^{1/6}$, respectively.

Fisher and Wagner (20) and Bransky and Wimmer (14) have made investigations of conductivity, stoichiometry, and Seebeck-effect on pure and Li-doped specimens. Their results showed V_{Co}' with charge compensation by h° as the dominant defect in agreement with the model suggested by several investigations. These experiments were not able to define a region of p_{O_2} and temperature in which V_{Co}'' was apparently the predominating defect.

Carter and Richardson (18) have studied the diffusion of Co^{60} in polycrystalline $Co_{1-x}O$ formed by the oxidation of metal discs. For temperatures between 800-1350°C at $p_{O_2} = 1$ atm, the self-diffusion coefficient (D) was given by

$$D = 2.5 \times 10^{-3} \exp\left(\frac{-34500}{RT}\right) \text{ cm}^2/\text{sec}.$$

They also measured the diffusion coefficient as a function of p_{O_2} and reported

$$D = 2.6 \times 10^{-9} (p_{O_2})^{0.35} \text{ cm}^2/\text{sec at } 1000^\circ\text{C}$$

$$D = 9 \times 10^{-9} (p_{O_2})^{0.30} \text{ cm}^2/\text{sec at } 1150^\circ\text{C}$$

$$D = 5 \times 10^{-8} (p_{O_2})^{0.28} \text{ cm}^2/\text{sec at } 1350^\circ\text{C}.$$

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Figure 14. Co-CoO phase boundary and lines of constant stoichiometry in CoO_{1+x} (Ref. 19)

Kofstad (3, p. 240) has investigated the plots of data of $\log D$ vs. $\log p_{O_2}$ from Carter and Richardson's (18) work and reported D to be proportional to about $p_{O_2}^{1/3}$ at 1 atm, and to about $p_{O_2}^{1/4}$ at 10^{-3} atm. These results are in general agreement with Fisher and Tannhauser (19), and the slightly larger slope at about 1 atm is within the limits of the reported experimental error. No report on the density or porosity of the oxide specimens was given.

Chen et al. (21) have studied Co self-diffusion and the isotope effect for Co diffusion in single crystals of $Co_{1-x}O$ in air. The results were given by

$$D = (5.0 \pm 0.4)10^{-3} \exp\left(\frac{-38900}{RT}\right) \text{ cm}^2/\text{sec}.$$

From the results of isotope effect of diffusion, they concluded that cation self-diffusion in $Co_{1-x}O$ takes place by a vacancy mechanism.

Price and Wagner (22) have measured the chemical diffusion coefficient in $Co_{1-x}O$ using an electrical conductivity technique. Between 800 and 1100°C and p_{O_2} between 0.5 to 10^{-6} atm they report

$$\tilde{D} = 4.33 \times 10^{-3} \exp\left(\frac{-24000}{RT}\right) \text{ cm}^2/\text{sec}$$

where $\tilde{D}$ is the chemical diffusion coefficient. Wimmer et al. (23) have also measured the chemical diffusion coefficient in $Co_{1-x}O$ by thermogravimetric and electrical conductivity measurements and reported

$$\tilde{D} = 4.8 \times 10^{-3} \exp\left(\frac{-22500}{RT}\right) \text{ cm}^2/\text{sec}$$

for temperatures between 900-1300°C and p_{O_2} between $1-10^{-5}$ atm. The results are in good agreement with tracer diffusion measurements showing

$$\bar{D}_{\text{Co}} = D/2.$$

Crow (24) has measured the Co tracer self-diffusion coefficient in single crystals of Co_{1-x}O and has presented a defect model on the basis of his own diffusion results and the experimental work of others on stoichiometry. He reported

$$D = 4.8 \times 10^{-3} \exp\left(\frac{-35900}{RT}\right) \text{ cm}^2/\text{sec at } 1 \text{ atm } p_{\text{O}_2}$$

$$D = 4.5 \times 10^{-4} \exp\left(\frac{-35800}{RT}\right) \text{ cm}^2/\text{sec at } 5 \times 10^{-3} \text{ atm } p_{\text{O}_2}.$$

Anion diffusion rates in Co_{1-x}O has been studied by several investigators (25-27) and is reported to be several orders of magnitude smaller than the cation diffusion rates. Thompson (25) has measured oxygen diffusion in polycrystalline Co_{1-x}O by an O^{18} isotope exchange technique. He reported,

$$D = 5.9 \times 10^{-6} \exp\left(\frac{-36000}{RT}\right) \text{ cm}^2/\text{sec}$$

at a p_{O_2} of 0.13 atm between 900-1100°C. Chen and Jackson (26), using the same technique as Thompson, reported

$$D = 50 \exp\left(\frac{-95000}{RT}\right) \text{ cm}^2/\text{sec}$$

for single crystals in temperature range of 1175-1560°C in air. A proton activation technique was used by Holt (27). In this method the penetration of O^{18} tracer in single crystals was determined by the nuclear reaction $\text{O}^{18}(\text{p}, \gamma) \text{F}^{18}$ in conjunction with autoradiography. From Holt's (27) Arrhenius plot, Chen and Jackson (26) have calculated $D = 2 \times 10^{-11} \text{ cm}^2/\text{sec}$ at 1140°C and at $p_{\text{O}_2} = 0.17 \text{ atm}$. This result is in general agreement with

results of Chen and Jackson (26). Holt (27) also used bicrystals in his study and reported preferential O^{18} penetration along grain boundaries. This may explain the high value of D obtained by Thompson (25) in polycrystalline samples where the diffusion may have occurred predominantly along grain boundaries.

The mechanism of diffusion of oxygen in $Co_{1-x}O$ is not well defined. Chen and Jackson (26) have made oxygen diffusion measurements in doped $Co_{1-x}O$ crystals. The diffusion coefficient at $1428^{\circ}C$ in air increased with Li^{+} concentration but decreased with Al^{3+} concentration. This was interpreted as indicating oxygen diffusion by a vacancy mechanism. Neutral interstitial oxygen has also been suggested as the important diffusion mechanism by Clauer et al. (11). Their conclusion is based on the results of creep studies in single crystals where they found creep rate to be proportional to $p_{O_2}^{1/2}$ in the temperature range of $1000-1200^{\circ}C$ at oxygen pressures between 1 and 10^{-3} atm.

THEORETICAL CONSIDERATIONS

Phenomenological Description of Diffusion

Fick (28) proposed a relationship to describe diffusion which was analogous to the Fourier expression for the conduction of heat. The one-dimensional flow of heat in a temperature gradient can be expressed by

$$J_H = -K \frac{\partial T}{\partial X} \quad (3)$$

where J_H is the heat flux per unit area, K is the thermal conductivity, and $\frac{\partial T}{\partial X}$ is the temperature gradient. On direct analogy, the diffusion flux of particles or species (in one dimension), defined as the quantity of material passing through a unit area of a plane perpendicular to the direction of diffusion per unit time, was proposed by Fick to be proportional to the negative concentration gradient in the diffusion direction. Mathematically, this is given by

$$J_i = -D_i \frac{\partial C_i}{\partial x} \quad (4)$$

where J_i is the flux of the i^{th} species across the plane, C_i is the concentration of the species at the plane, x is the dimensional coordinate in the direction of the concentration gradient, and D_i is a proportionality factor called the diffusion coefficient or diffusivity of species i . The negative sign signifies that the diffusion takes place from the region of high species concentration to low species concentration. In order that Equation 4 adequately describes the diffusion phenomenon, gradients in all intensive variables except concentration must be absent. An isothermal isobaric binary system, consisting of single phase region in which

diffusion occurs in only one direction, is assumed for deriving this equation.

Equation 4 is called Fick's First Law, and its direct use in the measurement of diffusion coefficients requires a fixed concentration gradient. Since such a steady state is often experimentally difficult to establish in a solid, a modified form is usually used which takes into consideration the change of local concentration with time. This is called Fick's Second Law and is expressed by

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x} \left(D_i \frac{\partial C_i}{\partial x} \right). \quad (5)$$

If it is assumed that D_i is independent of concentration, then Equation 5 simplifies to

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2}. \quad (6)$$

Various methods can be applied to solve Equation 6 for C_i , the concentration of the diffusing species as a function of position and time, i.e., $C(x,t)$, if certain initial and boundary conditions are satisfied. The application of Equation 6 for the specific case of tracer self-diffusion measurements will be presented later in this section.

Diffusion Mechanisms

The diffusion flux described by Equation 4 is the result of the movement of individual atoms through the medium. In a solid, there are several possible mechanisms by which atoms can move through the relatively restrictive structure. These mechanisms can be classified as:

Direct exchange or ring mechanism
Vacancy mechanism

- Divacancy mechanism
- Interstitial mechanism
- Interstitialcy mechanism
- Crowdion mechanism

The details of these mechanisms for atomic movements are illustrated in Figure 15. With the exception of the direct exchange or ring mechanism, the figure shows that diffusion mechanisms generally require the presence in the crystal of imperfections. All crystals do, in fact, contain imperfections which can be classified as:

- Point defects — vacancies, interstitials, or impurity atoms
- Line defects — dislocations and stacking faults
- Complex defects — defects resulting from the interaction or coalescence of elementary defects

Direct exchange and crowdion diffusion mechanisms are generally considered unimportant in oxides (29). A divacancy is formed when two vacancies are on adjoining sites and associate. The probability of this mechanism operating in oxides cannot be ruled out; however, it is not well known. The discussion, therefore, will be limited to vacancy, interstitial, and interstitialcy mechanisms.

Diffusion by the vacancy mechanism occurs when an atom jumps from its lattice position into a neighboring unoccupied lattice site or vacancy. The diffusing atom moves through the crystal by making a series of exchanges with vacancies which appear adjacent to it from time to time. This mechanism may largely be responsible for cation diffusion in oxides (10). Because cations and anions are located on interpenetrating sublattices in oxides, cations must move through the anion sublattice to accomplish a diffusional jump. It has been reported (29, 30) that the distortion of the anion sublattice in the process of diffusion is less for the vacancy mechanism of cation diffusion than for a direct exchange

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Figure 15. Diffusion mechanisms

mechanism. From geometrical considerations of atom packing in crystals, Azaroff (31, 32) has proposed two likely paths available for cation diffusion in crystals having anions in close packing. These include diffusion via vacancy jump mechanism either through alternating octahedral and tetrahedral sites, or along chains of octahedral sites within the anion packing.

Diffusion by the interstitial mechanism involves the jump of an atom from an interstitial site to an adjacent unoccupied interstitial site. It is assumed to be dominant in any nonmetallic solid in which a moving interstitial does not distort the lattice greatly (29). However, this would not be true in the NaCl structure.

Diffusion by the interstitialcy mechanism involves the jump of an atom from an interstitial site to an adjacent normal lattice site displacing the atom from that site to an occupied interstitial site. It may be a collinear or a noncollinear interstitialcy mechanism depending upon whether or not the atom displaced from the normal lattice site moves along the same direction as the first atom. The possibility of this mechanism operating in oxides has been reviewed by Brosnan (10). According to this, if interstitial occupation is allowable in a NaCl structure, less distortion would be required for an interstitialcy process than for a vacancy mechanism (for the same size of diffusing cations). Because of the presence of tetrahedrally coordinated cations in oxides with the NaCl structure, the interstitialcy mechanism was suggested to be important in oxide systems.

Atomic Theory of Diffusion

Diffusion in a crystalline solid involves movements or jumps of atoms or defects between definite sites in the crystal structure. Individual jumps are possible in all directions allowed by the structure and consecutive jumps follow no particular directional sequence. Statistical methods, therefore, must be applied in order to calculate the distance a diffusing atom has moved after a certain number of jumps. By means of Fick's laws, such calculations can lead to a fundamental interpretation of the diffusion coefficient in terms of atomic jumps.

Shewmon (29, p. 47) has given an exhaustive mathematical treatment of the problem. Describing the process as a three-dimensional random walk in which individual jumps are not correlated with one another, gives the diffusion coefficient as

$$D = \frac{1}{6} \Gamma \alpha^2 \quad (7)$$

where Γ is the total jump frequency of a diffusing atom and α is the jump distance. This equation applies to the simple case in which all jumps are of the same length, and all adjacent sites have an equal probability of being available to the jumping atom. The total jump frequency can be expressed as

$$\Gamma = k\omega \quad (8)$$

where k is the number of specific adjacent sites in the structure and ω is the jump frequency into a specific adjacent site. Thus, for a cubic crystal, Equation 7 becomes

$$D = \frac{k\alpha^2\omega}{6} = \gamma a_0^2\omega \quad (9)$$

where γ is a geometric constant and a_0 is the lattice parameter. For a FCC lattice such as the ions occupy in the NaCl structure, a vacancy jump mechanism corresponds to $\gamma \approx 1$ so the term may be dropped.

The frequency of jumping into a specific adjacent site, ω , can be expressed as

$$\omega = \omega_a P_v \quad (10)$$

where ω_a is the frequency at which the jumping atom acquires sufficient energy to overcome any barrier to a complete jump, and P_v is the probability that the adjacent site being approached is unoccupied. Applying Boltzman statistics, ω_a can be expressed by

$$\omega_a = \nu \exp\left(\frac{-\Delta G_m}{RT}\right) \quad (11)$$

where ν is the frequency of vibration toward a specific site, ΔG_m is the free energy associated with one mole of jumping species in the saddle point configuration, R is the gas constant, and T is the absolute temperature. By combining the last three equations, D is then given by

$$D = a_0^2 \nu P_v \exp\left(\frac{-\Delta G_m}{RT}\right). \quad (12)$$

When diffusion coefficients are characterized by tracer atom jumps, the random nature of the process may be disturbed so that a correlation factor ' f ' has to be introduced.

$$D^* = f D \quad (13)$$

where D^* is the tracer diffusion coefficient. The magnitude of f depends upon the structure type and the jump mechanism. The value of f for a vacancy jump mechanism in a FCC structure is 0.781 (33). Hence, for a FCC cubic lattice, Equation 12 can be given as

$$D^* = 0.781 a_0^2 \nu P_V \exp\left(\frac{-\Delta G_m}{RT}\right). \quad (14)$$

In Equation 12, ν is generally assumed to be the Debye frequency. If temperature is constant, the factor $[0.781 a_0^2 \nu \exp\left(\frac{-\Delta G_m}{RT}\right)]$ thus becomes constant and Equation 12 can be expressed as

$$D^* = (\text{Const}) P_V. \quad (15)$$

The probability of finding an adjacent site vacant, P_V , can be evaluated on the basis of the defect structure. Equations 12-15 can be rewritten in the form

$$D^* = f a_0^2 \nu P_V \exp\left(\frac{\Delta S_m}{R}\right) \exp\left(\frac{-\Delta H_m}{RT}\right) \quad (16)$$

where ΔS_m and ΔH_m are the entropy and enthalpy of one mole of jumping species at the saddle point and are frequently referred to as entropies and enthalpies of motion.

Defects in Oxides

All oxides may exhibit deviations from stoichiometry. In particular, oxides whose cations exhibit variable valence are the most likely to exhibit larger deviations from stoichiometry (34). Consequently, the accommodation of this excess or deficit of one component in a lattice gives rise to defects. In addition to defects introduced by deviation

from stoichiometry, oxides may also possess thermally-generated defects, defects introduced by the incorporation of impurity atoms into the lattice, and a variety of complexes due to association of individual defects.

Reviews on these and other defects in oxides are available in the literature (34-36). A brief description of the defect structure of an MO type oxide is made here. For the purpose of illustration, the general situations for pure stoichiometric and nonstoichiometric oxides are considered first, followed by a brief description of defects in Co_{1-x}O .

Pure stoichiometric oxides

In the case of a stoichiometric, or nearly stoichiometric oxide, thermally generated defects or disorder will occur. These defects may include Schottky, Frenkel, and antistructural disorders. Schottky disorder in an MO type oxide involves the formation of an equal number of cation and anion vacancies. Using the Kroger and Vink (36) notations, the reaction forming this defect can be given by

$$n\text{I} = V_M + V_O \quad (17)$$

where V_M and V_O are the metal and oxygen vacancies, respectively. In writing Equation 17, assumptions made by Van Gool (37) have been used. Since a vacancy is considered to be of zero mass, the equation is balanced as far as the mass balance is concerned. Although creation of sites have occurred, the numerical site relationship is maintained. Frenkel disorder involves the formation of equal number of cation vacancies and cation interstitials. This can be represented by

$$M_M = V_M + M_i \quad (18)$$

where M_M refers to a cation on cation site and i in the subscript which refers to the interstitial site. Both the Schottky and the Frenkel disorders can also occur with anion in the interstitial site. They are called anti-Schottky and anti-Frenkel disorders, and can be represented by

$$MO = M_{1-\delta}O_{1-\delta} + \delta M_i + \delta O_i \quad (19)$$

and

$$O_O = V_O + O_i, \quad (20)$$

respectively. δ is assumed to be very small. O_O refers to an anion on anion site. Antistructural disorder involves the interchange of cations and anions from their normal sites according to

$$M_M + O_O = M_O + O_M. \quad (21)$$

There can also be electronic disorder, whereby electrons are thermally excited from the valence band to the conduction band leaving holes in the valence band. This intrinsic process can be represented by

$$nil = e' + h^\circ \quad (22)$$

where e' and h° represent an electron and an electron hole, respectively. Symbols $'$ and $^\circ$ represent a negative and a positive charge, respectively.

All of the above defects may partially or completely ionize. Equations of such ionization reactions can be written in the same way as the above with proper charge compensation. For instance, a cation vacancy can ionize as follows:

$$V_M = V_M' + h^\circ \quad (23)$$

$$V_M' = V_M'' + h^\circ \quad (24)$$

The law of mass action can be applied to the above equations to determine the equilibrium constants of the disorder reactions. As an example, if K_S is the equilibrium constant for the Schottky defect formation reaction of Equation 17, then

$$K_S = [V_M][V_O] \quad (25)$$

where $[]$ represents the concentration of the defect. In formulating the equilibrium relations, it is assumed that the concentration of defects are low. Details of the assumptions made in writing these relations are given in the above cited literature. In subsequent discussions, whenever not mentioned, concentrations of M_M or O_O are taken as unity.

Pure nonstoichiometric oxide

In addition to the thermally generated defects present in stoichiometric oxides, the defect structure of a nonstoichiometric oxide at high temperature represents a situation in which the crystal lattice has to also accommodate the imposed external partial pressure of the components. In order to do this, the oxide must adjust the ratio of M:O until the chemical potentials of both components in the structure are equal to those in the surrounding atmosphere.

An excess of oxygen (or a metal deficiency) can be accommodated either by creating a new site to which an oxygen atom from the gas phase can attach, or by incorporating the oxygen atom into an available interstitial site. These situations can be represented by

or

In reaction of Equation 26, the V_M is produced during creation of a new oxygen site because of the one-to-one ratio of cation to anion sites in an MO structure.

The concentration of these defects is fixed by the equilibrium constants as

$$K_{26} = [V_M]/p_{O_2}^{1/2} \quad (28)$$

and

$$K_{27} = [O_i]/p_{O_2}^{1/2} \quad (29)$$

where $[O_0]$ is taken as unity. These defects may ionize by reactions similar to Equations 23 and 24.

An excess of metal can be accommodated as

or

The equilibrium constants for Equations 30 and 31 are given by

$$K_{30} = [M_i]/p_M \quad (32)$$

and

$$K_{31} = [V_O]/p_M \quad (33)$$

respectively.

From equilibrium relations of Equations 28, 29, 32 and 33, it is evident that the concentrations of defects can be expressed as a function of p_M or p_{O_2} . If K 's can be determined, the concentrations of various defects can be calculated in terms of p_{O_2} which is usually known.

In pure oxides having large deviations from stoichiometry, the concentration of defects introduced by stoichiometry deviations completely masks the presence of similar defects produced by thermal processes.

Defects in $Co_{1-x}O$

As has been reviewed earlier in Part II of this dissertation, $Co_{1-x}O$ is believed to be an oxygen rich (metal deficient) oxide in which the predominant defects are cobalt vacancies. The appropriate equations for the incorporation of oxygen with their corresponding equilibrium constants can be written as

$$\frac{1}{2} O_2(g) = O_O + V_{Co}, \quad K_{34} = [V_{Co}] p_{O_2}^{-1/2} \quad (34)$$

$$V_{Co} = V'_{Co} + h^\circ, \quad K_{35} = \frac{[V'_{Co}] p}{[V_{Co}]} \quad (35)$$

$$V'_{Co} = V''_{Co} + h^\circ, \quad K_{36} = \frac{[V''_{Co}] p}{[V'_{Co}]} \quad (36)$$

where the unsubscripted p represents concentration of electron holes.

Substituting Equation 34 in Equation 35 and Equations 34 and 35 in Equation 36, equilibrium constants for singly and doubly ionized cobalt vacancies can be rewritten as

$$K_{35} = \frac{[V'_{Co}] p}{K_{34}} p_{O_2}^{-1/2}$$

or

$$K_{34}K_{35} = K_{37} = [V'_{Co}]p \cdot p_{O_2}^{-1/2}, \quad (37)$$

and

$$K_{36} = \frac{[V''_{Co}] p^2}{K_{34}K_{35} p_{O_2}^{-1/2}}$$

or

$$K_{34}K_{35}K_{36} = K_{38} = [V''_{Co}]p^2 \cdot p_{O_2}^{-1/2} \quad (38)$$

The electroneutrality condition for these equations can be written as

$$[V'_{Co}] + 2[V''_{Co}] = p. \quad (39)$$

Applying Brouwer's approximation (38) and assuming $p = [V'_{Co}]$ in Equation 37 and $p = 2[V''_{Co}]$ in Equation 38, the concentrations of V'_{Co} and V''_{Co} can be determined. Hence corresponding to the reactions described by Equations 34-36, the concentrations of the neutral and ionized cobalt vacancies can be expressed by

$$[V_{Co}] \propto p_{O_2}^{1/2} \quad (40)$$

$$[V'_{Co}] \propto p_{O_2}^{1/4} \quad (41)$$

$$[V''_{Co}] \propto p_{O_2}^{1/6} \quad (42)$$

In the discussion on the atomic theory of diffusion it was shown by Equation 15 that, for cobalt tracer self-diffusion by a vacancy mechanism,

$$D^* = (\text{Const}) P_v$$

or

$$D^* \propto P_v.$$

In case of Co_{1-x}O , x is the mole fraction of vacant cobalt sites and is

therefore equivalent to $[V_{Co}^i]$ where $i = 0, 1$ or 2 , depending on the degree of ionization. The probability, P_v , that a specific cobalt site will be vacant is therefore equal to x , so that

$$D^* \propto x \quad (43)$$

Thus, from Equations 40 through 42, one can expect

$$D^* \propto p_{O_2}^{1/n} \quad (44)$$

where n can be $2, 4$ or 6 , depending on the predominating ionization state of the cobalt vacancies. Results from self-diffusion measurements can be used to find the index n , from which the ionization state of cobalt vacancies can be inferred. Similar results can be obtained by applying thermogravimetry, electrical conductivity, and Seebeck-effect measurements.

Tracer Self-Diffusion Measurements

Tracer self-diffusion is defined as the movement of a radioactive tracer species in a system which is chemically uniform throughout and in which no gradients in chemical potential occur. The tracer self-diffusion coefficient can be analyzed on the basis of the atomic theory of diffusion. In particular, Equations 7 and 12 allow expression of the tracer self-diffusion coefficient, D^* , in terms of the fundamental vibrational frequency and jump distance. In subsequent sections of this dissertation, the superscript $*$ will be dropped and the symbol D will be taken to mean the tracer self-diffusion coefficient for cobalt unless specifically noted otherwise.

Most tracer self-diffusion experiments are mathematically described

by the so-called "thin film" solution of Fick's Second Law in the form of the partial differential equation Equation 6. The assumption that D is not a function of composition is implicit in Equation 6 and is appropriate in chemically uniform media such as those used for tracer self-diffusion studies. A detailed description of the method of solution of Equation 6 is given by Crank (39, p. 10) and Jost (40, p. 16). It is assumed that two semi-infinite specimens of identical composition are welded together so that they share an interface at $x = 0$. At $t = 0$, all the tracer atoms are concentrated in a plane or "thin film" at $x = 0$. The general form of the solution to Equation 6 is then given by

$$C(x,t) = \frac{\beta}{t} \exp\left(-\frac{x^2}{4Dt}\right) \quad (45)$$

where β is a constant to be determined, and $C(x,t)$ represents the concentration of tracer atoms which have penetrated a distance x in time t . The differentiation of Equation 45 shows it to be a solution of Equation 6. It also satisfies the initial and boundary conditions of the problem since the equation is symmetrical about $x = 0$, and vanishes everywhere for $t = 0$ except at $x = 0$ where C becomes very large.

If α is the total amount of the tracer and the specimen is of infinite length on either side of $x = 0$ and is of unit cross sectional area, then

$$\alpha = \int_{-\infty}^{\infty} C \, dx \quad (46)$$

On substitution of Equation 45 in Equation 46 and integrating between the limits, Equation 46 yields

$$\alpha = 2\beta \sqrt{\pi D} \quad (47)$$

Hence,

$$C(x,t) = \frac{\alpha}{2\sqrt{\pi Dt}} \exp\left(\frac{-x^2}{4Dt}\right) \quad (48)$$

is the solution which describes the spreading by diffusion of an amount of tracer α deposited at time $t = 0$ in the plane $x = 0$. The geometrical conditions which are imposed by Equation 48 are usually difficult, though not impossible, to attain in ceramic materials. A somewhat simpler geometry is realized by considering a long cylinder, one end of which is in contact with a very thin film tracer source. This is called the "semi-infinite thin film" solution. A method, known as reflection and superposition, is used to modify Equation 48 in order to describe the semi-infinite thin film case by permitting solution only for $x > 0$ (39, p. 11). Accordingly, the solution is given by

$$C(x,t) = \frac{\alpha}{\sqrt{\pi Dt}} \exp\left(\frac{-x^2}{4Dt}\right) \quad (49)$$

The expression in Equation 49 describes a tracer self-diffusion experiment in which a thin film of the tracer is applied to one end of a long specimen of uniform cross section and is allowed to diffuse by annealing at high temperatures. After annealing, one of several possible methods can be employed to determine the distribution of tracer within the specimen. A plot of $\ln C$ vs. x^2 can then be made and a straight line curve is obtained as shown in Figure 16. The slope of this curve is equated to $-1/4Dt$, which is the slope predicted by the expression of Equation 49. The tracer diffusion coefficients then can be determined since t is known. Because in most ceramic systems the diffusion rates are very small and thus the penetration is also very small, application of tracer to chemical

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Figure 16. Graphical representation of a diffusion penetration plot showing relationship between $\ln C$ and x^2

and impurity diffusion measurements becomes more important. The concentration of a tracer can be determined with orders of magnitude greater sensitivity than is possible with chemical analysis (41).

There are several radioactive tracer methods by which the thin film semi-infinite geometry can be used to carry out tracer self-diffusion measurements in solids. These methods have been reviewed in detail by Leymonie (42), Boltaks (43), and Sharma (44). The three most common methods are the serial sectioning method, the decrease in surface activity method, and the autoradiography method. These procedures vary only in the method of analyzing the distribution of tracer after the high temperature anneal.

The serial sectioning method is the most frequently used method of studying diffusion by means of radioactive tracers and is the method used in this investigation. On the surface of a semi-infinite specimen, a very thin layer of the tracer is deposited by electrolysis, evaporation, or by precipitation. After annealing, the lateral faces of the specimen are lapped off so as to eliminate the effects of surface diffusion. Thin parallel sections are then successively removed by etching, lapping, or by electrochemical dissolution. The thickness of the layer removed in each section may be measured directly by opto-mechanical indicator or dial gauges, or indirectly by interferometers, or by weighing. The activity of each section is determined and converted into specific activity by dividing either by the thickness or the weight of the section. Finally a plot of log specific activity vs. penetration distance squared is made and the diffusion coefficient is calculated as described earlier in this section.

One of the advantages of this method is that the measurement does not

depend on the properties of the radiations which are emitted by the tracer (42). However, it has two drawbacks. Errors can be introduced in the measurements of very thin sections or by loss of tracer as a dust during sectioning. Another error can be introduced if the sections are not cut parallel to the diffusion plane. Shirn et al. (45) have shown that 1 to 8% error in the slope may result when the sections are removed at angles inclined by $1/2$ to 1° from the proper axis.

The decrease in surface activity method uses a measurement of the count rate from the surface of the specimen before and after annealing. During annealing some of the tracer penetrates to various depths from which its emission are detected as an attenuated count rate. The amount of attenuation depends on depth of origin of the emission and μ , the absorption coefficient for the radiation in the medium. The diffusion coefficient is calculated by (42):

$$A/A_0 = \exp(\mu^2 Dt) [\operatorname{erfc}(\mu^2 Dt)^{1/2}], \quad (50)$$

where A is the count rate of the annealed specimen, and A_0 is the count rate before diffusion. A master curve is usually drawn giving A/A_0 as a function of $(\mu^2 Dt)$ from which D can be calculated. The absorption of radiation in the specimen must be critically analyzed before D can be calculated. This limits the applicability of this method. Carter and Richardson (18) have used this method in Co_{1-x}O and Fe_{1-x}O , and also have compared it with the sectioning method which was used simultaneously.

The autoradiographic method of measuring diffusion coefficients determines C vs. x by cutting the annealed specimen along the diffusion direction and contacting the exposed surface with a photographic emulsion.

The intensity of exposure is then determined as a function of depth below the original surface and Equation 49 is used to calculate D . This method is usually used with radiations of short range, e.g., β , because they produce good resolution. A microphotometer is used to measure the intensity of the blackening of the emulsion. The method does not require any counter device. The method can be also used to examine grain boundary diffusion.

EXPERIMENTAL PROCEDURES

Single crystals of Co_{1-x}O used in these studies were grown in this laboratory by the arc-transfer method. The as-grown boules were approximately 0.9 cm in diameter and various lengths up to 2.5 cm. An analysis of impurities is given in Table 2 in Part I of this dissertation. The isotope Co^{60} , used as a cation tracer, was purchased from New England Nuclear¹ in the form of Co^{2+} in 0.5 N HCl solution with a specific activity of 111 mCi/mg. The analysis provided by the supplier indicated a radiochemical purity of >99.9%. Co^{60} has a half life of 5.26 years (46) and emits one β -particle (0.31 MeV) and two γ -rays (1.17 and 1.33 MeV) according to the decay scheme shown in Figure 17 (47).

A carrier solution was made by dissolving solid $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in distilled water to make a 0.02 M CoCl_2 solution. The appropriate amounts of tracer solution were added to the carrier to make a working tracer solution having an activity of approximately 10 $\mu\text{Ci/ml}$. Small amounts of this working solution were later used for depositing thin films on the diffusion specimens.

It was deemed desirable, for purpose of measuring section thickness, that the specimens be of constant known cross-sectional area throughout. In order to assure this, the boules were first machined into right circular cylinders. One end of the boule was cut perpendicular to the length using a low speed diamond saw. The boule was then affixed with wax² to a 10 cm long by 1 cm diameter drill stock with its length parallel to the

¹New England Nuclear, Boston, Massachusetts.

²Loc-Wax-20, Geoscience Instrument Corp., Mount Vernon, New York.

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Figure 17. Co^{60} decay scheme (Ref. 47)

center line of the drill stock. The drill stock was chucked into the head of a small lathe attached to the bed of a surface grinder, and a SiC wheel was used to grind the surface of the boule into a right cylinder of about 0.85 to 0.9 cm diameter. A slow-speed diamond saw was used to slice the cylinder perpendicular to its length to form short cylindrical diffusion specimens of ~2 mm thickness.

Each of the cylindrical specimens thus prepared was characterized by the techniques described in Part I of this dissertation. Only those specimens which were single crystals and free from growth defects were selected for the self-diffusion studies.

To conform to the geometry required by the semi-infinite thin film solution given by Equation 49, the faces of each specimen were made parallel to one another. One face of the specimen was attached with Loc-Wax-20 to a short length of 1 cm diameter drill stock which had both ends machined parallel. A mounting jig was used for this purpose. The drill stock was then gripped in the Jacobs chuck of a sectioning device. The mounting jig and the sectioner, later to be used for slicing thin sections of the diffusion-annealed specimens for the penetration measurements, have been described with illustrations by Berard (48). The faces of the specimens were first ground on 320 grit SiC paper and finally on 600 grit paper until the surface was in a plane perpendicular to the axis of the cylinder. After this treatment, the specimens were removed from the drill stock, cleaned in methanol and distilled water, and inspected under a low magnification microscope for flaws.

Annealing of specimens was carried out in a horizontal tube diffusion furnace constructed for these studies. The furnace had the features of

adequate control and capability of reaching temperatures above 1350°C in a few hours, control of atmosphere by using purified flowing gas mixtures, and capability of rapid insertion and withdrawal of the specimen in and out of the hot zone. An illustration is shown in Figure 18. The heating elements were SiC XL Hot Rods,¹ 20"x9"x1/2" in dimension. The hot face insulation consisted of 2800°F insulating firebrick² backed by layers of 2300°F insulating firebrick. The muffle was an impervious McDanel³ 998 alumina tube (99.8% Al₂O₃) 2" O.D. x 1-3/4" I.D. x 26" long. Gas-tight brass seals cooled by circulating water were attached to both ends of the muffle tube. A precalibrated Pt-Pt 10% Rh thermocouple was extended through the back seal with the measuring junction in the center of the hot zone. This thermocouple was used to measure the temperature of the specimen. The tip of the thermocouple always remained within 2 mm of the specimen. The reference junction was kept at 0°C by using a thermoelectric ice point reference junction.⁴ The specimen temperature was measured and recorded by a Brown Potentiometer⁵ strip chart recorder. A second Pt-Pt 10% Rh thermocouple outside the muffle was used to control the temperature of the furnace. The temperature controller consisted of a West Instruments

¹Trademark of Norton Company, Industrial Ceramics Division, Worcester, Massachusetts.

²A. P. Green Refractory Company, Mexico, Missouri.

³McDanel Refractory Porcelain Company, Beaver Falls, Pennsylvania.

⁴Model 2150-4C, Joseph Kaye & Co., Inc., Cambridge, Massachusetts.

⁵Minneapolis-Honeywell Regulator Co., Brown Instruments Division, Philadelphia, Pennsylvania.

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Figure 18. Schematic diagram of diffusion anneal furnace

Set Point Unit¹ with proportional control provided by an SCR unit.² It had the provision of controlling temperature both manually and automatically.

To obtain the desired oxygen partial pressure, mixtures of Ar and O₂³ were purified, dried, and blended in ratios required for each p_{O₂} using the gas train illustrated in Figure 19. Anhydrous magnesium perchlorate (anhydrone)⁴ was used to remove water, sodium hydrate asbestos absorbent (ascarite)⁵ to remove CO₂, and heated (550°C) Cu-turnings to remove O₂ by the oxidation of Cu to CuO. To insure complete mixing before entering the muffle tube, the gases were passed through a chamber packed with glass beads. The flow rates of the gases were regulated by two rotameter-type flow meters.⁶ The flowmeters had calibration curves, supplied by the manufacturer, for the gases that were used. An additional flowmeter was used to regulate the flow rate of the mixed gases into the furnace.

The flow rates of the individual gases needed to produce a known value of p_{O₂} was calculated by

¹Model JSCR, West Instrument Division of Gulton Industries, Inc., Schiller Park, Illinois.

²Model PSCR-15, West Instrument Division of Gulton Industries, Inc., Schiller Park, Illinois.

³Commercial grade, Ar and O₂, obtained from Air Products & Chemicals, Inc., Allentown, Pennsylvania.

⁴Trademark of J. T. Baker Chemical Co., Phillipsburg, New Jersey.

⁵Trademark of Arthur H. Thomas Co., Philadelphia, Pennsylvania.

⁶Model 610, Matheson Gas Products, East Rutherford, New Jersey.

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Figure 19. Schematic diagram of gas train

$$p_{O_2} = \frac{N_{O_2}}{N_t} p_t \quad (51)$$

where

N_{O_2} = flow rate of oxygen (ml/min)

N_t = total flow rates = $(N_{Ar} + N_{O_2})$ (ml/min)

p_t = total pressure inside the furnace = 1 atm.

Final check of the oxygen partial pressure was made using an oxygen meter¹ at the outlet of the reaction tube. The p_{O_2} values indicated by the oxygen meter are reported in the diffusion results.

All specimens to be used in the tracer diffusion measurements were annealed in air at 1350°C for 24 hours and air quenched. The aim of this pre-annealing and quenching was to have all specimens in the same stoichiometry to start with. An analysis of the condition of the crystals following this pre-annealing and quenching treatment is given in Appendix B. The method adopted for annealing was as follows. The cleaned specimens were arranged in an alumina boat (99.8% Al_2O_3) and placed in the cold zone just inside the tube end. The closure was placed on the end of the tube but a vent hole was left open to the atmosphere. The temperature of the furnace was increased in steps so as to reach about 1300°C in about six hours. The furnace control was then put into the automatic mode with a 1350°C set point. After the temperature of the interior thermocouple indicated a constant temperature, the specimen boat was inserted into the hot zone. The interior temperature usually registered a slight drop on insertion but returned to the set point temperature in less than five

¹Thermox Meter Model I, Thermo-Lab Instruments Inc., Pittsburgh, Pennsylvania.

minutes and remained constant afterward within $\pm 2^\circ\text{C}$. In order to quench the specimens after the annealing, the specimen boat was pulled out into the cold zone, the seal was opened, and the boat was withdrawn into air. This operation was usually accomplished in less than one minute.

Before each diffusional anneal, each specimen was given a second pre-annealing treatment at the temperature and p_{O_2} of the diffusion anneal for a period twice as long as the diffusion annealing time. This second annealing was performed in order to establish the stoichiometry of the specimen at the value desired for diffusion measurements. The procedure adopted for establishing the controlled atmosphere was to pass purified and dried Ar gas during the initial heating of the furnace. When the temperature was close to the required annealing temperature, the required flow of O_2 (purified and dried) gas was started. The specimen was inserted into the hot zone when both the temperature and the oxygen partial pressure showed constant values. After completion of annealing, the specimen was pulled out into the cold zone, the gas mixture flow was stopped, the seal was opened, and the specimen was air quenched.

The surface of the pre-diffusion-annealed specimen on which tracer was to be applied was ground lightly on 600 grit paper. Preliminary examinations of the samples showed that this grinding did not affect the parallelism of the faces. The grinding was found helpful in depositing a uniform thin layer of the tracer. The sample was thoroughly cleaned in distilled water. An aliquot of 20 λ of the working tracer solution was pipetted onto the surface after which 20 λ of NH_4OH was added to precipitate $\text{Co}(\text{OH})_2$. The specimens were first dried under an electric lamp for a few hours, and, after placing in the alumina boat, were further dried

in air above 300°C. The diffusion anneals were accomplished in the diffusion furnace with atmosphere and thermal treatment procedures the same as adopted for the pre-diffusion annealing. All diffusion anneals were performed on duplicate specimens.

After the diffusion anneal, the activated surface of the specimen was cleaned with a cotton swab soaked with acetone to remove any loosely bound tracer. The specimen was then mounted on the short length drill stock with Loc-Wax-20 using the mounting jig to ensure alignment. The mounted specimen was then chucked into the head of the small lathe and a thickness of $\sim 5\sqrt{Dt}$ was ground off the cylindrical surface of the specimen to eliminate any effect of surface diffusion. The mounted specimen was then placed in the Jacobs chuck of the sample holder and inserted into the sectioning device. The specimen was sectioned by grinding on a pre-weighed 320 grit paper disc. The sample holder was turned continuously during the sectioning to ensure parallel sectioning. The paper holding the ground material was weighed, and the increase in weight was taken to be the mass of the thin section. The weighings were done with a Cahn microbalance¹ capable of weighing accurately to the nearest 2 μg . The sections containing active material were covered with mylar tape and stored for later activity counting. The thickness of each section removed was determined by using the weight of the section removed, the cross sectional area of the specimen, and the density of CoO taken as 6.437 gm/cm^3 (49). The diameter of the specimen was measured with a micrometer calipers taking the mean of ten readings. The sections were approximately

¹Model G-2 Electrobalance, Ventron Instrument Co., California.

10 μm in thickness, and at least 20 sections were removed from each specimen.

The radioactivity counting of each specimen was carried out in a γ -ray counting arrangement consisting of a 2"x2" NaI (thallium activated) scintillation detector,¹ a spectrometer,² a single channel analyzer,³ a combination of Scaler,⁴ Timer/Scaler⁵ and a high voltage power supply.⁶ No decay time corrections were necessary due to the long half-life of Co^{60} .

All the grit papers on which the sections were ground, weighed, and counted were of the same size. Provision was made in the counting chamber to count every section in identical geometry. All sections were counted for 1000 sec. The counting rate always remained large enough that increase in the counting time was not necessary for counting the deepest sections.

Calculations of the tracer self-diffusion coefficients were done on the basis of the semi-infinite thin film solution of Equation 49. The expected distribution for this case consists of a very high concentration of activity at the surface ($x = 0$) which drops off exponentially with the square of the distance from the surface. Considering the specific

¹Model DS-200(V), Nuclear Chicago, Des Plaines, Illinois.

²Model 816, Canberra Industries, Meriden, Connecticut.

³Model 830, Canberra Industries, Meriden, Connecticut.

⁴Model 871, Canberra Industries, Meriden, Connecticut.

⁵Model 892, Canberra Industries, Meriden, Connecticut.

⁶Model 251, Mech-Tronics Nuclear Corporation, Melrose Park, Illinois.

activity as A/ℓ where ℓ is the thickness of the section, then

$$\ln \frac{A}{\ell} = \ln A_0 + \frac{-x^2}{4Dt} \quad (52)$$

where A_0 is constant and proportional to the initial amount of tracer. Hence D can be calculated directly from the slope of the $\ln(\frac{A}{\ell})$ vs. x^2 penetration plot.

RESULTS AND DISCUSSION

Two types of experiments were performed in this investigation. In one type of experiment, tracer self-diffusion coefficients were measured as a function of temperature at a constant deviation from stoichiometry of $x = 0.005$. The measurements were made at 1037, 1150, 1250, and 1350°C. The second type of experiment was concerned with measuring tracer self-diffusion coefficients as a function of deviation from stoichiometry at a constant temperature of 1150°C. Four sets of measurements in this second experiment were carried out by fixing x at 0.002, 0.004, 0.006, and 0.008. The ranges of temperature and deviation from stoichiometry in these experiments were selected such that the measurements covered a wide range but remained within region A of the Fisher and Tannhauser (19) phase diagram, Figure 14. As has been reviewed earlier in this dissertation, the defect structure of Co_{1-x}O in this region has been reported to consist predominantly of singly-ionized cobalt vacancies with electron holes as free charge carriers.

Constant x -Variable Temperature Experiment

A typical penetration plot from this experiment is shown in Figure 20. Plots for all of the specimens investigated at different temperatures are given in Appendix A. The curves shown in all these plots are based on a least-squares fit. The initial few points (usually up to 20 μm from the surface) in most of these penetration plots were either of very high activity or showed constant counts. They were dropped from the least-squares fits.

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Figure 20. Diffusion penetration plot of a Co_{1-x}O specimen

$x = .005$, $T = 1037^\circ\text{C}$, $t = 24$ hr.

● indicates point dropped in the final least squares fit

Units for A and l are counts per 1000 sec and cm, respectively.

A 95% prediction interval (50) was used to test each data point in a penetration plot with points outside this interval being rejected. Each time a point was rejected, a new least-squares fit was determined and a new prediction interval was calculated. When no further points were rejected, the final fit was used to calculate a 95% confidence interval for D from Equation 52 as

$$D = \frac{1}{4(b + \tau S_b)t} \quad (53)$$

In this expression b is the regression coefficient of $\ln(A/\ell)$ on x^2 , S_b is the standard error of the regression coefficient and τ is the t -statistic for a 95% confidence interval on the regression coefficient.

Diffusion coefficients calculated in this way are tabulated in Table 3 along with time of diffusion anneal and p_{O_2} required to fix the stoichiometry at $x = 0.005$ for different temperatures. The reasonably narrow confidence intervals for diffusion coefficients are consistent with the nature of the penetration plots which showed activities to fall almost linearly with square of the penetration distance. Except for the first set of measurements at 1350°C, the values of the diffusion coefficients for duplicate specimens are in good agreement. No reason was found for the discrepancy in the values of D between specimens 1 and 2 at 1350°C except that the two specimens showed extreme differences in hardness. Because of the inherent difficulties in producing polished sections of radioactive specimens, they could not be examined for possible differences in their microstructures. However, the microstructure of nonradioactivated specimens which showed different hardnesses did not reveal any significant differences as shown in Figure 21.

Table 3. Summary of diffusion coefficient measurements at constant deviation from stoichiometry of $x = 0.005$

Specimen	Temperature °C	P_{O_2} atm	Time hr	D cm^2/sec
1	1350	0.031	4	$(1.11 \pm 0.84 - 0.33) \times 10^{-8}{}^a$
2				$(2.18 \pm 0.09 - 0.08) \times 10^{-8}$
1R ^b				$(1.97 \pm 0.07 - 0.06) \times 10^{-8}$
2R				$(2.15 \pm 0.07 - 0.06) \times 10^{-8}$
3	1250	0.063	6	$(1.39 \pm 0.40 - 0.26) \times 10^{-8}$
4				$(1.11 \pm 0.07 - 0.06) \times 10^{-8}$
5	1150	0.105	12	$(5.01 \pm 0.14 - 0.12) \times 10^{-9}$
6				$(5.35 \pm 0.50 - 0.42) \times 10^{-9}$
7	1037	0.21	24	$(1.96 \pm 0.07 - 0.06) \times 10^{-9}$
8				$(2.23 \pm 0.43 - 0.31) \times 10^{-9}$

^aDiscarded in the calculation of activation energy reported in Table 4.

^bR indicates repeated measurement.

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Figure 21. Microstructures of annealed Co_{1-x}O specimens which showed different hardness

(a) Specimen of moderate hardness

(b) Soft specimen

A

B

An Arrhenius plot of data giving the temperature dependencies of the diffusion coefficient is given in Figure 22. The Arrhenius relation is based on the equation

$$D = D_0 \exp \left(\frac{-Q}{RT} \right) \quad (54)$$

where D_0 is a constant called the frequency factor, Q is the activation energy, and R and T are the gas constant and absolute temperature, respectively. A least-squares fit of the plot $\log D$ vs. $1/T$, yielded

$$D = (3.89 \begin{smallmatrix} + 4.95 \\ - 2.18 \end{smallmatrix}) \times 10^{-4} \exp \left(\frac{-31600 \pm 2400}{RT} \right) \text{ cm}^2/\text{sec} \quad (55)$$

for the experiments performed between 1037 and 1350°C at $x = 0.005$ ($p_{O_2} = 0.21 \cdot 10^{-1.5}$ atmosphere). The limits on D_0 are calculated from the 95% confidence interval on the intercept of the least-squares fit of $\log D$ vs. $1/T$. The limits on Q are calculated from the 95% confidence interval on the regression coefficient for the fit. Table 4 compares this result with the reported activation energies from other investigations. Some of these studies are compared on the Arrhenius plot given in Figure 23. As is evident, both from Table 4 and Figure 23, the activation energy obtained in this work for constant stoichiometry agrees very well with that computed by Carter and Richardson (18) from data on polycrystalline specimens corrected to the same stoichiometry as in this experiment.

Since x , and therefore p_v , are fixed at a constant value in this study, Equation 16 can be written

$$D = (\text{Constant}) \exp \left(\frac{-\Delta H_m}{RT} \right) \quad (56)$$

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Figure 22. Arrhenius plot for the diffusion of Co^{60} in Co_{1-x}O single crystals at $x = 0.005$

Table 4. Comparison of activation energies for Co diffusion in Co_{1-x}O

Investigators	Q Cal/mole	D_0 cm^2/sec	Range of temperature $^{\circ}\text{C}$
Chen <u>et al.</u> (21) ^a (SC, air) ^b	38000 ± 770	$(4.19 \pm 1.22) \times 10^{-4}$ $- 0.94$	963-1638
Carter and Richardson (18) ^a (PC, air) ^b	37700 ± 1620	$(3.6 \pm 3.14) \times 10^{-3}$ $- 1.68$	950-1353
Carter and Richardson (18) ^c (PC, $x = 0.005$)	28800	1.37×10^{-4}	1000-1350
Fryt <u>et al.</u> (51) ^d (PC, variable x)	37800 ± 500	$(5.2 \pm 0.6) \times 10^{-3}$	950-1350
This work (SC, $x = 0.005$)	31600 ± 2400	$(3.89 \pm 4.95) \times 10^{-4}$ $- 2.18$	1037-1350

^aValues recalculated from original data points. Limits represent 95% confidence interval.

^bSymbols SC and PC refer to single crystalline and polycrystalline specimens, respectively.

^cValues calculated from empirical relations in Reference 18. Because of insufficient number of data points, 95% confidence interval was not calculated.

^dValues taken from literature. Confidence level or limits unknown.

This is a form of the Arrhenius equation, Equation 54, with ΔH_m being the activation energy Q and the various constants being multiplied together to constitute D_0 . Therefore, the activation energy measured in this study and given in Equation 55 is actually the enthalpy of motion of cobalt ions probably jumping by a vacancy mechanism.

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Figure 23. Comparison of D for Co^{60} diffusion in Co_{1-x}O

Symbols SC and PC represent single crystalline and polycrystalline specimens, respectively.

In the work of Chen et al. (21) and Carter and Richardson (18) in air, however, the value of x , and therefore P_v , was not constant, but rather varied with temperature while the p_{O_2} remained fixed at 0.21 atmosphere. Figure 24 shows that $\ln x$ vs. $1/T$ at constant p_{O_2} is a linear relationship. This can also be predicted by means of defect relations. Thus, at constant p_{O_2} but variable temperature, x will vary according to an equation of the form

$$x = A \exp \left(-\frac{E}{RT} \right) = P_v \quad (57)$$

The value of E determined from Figure 24 was calculated to be 7250 ± 450 cal/mole. For Chen et al. and Carter and Richardson's work in air, therefore, Equation 57 must be substituted into Equation 16 to give

$$D = [f a_0^2 v A \exp \left(\frac{\Delta S_m}{R} \right)] \exp \left(-\frac{E + \Delta H_m}{RT} \right) \quad (58)$$

where now the bracketed term is to be identified as D_0 in the Arrhenius equation and the activation energy is

$$Q = E + \Delta H_m \quad (59)$$

Thus, the activation energies determined by Chen et al. and Carter and Richardson for Co diffusion in air are expected to be greater than the activation energy for this study by about 7200 cal/mole. Table 4 shows that this is approximately the result found.

As is evident from Table 4 and Figure 23, essentially no difference is found in the activation energies for diffusion in single crystal and polycrystalline specimens. In the latter, because of the grain boundaries, the diffusivities of cations might be expected to increase. Two points

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Figure 24. Variation of stoichiometry with temperature in
air from Fisher and Tannhauser (Ref. 19)

can be argued. It is possible that grain boundary diffusion may not be greatly different than volume diffusion for Co in Co_{1-x}O . It is also possible that the method of measurement used by Carter and Richardson (18) may not have been sensitive enough to measure the effects of grain boundary diffusion. The second possibility cannot be ruled out since the specimens of Carter and Richardson were of very large grain sizes, larger than the usual diffusion length of 300-400 μm in these types of experiments.

Constant Temperature — Variable x Experiment

Similar to the last experiment, penetration plots from this experiment, also showed linear relationships. All the penetration plots are given in Appendix A. The same procedure, as described earlier, was adopted for analyzing these data. Diffusion coefficients with 95% confidence intervals were calculated from the slopes of the penetration plots and are tabulated in Table 5 along with data on x and the p_{O_2} required to fix the deviation from stoichiometry. The diffusion coefficients increased with increasing x or p_{O_2} showing that D is indeed a function of oxygen pressure. A plot of D vs. x , as shown in Figure 25, gives a straight line. This supports the derivation of Equation 43, according to which

$$D \propto x$$

A least-squares fit of this plot indicates very little scatter of data. This may be indicative that a single diffusion mechanism is operative in the experimental region.

The dependence of the diffusion behavior on defect structure can be further elucidated by $\log D$ vs. $\log p_{\text{O}_2}$ plots, as shown in Figure 26.

Table 5. Summary of diffusion coefficient measurements at constant temperature of $1150 \pm 2^\circ\text{C}$

Specimen	x	p_{O_2} atm	D cm^2/sec
9	0.008	0.562	$(7.59 \pm 0.34) \times 10^{-9}$ $- 0.31$
10			$(8.33 \pm 1.95) \times 10^{-9}$ $- 1.33$
12	0.006	0.21	$(6.14 \pm 0.76) \times 10^{-9}$ $- 0.61$
5	0.005	0.105	$(5.01 \pm 0.14) \times 10^{-9}$ $- 0.12$
6			$(5.35 \pm 0.50) \times 10^{-9}$ $- 0.42$
13	0.004	0.0398	$(4.28 \pm 0.41) \times 10^{-9}$ $- 0.35$
14			$(4.67 \pm 0.99) \times 10^{-9}$ $- 0.70$
15	0.002	0.0031	$(1.91 \pm 0.05) \times 10^{-9}$ $- 0.04$
16			$(1.80 \pm 0.04) \times 10^{-9}$ $- 0.04$

As described earlier, the range of p_{O_2} in this experiment covered most of Region A of the Fisher and Tannhauser (19) phase diagram (figure 14).

For this range, based on Equation 41, the dependency of the diffusion coefficient on p_{O_2} is given by

$$D \propto p_{\text{O}_2}^{1/n}; \quad n = 4 \quad (60)$$

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Figure 25. Cobalt tracer self-diffusion coefficient in Co_{1-x}O
at $1150 \pm 2^\circ\text{C}$ as a function of stoichiometry

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Figure 26. Tracer self-diffusion coefficient of Co in Co_{1-x}O as a function of p_{O_2} at 1150°C

SC: single crystals; PC: polycrystalline

A least-squares fit to the plot in Figure 26 gives

$$D = (9.74 \begin{smallmatrix} + 1.11 \\ - 1.00 \end{smallmatrix}) \times 10^{-9} p_{O_2}^{1/(3.59 \begin{smallmatrix} + 0.47 \\ - 0.37 \end{smallmatrix})} \text{ cm}^2/\text{sec} \quad (61)$$

The limits shown represent 95% confidence intervals calculated from the least-squares fit. A value of $n = 3.59 \begin{smallmatrix} + .47 \\ - .37 \end{smallmatrix}$ thus obtained is in agreement with the assumption of singly-ionized cobalt vacancies. Since the index n is calculated directly from the slope of the $\log D$ vs. $\log p_{O_2}$ curve, a small change in the slope is reflected in a significant change of the value of n .

Table 6 gives a comparison of values of n calculated by different investigators. The value obtained in this work agrees very well with those of Eror and Wagner (13) and Fisher and Tannhauser (19), both of whom have calculated n by electrical conductivity and thermogravimetry experiments.

There was not a sufficient number of data points in this study to confirm a change in the slope of $\log D$ vs. $\log p_{O_2}$ at high p_{O_2} values, as has been observed in the conductivity measurements of Fisher and Tannhauser (19) and the self-diffusion measurements of Carter and Richardson (18).

Table 6. Comparison of values of n in $D = D' p_{O_2}^{1/n}$

Investigators	Range of temp. °C	Range of p_{O_2} atm	n
Erör and Wagner (13) (SC, conductivity and gravimetry)	900-1200	10^{-4} - 1.0	3.86 - 3.98
Fisher and Tannhauser (19) (PC, conductivity and gravimetry)	900-1450	10^{-12} - 1.0	3.8 - 4.3 ^a 5.7 - 6.1 ^b
Carter and Richardson (18) (PC, self-diffusion)	900-1350	3.5×10^{-3} - 1.0	2.85 - 3.5
Fryt et al. (51) (PC, oxidation)	1000-1250	3.5×10^{-3} - 1.0	3.85 ± 0.1
Beigun et al. (52) (self-diffusion and hole mobility)	950-1350	Not known	2.5 - 3.3
This work (SC, self-diffusion)	1037-1350	3.1×10^{-3} - 0.56	3.59 ± 0.47 - 0.37

^aIn region A of phase diagram, Figure 14 (19).

^bIn region B of phase diagram, Figure 14 (19).

CONCLUSIONS

- 1) The arc transfer method of crystal growth allows growth of Co_{1-x}O single crystals of size and quality adequate for performing diffusion experiments.
- 2) The arc current and the arc gap (electrode separation distance) are critical parameters in producing good quality Co_{1-x}O crystals. A current of about 6 A and an arc gap in the neighborhood of 1-2 mm are optimum values when growing Co_{1-x}O crystals using 5 mm diameter Co rods.
- 3) Penetration plots and confidence intervals on tracer self-diffusion coefficients indicate that the experimental method used produces results which are reproducible in Co_{1-x}O single crystals.
- 4) The results of the constant stoichiometry study are in agreement with those of Chen et al. (21) and Carter and Richardson (18) performed in air, provided that a correction is made for changes in stoichiometry in the latter experiments.
- 5) The Co tracer self-diffusion coefficient as a function of temperature at a constant stoichiometry of $x = 0.005$ can be represented by

$$D = (3.88 \begin{smallmatrix} + 4.95 \\ - 2.18 \end{smallmatrix}) \times 10^{-4} \exp \left(\frac{-31600 \pm 2400}{RT} \right) \text{ cm}^2/\text{sec}$$

between 1037-1350°C.

- 6) The dependence of D on p_{O_2} at a constant temperature of 1150°C can be given by

$$D = (9.74 \begin{smallmatrix} + 1.11 \\ - 1.00 \end{smallmatrix}) \times 10^{-9} p_{\text{O}_2}^{1/(3.59 \begin{smallmatrix} + 0.47 \\ - 0.37 \end{smallmatrix})} \text{ cm}^2/\text{sec}$$

This equation is valid over the range of $p_{O_2} = 10^{-2.5} - 10^{-0.25}$ atm ($x = 0.002 - 0.008$).

- 7) The results of the constant temperature experiment indicate that, at 1150°C with $x = 0.002 - 0.008$, the probable mobile defects under these conditions are singly-ionized cobalt vacancies. Because no change in ΔH_m is seen between 1037-1350°C at $x = 0.005$, it may be inferred that the same mobile defect prevails over the entire temperature range at this stoichiometry.
- 8) Co tracer self-diffusion coefficients in $Co_{1-x}O$ single crystals were found to be essentially identical with those measured on polycrystalline specimens by other investigators. This suggests that further work should be done in polycrystalline $Co_{1-x}O$, especially at fine grain sizes, to determine whether grain boundaries enhance Co diffusion in this material.

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APPENDIX A: PENETRATION PLOTS FOR Co^{60} DIFFUSION
IN SINGLE CRYSTALS OF Co_{1-x}O

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Figure 27. Penetration plots for measurements at constant deviation from stoichiometry of $x = 0.005$

Numbers in parentheses refer to specimens reported in Table 3.

● indicates point dropped in the final least squares fit

Units for A and λ are counts per 1000 sec and cm, respectively.

Figure 27 (continued)

Figure 27 (continued)

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Figure 28. Penetration plots for measurements at constant temperature of $1150 \pm 2^\circ\text{C}$

Numbers in parentheses refer to specimens reported in Table 5.

● indicates point dropped in the final least squares fit

Units for A and λ are counts per 1000 sec and cm, respectively.

Figure 28 (continued)

Figure 28 (continued)

Figure 28 (continued)

APPENDIX B: ANALYSIS OF PRE-DIFFUSION ANNEALING TREATMENTS

As described in Part I of this dissertation, single crystals of Co_{1-x}O grown by the arc-transfer method had Co_3O_4 as a second phase distributed randomly throughout the boule at room temperature. Preliminary experiments were done to determine if annealing at high temperature in air or controlled p_{O_2} atmosphere had any effect in eliminating the second phase precipitates. Various annealing treatments at temperatures up to 1350°C and at oxygen partial pressures down to 10^{-6} atmosphere for as long as 24 hours were used. None of these treatments were effective in removing the precipitates when the cooling rate was not rapid enough. The annealed specimens usually showed larger second phase precipitates than as-grown crystals; however, the total volume of precipitates apparently remained constant. Irrespective of the annealing oxygen partial pressures, only crystals which were subjected to a rapid quenching, estimated at $\sim 50^\circ\text{C}/\text{sec}$, showed complete absence of the second phase. Optical micrographs of a specimen subjected to a rapid air quench after a 24 hour anneal in air at 1350°C are shown in Figure 29. In order to eliminate Co_3O_4 inclusions, it was therefore deemed sufficient to pre-anneal all specimens at 1350°C in air for 24 hours and quench before the second pre-annealing and quenching at the temperature and p_{O_2} of the diffusion anneal.

In order to determine the annealing time necessary to establish a uniform stoichiometry in the crystals, a theoretical analysis based on known diffusion rates was performed.

The diffusion coefficient of Co in Co_{1-x}O is of the order of $10^{-9} \text{ cm}^2/\text{sec}$ in the temperature range of this investigation. Estimating the

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Figure 29. Microstructure of Co_{1-x}O single crystal specimen used in quenching study

(a) As grown (200X)

(b) Annealed at 1350°C , 24 hours in air and quenched (500X)

A

B

order of magnitude of the distance traversed by a Co ion to be $\sim\sqrt{Dt}$, very long annealing times would be required if Co ions must move millimeter distances in order to homogenize the crystal. Oxygen diffusion coefficients are about three orders of magnitude less than Co diffusion coefficients in Co_{1-x}O (25-27). Therefore, the possibility of homogenization of the crystal by redistribution of oxygen from the surface inward (or vice versa) is very unlikely.

It is possible to hypothesize a model for stoichiometry changes and homogenization which assumes oxygen ions to be immobile with redistribution of Co occurring by movement of Co vacancies over long distances. This model has been considered by Seitz (53) and by Wimmer *et al.* (23). Two situations can be imagined. In the oxidizing condition, an excess of oxygen will be created at the surface by attachment from the gas phase. The corresponding excess of Co vacancies generated at the surface can rapidly diffuse inward with consequent slight movement of individual Co ions outward to achieve homogenization. In the reducing condition, oxygen atoms will be removed from the surface into the gas phase leaving behind an excess concentration of Co ions. Cobalt vacancies from the interior can then diffuse out rapidly to the surface to homogenize the crystal. In both cases, it is necessary for Co vacancies to move rapidly over long distances, and thus a high Co vacancy diffusion coefficient is required. The Co vacancy diffusion coefficient is given by

$$D_v = \frac{D_{\text{Co}}}{[V_{\text{Co}}]} = \frac{D_{\text{Co}}}{x} \quad (62)$$

where D_{Co} is the cobalt self-diffusion coefficient, $[V_{\text{Co}}]$ is the mole

fraction of vacant cobalt sites and x is the deviation from stoichiometry in Co_{1-x}O . In the range of stoichiometries investigated in this study (x on the order of 10^{-3}), the order of magnitude of D_v will be $10^{-6} \text{ cm}^2/\text{sec}$ which will permit vacancies to travel millimeter distances in times on the order of hours.

Assuming that D_v is constant over the stoichiometry range investigated, a calculation of Co vacancy distribution in an annealed specimen can be made using a solution to Ficks Law given by Crank (39, p. 45). The geometry involves a membrane (crystal) of infinite cross section and thickness ℓ , having its two surfaces held at fixed vacancy concentrations C_1 and C_2 and having an initial distribution of vacancies given by $f(y)$ where y is the thickness coordinate. Thus for

$$\begin{aligned} C &= C_1 & y &= 0 & t &\geq 0 \\ C &= C_2 & y &= \ell & t &\geq 0 \\ C &= f(y) & 0 < y < \ell & & t &= 0 \end{aligned}$$

Crank shows that

$$\begin{aligned} C = C_1 + (C_2 - C_1) \frac{y}{\ell} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{C_2 \cos n\pi - C_1}{n} \sin \frac{n\pi y}{\ell} e^{-Dn^2\pi^2 t/\ell^2} \\ + \frac{2}{\ell} \sum_{n=1}^{\infty} \sin \frac{n\pi y}{\ell} e^{-Dn^2\pi^2 t/\ell^2} \int_0^{\ell} f(y) \sin \frac{n\pi y}{\ell} dy \end{aligned} \quad (63)$$

In this equation D is to be taken as the cobalt vacancy diffusion coefficient, C_1 and C_2 are fixed by the temperature and p_{O_2} of the surrounding gas phase, and $f(y)$ is fixed by the previous history of the crystal.

For the purpose of calculation, it was assumed that during initial

growth, a uniform or homogeneous crystal resulted. Thus, $f(y)$, the initial distribution of cobalt vacancies, was taken as a constant C_0 determined by the melting temperature in air. During annealing, both surfaces are held at the same stoichiometry so that $C_1 = C_2$ for all t . Under these conditions, Crank (39, p. 45) has shown that Equation 63 reduces to

$$\frac{C - C_0}{C_1 - C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} e^{-[D(2n+1)^2 \pi^2 t / 4\ell^2]} \cos \frac{(2n+1)\pi y}{2\ell} \quad (64)$$

where the thickness is now 2ℓ .

Equation 64 was used with a computer to calculate the distribution of Co vacancies after the original 1350°C air anneal. The thickness of all crystals were about 2 mm. Conditions of 1350°C in air establish the surface stoichiometry at $x = 0.0085$. The original, as-grown stoichiometry was taken as $C_0 = x_0 = 0.02$ as estimated from phase diagram in Figure 14 (19).

The distribution of Co vacancies calculated in this manner for the original, highest-temperature anneal was found to be uniform throughout. Equation 64 could then be used to calculate the cobalt vacancy distribution after each of the pre-diffusion anneals under condition of temperature and p_{O_2} dictated by the range of stoichiometries to be investigated. Each pre-diffusion anneal was carried out for a time twice as long as the diffusion anneal time. The results of these calculations show complete uniformity of cobalt vacancy concentration throughout the 2-mm thickness of the crystals for all treatments. These calculations are supported by indirect evidence of rapid $Co_{1-x}O$ equilibration reported by Carter and Richardson (18).