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Oxygen annealing of silver for obtaining low electrical resistivity: technique and interpretation

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A single crystal Ag rod has been annealed in stages in a deliberate but low oxygen partial pressure. The change in the residual resistivity ratio (RRR) after each anneal is reported. During the course of the anneals the RRR is increased from 140 to 9500. The details of the annealing procedure are given, and the dynamics of internal oxidation of impurities in Ag are discussed. It is shown that for achieving high RRR, high annealing temperatures and low partial pressure of oxygen should be employed. In addition, the necessity of including size effects in the interpretation of electron transport phenomena in incompletely oxygen annealed samples is demonstrated.

1. Introduction

The deliberate internal oxidation of the impurities in nominally pure metals has been a matter of interest and importance to metallurgists for many years. Recently it has become apparent that this process could also be important to physicists interested in studying the conduction electron structure of metals. Most of the available techniques for these studies, such as those employing the de Haas-van Alphen effect, or high field galvanomagnetic effects, etc, require that the conduction electrons have a long mean free path. Consequently, these studies are performed at low temperatures and in the purest available materials – which minimizes electron scattering by phonons and impurity atoms, respectively.

The quantity used by most experimentalists for measuring the purity of the samples studied is the "residual resistivity ratio" (RRR). The RRR is defined as the resistivity at room temperature, ρ_{293} divided by the resistivity at temperatures near 0 K, ρ_0 . ρ_{293} arises primarily from thermal scattering of electrons and is very nearly independent of impurity content, while ρ_0 is due to scattering by impurities and lattice imperfections only. In a given nominally pure material, the RRR is determined almost entirely by the electron mean free path at 0 K. So although the RRR is not a good quantitative measure of the chemical purity of a metal, for those researchers probing the electronic structure of metals by most of the usual techniques, it is the most *relevant* measure of purity.

In recent years the RRR of a single crystal of Cu has been improved (increased) by as much as a factor of approximately 15 by oxygen annealing [1]. In this technique a Cu specimen is annealed in a "dynamic" vacuum having a controlled leak of either pure oxygen or air. The oxygen diffuses into the sample and, in some way not yet entirely understood, combines with and sequesters the impurities so as to render them ineffective as electron scattering centres.

To our knowledge, the oxygen annealing of metals, other than Cu, for the purpose of improving the residual resistivity ratio has never been very successful. Nor do we know of any quantitative discussion of how the two controllable parameters, temperature and oxygen pressure, could be chosen to maximize this improvement. Finally, we note that in samples that are oxygen annealed (knowingly or otherwise) certain pitfalls in the interpretation of electronic transport phenomena are generally overlooked.

In this paper we report the details of a successful oxygen annealing of a single crystal Ag sample which improved the RRR by a factor of 100, thus producing the highest RRR yet reported for this metal. In addition we address ourselves to the question of the influence of

TABLE I Annealing history and resulting residual resistivity ratios of a silver crystal

Anneal no.	Annealing temperature (°C)	Vacuum (Torr)	Annealing time (h)	Resulting RRR
1	900	*	150	140
2	900	1.0×10^{-5}†	3	162
3	500	4.0×10^{-5}	3	179
4	600	4.0×10^{-5}	3	230
5	700	4.0×10^{-5}	3½	770
6	700	3.5×10^{-5}	3	1000
7	800	4.2×10^{-5}	3	1150
8	900	3.5×10^{-5}	4	1670
9	900	3.0×10^{-5}	12½	2950
10	900	6.0×10^{-6}†	24	1350
11	900	4.5×10^{-5}	27½	6800
12	900	4.0×10^{-5}	25½	8400
13	900	5.0×10^{-5}	30	8900
14	900	2.0×10^{-4}	48	9500

*Sample was sealed in a vacuum
†No deliberate oxygen leak

temperature and oxygen pressure on oxygen anneals and the interpretation of the resultant resistivities.

2. Experimental

A single crystal Ag rod, about 20 cm long, was produced by the Bridgemen method in an ultra-pure graphite crucible approximately 30 cm long. It was grown under flowing argon that had been passed through a cooled molecular sieve to remove any residual oxygen in the gas.

A spectrographic analysis of this sample indicated the presence of Si, Mn, Mg, Cu, and Fe impurities in the crystal, and nuclear activation analysis gave a quantitative analysis of 1.0 ± 0.3 at. ppm Mn*. Quantitative spectrographic analysis employing carefully prepared blanks and standards of Si, Mn, Mg, Cu, and Fe in a AgCl precipitate indicated impurity levels of < 4.5 ppm Mg, < 2 ppm Mn, < 1.7 ppm Cu, 2 to 4 ppm Si, and 2 to 4 ppm Fe in the sample†. The agreement between the Mn content obtained by this method and by the nuclear activation analysis is reasonable and provides a measure of confidence in the spectrographic analysis of the other four elements. In addition, the data of McLellan [2] on the solubility of carbon in the noble metals indicate that there would probably be ≈ 300 atomic ppm carbon in a Ag crystal grown in a carbon crucible. The Ag crystal was highly imperfect inasmuch as X-ray examination showed that it contained a large number of low-angle grain boundaries.

The single crystal Ag rod with a diameter of approximately 2.5 mm was subjected to the following thermal treatments. It was initially sealed under vacuum in a quartz tube and annealed for approximately one week at 900°C (see Table I). After this and each subsequent anneal the RRR was measured. A second 3 h anneal in a "dynamic" vacuum at 900°C improved the RRR noticeably, giving strong evidence that small amounts of residual gases play a role in the RRR obtained. The vacuum system was then improved so that pressures of approximately 5×10^{-6} Torr could be obtained. Anneals 3 to 14 were then performed on the same sample as anneals 1 and 2 for the indicated times and with the resulting RRR's shown in Table I. During these anneals (except for number 10) pure oxygen was leaked into the system yielding the vacuum pressures given in Table I. The gases giving rise to these pressures are approximately 90% O_2, 10% N_2, the N_2 coming from the, at most, 5×10^{-6} Torr air leak. (Air, H_2O, hydrocarbons all probably contribute to the 5×10^{-6} Torr residual pressure.) Anneal 10, as anneal 2, was carried

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*I should like to thank Drs Melvin Freedman and James Tanner of the Food and Drug Administration for performing the neutron activation analysis.

†I am grateful to Mr Samuel H. Cress for performing the spectrographic analysis and Mr Dean I. Walter for preparing the standards.

out without the deliberate oxygen leak and the gases present in the system during these treatments should be at most 80% N_2 and 20% O_2. Prior to each anneal the sample surface was cleaned by etching in warm, dilute nitric acid in order to prevent any surface contaminants from diffusing into the specimen.

After the final anneal, a vacuum fusion analysis was performed to determine the oxygen content of the specimen with the gases released analyzed with a mass spectrograph*. An attempt was made to make a separate determination of the oxygen in Ag solution and the oxygen bound to the impurities by dissolving portions of the sample at 900°C in a tin bath for the former determination and at 1900°C in a platinum-tin bath for the latter. Within the sensitivity of the experiment, about 15 at. ppm, no oxygen was detected in solution. This is in agreement with the expected oxygen solubility in Ag at the oxygen pressure of anneal 14. The total oxygen content was determined as being 55 ± 20 at. ppm.

Although there is some uncertainty as to the nature of the stable impurity oxides under the prevailing conditions, this last result cannot be considered in agreement with the impurity content as given by the spectrographic analysis and nuclear activation results. The measured metallic impurity content appears to be low by a factor of about 2. In addition, taking the literature data for the resistivity induced in Ag per ppm of the impurities contained in our sample and using the upper bound for impurity content given by the analysis, we would expect an RRR of about 300 after anneal 2. (For those impurities for which these resistivity data are not available for Ag, we have estimated it from the data on Cu.) This also implies that the spectrographic results are low by a factor of at least 2 or alternately that our sample contains an equivalent amount of the refractory metals. A few ppm of these particular elements would not have been detected in the spectrographic analysis that was made. In either case, we estimate the total metallic impurity content to be approximately 35 at. ppm and the oxygen content after anneal 14 to be 50 at. ppm.

Finally, no quantitative measurement of this effect was made, but the oxygen anneal caused a very noticeable hardening of the sample. Whereas the "as-grown" Ag rods (several crystals were grown, only one was oxygen annealed) were unable to support their own weight, the oxygen annealed sample could be casually handled without bending and was even somewhat "springy". This effect is probably associated with dispersion hardening.

3. Discussion

3.1. Dynamical considerations of internal oxidation

The internal oxidation of trace impurities in a pure metal is a process governed primarily by the mechanism of diffusion. Many of the equations needed to discuss our work have been developed by Meijering and Druyvesteyn [3]. Although they were concerned with a very different physical situation (1 to 2% impurities and annealing in air at standard pressure) many of their results and those of earlier workers obtain and can be summarized as follows; at a given temperature, θ, and pressure, P, the host metal has a certain oxygen solubility, $C_1(\theta, P)$, proportional to $P^{1/2}$ [3]. In most situations it is an excellent approximation to assume that the oxygen content at the surface of the material is C_1, and this should apply here also, in spite of the low partial pressures of oxygen used. From the surface the oxygen diffuses into the metal at a rate governed by C_1 and by the oxygen diffusion constant, D_1, combining with the impurities to form oxides (see Fig. 1). If the impurity concentration is sufficiently large, an oxygen atom diffusing from the region where the impurities are oxidized into the region where they are not oxidized will not penetrate very far before becoming bound to an impurity. Thus there will be a relatively narrow region between the totally oxidized and totally non-oxidized regions which we call the "oxidation boundary". Note, however, that for pure metals being oxygen annealed to enhance the RRR, the impurity concentration is typically at the trace level, and therefore the oxidation boundary can be expected to be far less sharp.

The rate at which the oxidation boundary moves into the metal depends not only on C_1 and D_1, but also on C_2, the impurity concentration. C_2 enters here because impurities serve as a sink for oxygen atoms. When the relationship $C_1D_1 \gg C_2D_2$ (D_2 is the impurity diffusion coefficient) does not hold, impurities will diffuse toward the surface, combining with the oxygen atoms and slowing the movement of the oxidation boundary. Under these circumstances the

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*I should like to express my appreciation to Mr W. A. Fraser for performing the vacuum fusion analysis.

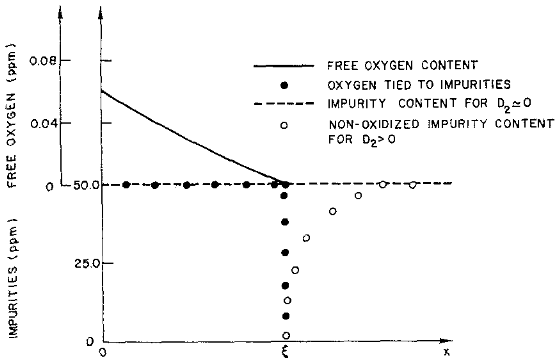

Figure 1 Schematic plot of impurity and oxygen content (as atomic fraction of Ag content) versus distance from sample surface, x. Note the change of scale employed at 50.0 on the vertical axis. The free oxygen content shown at the sample surface, 0.06 ppm, corresponds to the temperature and oxygen presure of anneal 7. The thickness of the oxidation front, located at ξ, is finite but appears infinitesimal relative to the magnitude ξ would obtain after the first few minutes of oxygen annealing. It is only within the oxidation front that both free oxygen and non-oxidized impurities are found.

rate of oxidation boundary penetration depends also on D_2.

The carbon content of the sample will play no role in these processes. Both carbon and oxygen are located at interstitial sites in Ag and bound states of C and O or O_2 are excluded by dimensional considerations. Thus we expect that the C simply diffuses to the surface where it combines with an O atom and leaves the sample. In fact, since C is both a smaller and less massive atom than O, we expect its diffusion constant in Ag, D_C, to be greater than D_1 (to our knowledge D_C has not been determined). Taking $D_C = D_1$ as a lower limit on D_C, and assuming that oxidation takes place at the surface sufficiently rapidly to keep the surface concentration of C at or near zero, anneal number 2 would remove essentially all the C from the Ag crystal.

There is no *a priori* reason for believing that in a Ag crystal lattice an oxidized impurity, with its attendant strain field, will have a much smaller scattering cross-section for conduction electrons than will the same impurity alone. In our experiment, the reduction in the residual resistivity by a factor of about 100 must come about because the impurity oxides cluster or precipitate out of solution. The precipitation is to be expected also by virtue of the low solubility of metal oxides in noble metals. With our present state of knowledge of systems of this kind it is not possible to make a reliable thermodynamic analysis of what impurity oxides internal to a host metal are formed and are stable under specific conditions. We do not know the exact composition of the oxide inclusions or the contribution of the oxide surface energy terms. The formation of clusters will also distort the Ag lattice and this too can make a contribution to the thermodynamics of the problem. In a Cu lattice for example, Fe_3O_4 can be readily reduced in an oxygen pressure of 5×10^{-2} μm at temperatures where they would normally be stable at pressures as low as 7×10^{-8} μm [4]. In brief, we do not know the thermodynamics of small impurity oxide particles in an Ag lattice. However, from the work of Domenicali and Christenson [4] it is known that the Fe impurities at the 1000 ppm level in Cu will precipitate out in particles sufficiently large to manifest the magnetic properties of bulk Fe_3O_4. In addition MacDonald and Pearson [5] have shown that melting Cu in graphite crucibles reduces the oxides of the impurities so that the impurity metals enter solid solution.

There is, therefore, substantial reason to believe that the impurities are present in our crystal in solid solution prior to the oxygen anneal and that internal metallic oxides in clusters are formed as a result of oxygen annealing. This clustering will occur, however, only if the impurity atoms are free to move through the crystal. As pointed out in [3] the impurity oxide molecules cannot move as a whole through the lattice. Impurity oxide molecules could dissociate thus freeing the impurity to diffuse, but if the oxidation boundary is well passed this impurity, (the impurity well to the left of ξ in Fig. 1) then the oxygen content in solution will be sufficiently high that the impurity will very quickly recombine with an oxygen atom and again be immobilized. Thus, the longer a given region can be kept at a low oxygen concentration, the greater the probability of increasing the RRR.

In fact there is experimental evidence that the clustering of impurities in a region takes place just as the oxidation boundary moves through the region [3]. This suggests that to achieve the highest possible RRR, one should choose conditions which increase the thickness of the oxidation boundary (which is the region of the sample with the lowest, non-zero oxygen concentration) and decrease the speed with which it advances through the crystal. We now present a physical model which bears upon these two factors, agrees with the more mathematical approach of [3] and, hopefully, provides some insight into the oxygen annealing process. Unless otherwise stated we shall always assume that $C_2 \gg C_1$ and $C_1D_1 \gg C_2D_2$.

Meijering and Druyvesteyn [3] have suggested a definition of the thickness of the oxidation boundary as the distance between the plane where 0.1 of the impurities are oxidized and 0.9 of the impurities are oxidized. Using quantitative numerical techniques based on the equations they derived, these workers obtained 0.50 $a/\sqrt{C_2}$ for the distance between the 0.1 and 0.9 oxidized planes, where a is the lattice parameter. The essential points here are the order of magnitude of the result, its independence of C_1 and D_1, the two controllable parameters, and the inverse dependence of the oxidation boundary thickness on the square root of the impurity concentration. All three of these aspects of their result can be understood on the basis of a simple model which supposes that the oxidation boundary thickness will be approximately the mean square distance an oxygen atom will diffuse, from the edge of the oxygenated region, into the non-oxygenated region, before meeting an impurity.

This diffusion distance can be determined in the following way. In a one dimensional treatment, the jump frequency, ν, of a diffusing particle is given by

$$\nu = \frac{2D}{\delta^2} \qquad (1)$$

where D is the diffusion coefficient, isotropic in a cubic lattice, and δ the length of the jump. Oxygen occupies interstitial positions in an fcc lattice (the centres of the twelve edges and the cube centre) each of which is surrounded by twelve equivalent points. Here the projection of an average jump length in say a cube edge direction is $+ a/2$, $- a/2$, or 0 so that $\delta^2 = a^2/4$ for 2/3 of the jumps and zero for the remaining 1/3. Thus, oxygen in an fcc crystal has a jump rate frequency, ν, of $12D_1/a^2$. Each jump to a neighbouring interstitial means the diffusing oxygen is surrounded by four (out of the six) nearest lattice points that did not surround its previous interstitial position. Thus, the average frequency with which an oxygen atom meets an impurity is $(12D_1/a^2) \times 4C_2 = 48C_2D_1/a^2$, or the average time for this to occur is T where

$$T = \frac{a^2}{48C_2D_1}\,. \qquad (2)$$

[We have neglected here that one of the twelve surrounding interstitial oxygen sites (the one previously occupied) is known not to have an impurity associated with it. Thus T will be somewhat greater than given here.] The mean square distance, ΔX, a particle diffuses in a time T is $\Delta X = \sqrt{(2DT)}$, so that the oxygen will diffuse a distance ΔX_0 before being captured by an impurity given by

$$\Delta X_0 = \sqrt{\frac{a^2}{24C_2}} \approx \frac{0.2a}{\sqrt{C_2}} \qquad (3)$$

which is very nearly the Meijering and Druyvesteyn result [3]. If there is a certain amount of impurity oxide dissociation in times short compared to the time necessary for the oxidation boundary to move its own thickness then the oxygen atoms will have a second (and third, etc) opportunity to diffuse. For this case the magnitude of ΔX_0 will increase, but not its functional dependence.

For simplicity we take the Meijering and Druyvesteyn result for the distance between the planes where 0.99 and 0.01 of the impurities are oxidized, 0.99 $a/\sqrt{C_2} \approx a/C_2$, as the thickness of the oxidation boundary. The length of time available for the impurities to precipitate out as oxides at some region of the crystal is approximately equal to the difference in the time from when oxidation begins in the region to when dissolved (but unbound) oxygen concentration begins building up (all impurities having been oxidized), thus preventing diffusion of the impurities by combining with them. This time, T_p, is just the time necessary for the oxygen boundary to move a distance equal to its own thickness, of the order of $a/\sqrt{C_2}$. T_p varies inversely with the velocity of penetration of the oxidation front. The velocity is readily obtained from the expression for the position of the oxidation front, ξ, as a function of time [3]

$$\xi^2 = \frac{2C_1D_1t}{C_2} \qquad (4)$$

where ξ is measured from the sample surface, t is time and $t = 0$ when the oxygen anneal begins. (Note that Equation 4 assumes impurity monoxide. If the average number of oxygen atoms binding to each impurity atom is r, then C_2 should be replaced by rC_2. As best we can determine, for our Ag crystal, $C_2 = 35$ ppm,

$r = 1.5$ so that the effective impurity content is $rC_2 \approx 50$ ppm.) Therefore,

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = \frac{C_1 D_1}{C_2} \frac{1}{\xi} \qquad (5)$$

and

$$T_\mathrm{p} \approx \frac{a/\sqrt{C_2}}{\mathrm{d}\xi/\mathrm{d}t} = \frac{a\sqrt{C_2}\xi}{C_1 D_1}\,. \qquad (6)$$

For the physical picture leading to Equation 3 and 6 to be reasonable it is necessary that $T/T_\mathrm{p} = (aC_1/48\xi C_2{}^{3/2})$ is very small; that is a freely diffusing oxygen atom must meet an impurity in a time short compared to the time necessary for the oxidation front to move a distance equal to its own thickness. T/T_p is easily evaluated by using the oxygen solubility in Ag at atmospheric pressure as given by Smithells [6], the fact that C_1 is proportional to $P^{1/2}$ (P is the oxygen partial pressure) and taking $\xi = 10^{-4}$ cm and $C_2 = 0.5 \times 10^{-4}$. One finds that $T/T_\mathrm{p} \approx 10^{-6}$ at 900°C and 10^{-5} at 500°C, thus easily fulfilling the requirements of the model.

3.2. Electrical resistivity

The contribution to the electrical resistivity, ρ, from electron-impurity scattering will be reduced by a factor proportional to $N_\mathrm{c}/N_\mathrm{i}$, where N_c is the number of impurity oxide clusters, and N_i the number of impurity atoms, per unit volume of crystal. The factor would equal $N_\mathrm{c}/N_\mathrm{i}$ if the electron scattering cross-section of a cluster and a single impurity were equal. N_c is proportional to γ^{-3}, where γ is the average distance between clusters. The *maximum* value γ can achieve will be of the order of the mean square impurity diffusion distance in the time T_p, that is $\gamma \lesssim \sqrt{(2D_2T_\mathrm{p})}$. The effective impurity diffusion time will be proportional to T_p – reduced from it, by the average fraction of the time the impurities are bound to oxygen atoms. So finally

$$\frac{N_\mathrm{c}}{N_\mathrm{i}} \propto \left[\frac{1}{\sqrt{(2D_2T_\mathrm{p})}}\right]^3 = \left[\frac{C_1D_1}{2D_2a\sqrt{C_2}\xi}\right]^{3/2} \qquad (7)$$

and achieving the highest possible residual resistivity involves making $N_\mathrm{c}/N_\mathrm{i}$ as small as possible. Obviously, the magnitude of $N_\mathrm{c}/N_\mathrm{i}$ and the RRR ultimately obtained will depend on the particular impurities in the host metal and their binding energies with oxygen. However, for any given impurity the maximum RRR will be achieved by obtaining the smallest possible value for the right hand side of Equation 7. This can be achieved by deliberate selection of the temperature and oxygen pressure of the anneal. In this regard, it may well be that no very successful oxygen anneal of Ag has been reported previously because of the extraordinarily high value of D_1 in Ag.

This entire analysis has been based on the hypothesis that the greatest part of the clustering of impurities in a given region of the Ag crystal can take place as the oxygen boundary moves through this region. Since the RRR in our experiment was increased by a factor of 100, a check of this hypothesis can be made by verifying that the mean impurity diffusion length ΔX, during a time T_p, is large enough that impurity oxide clusters can attain a size of the order of 100 impurity atoms. For an impurity concentration of 35 at. ppm, for example this requires $\Delta X_\mathrm{i} \gtrsim 45a$. But at 900°C, $\Delta X_\mathrm{i} = \sqrt{(2D_2T_\mathrm{p})} \approx 1000\,a$ which exceeds the minimum required distance by a factor of about 22. (For D_2 we have used a "typical" impurity diffusion coefficient in Ag since values for the impurities found in our Ag crystal are not available.)

It is of interest to note that the final value of the low temperature resistivity attainable by oxygen annealing, ρ_f, is relatively insensitive to initial residual resistivity, ρ_i (or impurity content, C_2) even though $\rho_\mathrm{i} \propto C_2$. Equation 7 multiplied by C_2 is proportional to ρ_f and varies only as $C_2{}^{1/4}$. It is probably for this reason that we were able to obtain an increase by a factor $\approx$ 100 in the RRR of our Ag specimen. The initial RRR of 140:1 is rather low for a noble metal but the final 9500:1 (the material is probably closer to 14 000:1 reduced to 9500: 1 by size effect) is within a factor of 2 of the highest results reported on any noble metal – regardless of initial purity.

Finally, we note that oxygen annealing a given specimen at a constant temperature and pressure will produce a different result near the surface of the specimen than deeper in the interior. This is obvious from the presence of ξ in the denominator of either Equations 5 or 7, and shows that better results may be obtained in the interior, i.e. larger but fewer clusters of impurity oxide. This inhomogeneity will effect the various electronic phenomena, unless the electron mean free path is limited in all parts of the specimen by other scattering centres, such as crystal imperfections and, perhaps, impurities that do not oxidize in the host lattice under the annealing conditions. Under these latter circumstances the inhomogeneity of the clusters will not produce a significant corresponding inhomogeneity of the electronic conductivity.

In conclusion, to obtain the maximum RRR by an oxygen anneal, the anneal should be performed at the highest possible temperature in order to increase D_2 (and thereby the denominator of Equation 7) and the lowest possible oxygen pressure (to decrease C_1) consistent, of course, with oxidizing the impurities and penetrating the entire thickness of the specimen in some reasonable time.

4. Size effect considerations

The initial reduction of resistivity that occurs when oxygen annealing of a metal takes place is generally recognized as being the result of a thin exterior layer of highly conductive (oxygenated) material that short circuits the bulk of the specimen. What has always been neglected, to our knowledge, but should be considered for a quantitative analysis of this effect, is the electrical resistivity size effect [7]. A thin layer of highly conducting material on a much less conductive base can be expected to have electrical resistivity properties much like a thin film. In a thin film, current carrying electrons, whose drift velocity produces the current, will collide with the surfaces and be reflected back into the film with a loss of their drift velocity. The external surface of an oxygenated layer of material has precisely the same effect. At the other boundary there is no reflection of electrons, but rather they pass into the much more resistive non-oxygenated region and quickly lose most of their drift velocity. They are replaced on the average by electrons with very low drift velocities coming from the non-oxygenated region. For considerations of electrical conductivity, the net effect should be very nearly the same as would obtain at a true surface, and this would imply that the experimental transport properties of a surface oxygenated specimen should be analysed with the help of the size effect theories of Fuchs [8] and Sondheimer [7]. If so, it would also suggest an alternative technique of preparing thin, highly conductive uniform thickness samples. These samples would not be troubled by the constitutional imperfections that accompany the preparation of thin films or the difficulties in handling very thin conventionally prepared specimens.

In order to test the necessity of including size effect considerations when discussing the electrical resistivity of *partially* oxygenated pure metals, we apply the results obtained in [3] analogous to Equation 4 but appropriate to cylindrical rods. If the depth of oxygen penetration in the cylinder is less than approximately half the radius, this equation is not appreciably different from Equation 4. Having the depth of oxygen penetration as a function of the quantity $2C_1D_1t/C_2$, it is a simple matter to obtain the RRR as a function of this same quantity by using the standard equations of parallel circuits and the resistivities for the non-oxygenated and oxygenated regions. We require, however, the resistivities of these two regions.

The first of these two resistivities is obtained from the measured value before anneal 2. (Since some of the resistivity before anneal 2, which removes the carbon, is due to the presence of the carbon, the value of the resistivity of the carbon free but non-oxygenated Ag lies somewhere between that obtained before and after anneal 2. For the purposes of the qualitative discussion that follows, this small difference is of no significance.) The second could be obtained from the results of anneal 14 (when the entire sample has been oxygenated) if it were not for the fact that in the given physical situation, it is known that there is some size effect even in the completely oxygenated sample. Using a free electron model the electron mean free path at low temperatures in a Ag specimen with an RRR of 10 000:1 (20 000:1) is 0.057 (0.114) cm. Since our sample diameter is only 0.26 cm, there is some reduction in conductivity because of size effect and the results given in [7] for cylinders give a bulk RRR somewhere between 10 000:1 and 20 000:1 – probably about 14 000:1. Therefore, the RRR of the partially (surface) oxygenated states of the sample has been calculated at the various stages of oxidation as a function of $2C_1D_1t/C_2$ for three sets of conditions; an assumed bulk RRR of 10 000:1 for the oxygenated Ag with no size effect in the surface oxygenated region, a bulk RRR of 10 000:1 for oxygenated Ag but including the influence of a size effect on the resistance of the oxygenated region, and a bulk RRR of 20 000:1 for oxygenated Ag – also including the influence of size effect. The actual physical situation should lie somewhere between these latter two cases, and more important this analysis shows that unrealistic results are obtained if size effect in the oxygenated layer is ignored.

For the two cases where size effect was considered, the surface scattering was obtained

TABLE II The three calculated sets of values of the impurity content, columns 7 to 9, are obtained by dividing the numbers in column 6 by the numbers in the same row of columns 3 to 5

Anneal	Change RRR	Theoretical change in $\frac{2tC_1D_1}{C_2} \times 10^8$			Experimental change in tC_1D_1	Calculated C_2 (ppm)		
		No size effect	10 000:1 RRR plus size effect	20 000:1 RRR plus size effect		No size effect	10 000:1 RRR plus size effect	20 000:1 RRR plus size effect
1	—	—	—	—	—	—	—	—
2	140–162	1.20	156.9	132.1	74.76	6.24×10^4	4800	5700
3	162–179	2.15	128.0	107.3	1.83	8500	140	170
4	179–230	13.22	474.7	445.8	11.49	8700	240	260
5	230–770	853.7	7 443.0	5 015.6	52.51	620	70	100
6	770–1000	771.9	3 633.0	2 559.4	41.68	540	110	160
7	1000–1150	619.2	2 642.0	1 733.8	136.73	2210	520	790
8	1150–1670	3 054.8	11 146.0	6 770.0	416.1	1360	370	610
9	1670–2950	11 393.0	36 740.0	19 237.0	1204.8	1080	330	630
10	—	—	—	—	—	—	—	—
11	1300–6800	122 191.0	273 278.0	104 770.0	3248.5	270	120	310

using Sondheimer's [7] results for a flat plate geometry. For an annular ring of thickness less than half the radius, this is a good approximation. For all three cases a graph of RRR versus $2C_1D_1t/C_2$ was prepared. From these one could read off the change expected from theory of the quantity $2C_1D_1t/C_2$ that would yield the changes in RRR that were observed experimentally with each of the anneals listed in Table I. These are given in columns 3 to 5 of Table II. The actual experimental incremental values of the quantity C_1D_1t are also known for each anneal, obtained from our knowledge of the pressure and diffusion coefficient of oxygen and the time of each anneal. From the quotient of the latter divided by the former, a value of C_2 can be obtained which should agree to within an order of magnitude, with what we know to be the effective impurity concentration – approximately 50 ppm. [The relevant quantity here is rC_2 (50 ppm) see note after Equation 4.]

The agreement cannot be expected to be better than qualitative because the above represents the idealized case, and the situation is really more complicated. Firstly, because the diffusion coefficient of the impurities, D_2, rises much more rapidly with temperature than D_1, at 900° C the condition $C_1D_1 \gg C_2D_2$ is not well fulfilled, though it is at 500° C. At high temperatures, then, the apparent magnitude of C_2 determined as just outlined will be too great because the migration of impurities from deeper in the sample will slow the advance of the oxidation front. Secondly, though the amount of material we removed by etching our specimen between anneals was negligible compared to the rod diameter, we cannot be sure it was also negligible compared to the thickness of the oxygenated layer, particularly for the first few anneals. This too would raise the apparent value C_2. Thirdly, concentration of non-oxidized impurities will not rise from 0 to C_2 as a step function at the oxidation front in those cases where a previous high temperature (800° C or more can be considered high temperature for this purpose) oxygen anneal has resulted in significant impurity diffusion near this oxidation front (see Fig. 1). If a lower temperature anneal for which C_2D_2 is negligible is then performed, the oxidation front will be moving, initially at least, through a region of lower impurity content then C_2. Thus only qualitative agreement can be expected between the true value of C_2, and the various values calculated in the manner outlined above.

In Table II the results of these calculations of C_2 from the residual resistivity data are given in columns 7 to 9. The most striking thing to note is that the values of C_2 obtained under the assumption that no size effect corrections need be made for the electrical resistivity are completely out of line with the roughly 50 ppm that we expect. This is particularly noticeable and significant for anneals 3 and 4 where the layer of oxygenated material is thinnest and size effect is most important. Anneal 2 gives unrealistic results for all three sets of conditions. This is to be expected because at the temperature and oxygen pressure of this anneal, either the impurity oxide complexes formed are near instability, or the diffusion of the impurities is almost fast enough to reduce to zero the speed with which the oxidation front moves into the sample. We know this from the results of anneal 10 where reducing the vacuum pressure by $\frac{1}{2}$ (the reduction in oxygen partial pressure might have been greater) actually produced a reduction in RRR. While a number of workers have reported that visible impurity oxide precipitate has vanished after annealing in a hard vacuum, the alternate possibility – that the decrease in RRR during anneal 10 is the result of nonoxidized impurities diffusing into the oxygenated region – cannot be excluded by the present data.

The remaining data in the last two columns of Table II are qualitatively correct. Anneals 3 to 6 give the correct value of C_2 (within a factor of 2 to 5). For anneals 8 and 9 and also 7, the temperature is sufficiently high that impurity diffusion is non-negligible, so the apparent (calculated) value of C_2 increases. During anneal 10, either some impurities diffuse into the oxygenated region, or there is deoxidation of some of the impurity oxide. In either case, the amount of unoxidized impurity seen by the oxidation front during the next oxygen anneal (number 11) will be less than C_2. It is seen that the calculated C_2 for anneal 11 is one third to one half that for previous anneals at comparable temperatures and pressures.

We conclude that any analysis of the electrical resistivity and other electrical transport phenomena in partially oxygenated specimens must take account of size effect considerations. We also feel that the results of anneal 2 indicate that some of the existing transport data available in the literature must surely have been unknowingly obtained on partially oxygenated samples.

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