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Oxygen Annealing of Copper: A Review*

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Summary

Annealing in the presence of a reduced pressure of oxygen is a useful technique for significantly decreasing the low temperature electrical resistivity of copper. The same technique is sometimes used on dilute alloys to produce dispersion hardening by the formation of oxide particles. This paper reviews the literature on the oxidation process in copper. Particular emphasis is on oxidation to decrease electrical resistivity, but brief discussions are also presented of oxide dispersion hardening and chemisorption. Decreased low temperature resistivities obtained in other metals and with other gases are also discussed.

I. INTRODUCTION

Annealing of copper and its alloys in the presence of oxygen has been practiced for many years. It is usually done for one of two reasons: to decrease the low temperature electrical resistivity of already quite pure copper by an effective precipitation of some impurities or, with alloys of relatively low solute concentration, to create a hardening dispersion of oxide particles within the copper matrix. In this paper we are primarily concerned with oxidation as a means of decreasing the resistivity of "pure" copper at cryogenic temperatures.

The resistivity measured at room temperature, where the resistance is due almost entirely to lattice vibrations (phonons), undergoes no significant change on oxidation unless the copper was initially quite impure. However, the resistivity measured at liquid helium temperature (4K), where essentially all resistance is due to impurities, shows a dramatic drop, often by more than an order of magnitude. We thus have a large increase in the residual resistance ratio, RRR, which is a common measure of effective purity:

$$\mathrm{RRR} \equiv R\,(295\mathrm{K})/R\,(4\mathrm{K}) \simeq \rho\,(295\mathrm{K})/\rho(4\mathrm{K}) \tag{1}$$

where R is the resistance and ρ the resistivity of a given specimen. To first order, this quantity is independent of specimen geometry, hence the second equality. Some typical RRR values for copper are: oxygen-free copper ~ 100 as received and ~ 800 after oxidation; five nines (99.999%) copper ~ 1500 as received and $\gtrsim$ 10,000 after oxidation.

Oxygen-annealed copper can be returned to its initial state by a suitable reduction process. This indicates that nothing is leaving the copper and thus its *chemical* purity is actually being lowered by the oxidation. Yet the oxidized copper is a better conductor at low temperature, and thus we can describe the result as an increase in *electrical* (*versus* chemical) purity. This occurs because oxygen ties up transition metal impurities such as Fe, Mn and Cr, as oxides, which greatly decreases their ability to scatter electrons.

Copper prepared by oxygen annealing has been used in a large number of metal physics experiments. In these investigations low resistivity is essential as, invariably, the magnitude of the effects studied decreases drastically as the scattering of the electrons increases. Thus the experiments are done at low temperatures to reduce thermal scattering and with metals

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of the highest available purity (as measured by RRR) so that the impurity scattering will be minimized.

In the next two sections we review the literature on mechanisms of oxidation and the use of oxidation to decrease the electrical resistivity. In the fourth section, experiments on similar oxidation effects in other metals and on effective purification using other gases are reviewed. The fifth section provides an introduction to the literature on oxide dispersion hardening of copper and discusses briefly some chemisorption experiments.

In the reference list we have included the titles of the referenced articles in order to assist the reader in deciding which of the many articles might best provide the information he seeks.

II. THE INTERACTIONS OF OXYGEN WITH COPPER

Here we review what is known and what has been speculated about the interaction of oxygen with commercial copper, with dilute copper alloys and with very pure copper. We mention surface processes briefly, but our main interest is in the interactions which take place within the bulk metal, the so-called internal oxidation. As a general introduction to the oxidation of metals, the article by Cupp[1] is recommended.

A. Surface oxidation

When copper is heated in air at near one atmosphere, a complex oxidation process takes place at the surface and an oxide scale forms. At relatively low temperatures ($T < 375°C$) the scale is black cupric oxide, CuO. Near the melting point (1083°C) red cuprous oxide, Cu_2O, forms. At intermediate temperatures a complex layering of the two is seen[2]. Details of the scaling, such as composition and adherence *versus* various parameters, are given by Tylecote[3] and the theory is reviewed by Hauffe[4]. Both oxides are usually considered stable at room temperatures, but a slow decomposition of Cu_2O to CuO has been suggested[5].

Impurity oxides may form at a metal surface when the impurity diffuses faster through the metal than does oxygen. This does not occur for metals in copper[6] owing to a high oxygen diffusion rate, of the order of 5×10^{-6} cm^2/sec at 1000°C[7], which exceeds metallic diffusion rates by several orders of magnitude.

B. Internal oxidation

At 1000°C the decomposition oxygen pressure of the copper oxides is around 10^{-5} Torr, quite high compared with all other common metal oxides[8,9]. This is a reflection of the small free energy of oxide formation (—21 kilocalories per atom of oxygen at 1000°C) for copper[10] and it allows internal oxidation of metallic impurities, without surface scale formation, by annealing in a reduced pressure of oxygen.

Several methods may be used to supply the relatively low oxygen pressure. A controlled air leak* into a vacuum furnace is a common approach[11] as is the use, sometimes inadvertent, of small amounts of oxygen in a carrier gas. An ingenious technique was developed by Rhines[12] for his study of the oxidation of some 40 elements as impurities in copper. The specimen is tightly packed in a mixture of Cu and Cu_2O powders in a sealed container so that, at the annealing temperature, oxygen is provided by dissociation of the Cu_2O. This device has since come to be called a "Rhines pack". In an extensive investigation of this technique, Wood[13] has shown, surprisingly, that Cu_2O is vaporized as molecules and dissociated at the specimen surface. Similar packs using NiO and CoO, which have relatively high dissociation pressures[9] but well below that of Cu_2O, were also used for oxidation with some success.

Clearly, internal oxidation requires a finite solubility of oxygen in copper. Data on solubility are given by a number of authors[5,14–16]. The determination is difficult. The best values probably are 0.0017 wt.% O_2 at low temperatures, increasing to 0.008 wt.% O_2 at 1065°C — 68 and 320 at. p.p.m. of O respectively. Commercial copper which is not deoxidized or prepared as "oxygen free" may contain up to 0.04 wt.% O_2, essentially all as cuprous oxide. These oxide particles are relatively large (2—10 μm)[17] triangular platelets

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* In this paper we refer frequently to gas pressures used for various annealing procedures. When no reference is made specifically to oxygen, one should assume that the stated pressure is for air.

and tetrahedra[18]. Their effect on the electrical resistivity of commercial copper is well known[19]; they give a significant increase. Cuprous oxide does not have a significant effect on the resistivity of the relatively high purity copper which is the main consideration of this paper.

Two further conditions, mentioned earlier, are essential for internal oxidation: the oxygen must diffuse faster in the solvent metal than does the impurity, or oxidation will occur at the surface, and the impurity must have a greater affinity for oxygen than the solvent metal.

High temperature internal oxidation of copper takes place in two steps[20]: 1. Impurities with a larger free energy of oxide formation than copper are oxidized. 2. Oxygen goes into solid solution in the copper and, when the copper is cooled, a small amount of cuprous oxide is precipitated.

The oxidized impurities in dilute alloys tend to form as a dispersion in the matrix of the base metal. Fine particles are favored by low solute concentrations, low temperatures and high oxide stability[1]. However, if the temperature is too low, the oxides tend to form on the grain boundaries[12]. Alloys used for dispersion hardening (see Section V), which have a relatively high (~ 0.1%) concentration of impurities, also show a variation of oxide particle size and density with distance from the surface[1,21].

One further important parameter is the time required for complete internal oxidation. Cupp[1] lists some qualitative observations on the rate of advance of the oxidation front into a metal. The rate decreases with time, increased solute content, lower oxygen pressure and lower temperature. Furthermore, observations on copper by Rhines *et al.*[22] suggest that below 750°C very complex processes take over and not even qualitative statements can be made.

Theoretical work[22,23] on the diffusion of oxygen into metals at high temperatures has shown that a quite simple theory is generally adequate to give good agreement with experiment. (Rhines *et al.*[22] have also treated the more complex theoretical problems of oxidation from surface scale and oxidation of ternary alloys with some success.) The major feature of the simple theories of internal oxidation is the relationship between the depth of oxidation, d, and the elapsed time, t,

$$d^2 = Kt. \qquad (2)$$

The proportionality constant, K, contains the product, $N_o D_o$, of the saturation solubility and the diffusivity of oxygen in pure copper as well as the inverse of the solute concentration. K is observed to depend on temperature, at least roughly, as $\exp(-T^{-1})$. Determination of $N_o D_o$ is difficult, and Verfurth and Rapp[23] conclude that "unequivocal values for N_o, D_o or even the product $N_o D_o$ in copper are not available from the literature". Thus we return to the experimental work of Rhines *et al.*[22] and evaluate limits of K for the elements showing the fastest (Al) and the slowest (Si) oxidation in copper of the five investigated (the others: Be, Sn, Zn). We find: $K(\text{Al}) = 4 \times 10^{-6}$ cm^2/sec and $K(\text{Si}) = 0.4 \times 10^{-6}$ cm^2/sec for $T = 1000$°C at concentrations of 0.03 and 0.18 at.% respectively. There is no good way to determine K for other elements from these data, but for a very dilute (up to ~ 6 p.p.m.) alloy the higher value of 4×10^{-6} cm^2/sec is probably a reasonable estimate.

Several experiments, described below, have shown that reduction of the oxidized copper is also possible. This may be accomplished by vacuum annealing, by surface reaction with a reducing gas such as CO, or by the diffusion of hydrogen into the metal. Complete reduction of the oxides is observed to require a higher temperature or a longer time than was used for the oxidation. This observation suggests several possible mechanisms. One is that the low impurity concentration, predominantly iron, prevents the true oxide compounds from forming and that, instead, more easily dissociated nonstoichiometric iron—oxygen complexes are created. There is some justification for this concept in the observations of Verfurth and Rapp[23] on the oxidation of the aluminium in copper. Pawlek *et al.*[24] have suggested that the oxides form but that their free energy is strongly concentration dependent. One should note that there are no observations to show that actual precipitation of the impurity oxides occurs at these low concentrations.

III. OXIDATION TO DECREASE ELECTRICAL RESISTIVITY

The history of the effect of oxygen annealing on the electrical resistivity of copper as recorded in the literature has three more or less distinct historical phases. In this discussion we treat each of these time periods separately.

A. The period 1906 to 1958

During this period most of the interest was centered on the room temperature resistivity of copper. The International Annealed Copper Standard (IACS) resistivity of $\rho = 1.7241$ $\mu\Omega$.cm at 20°C was defined in 1913[25] although apparently in general use for some years previous. Early papers tend to give conductivity values solely in terms of percent of the IACS figure.

The first indication that oxygen could increase the conductivity, σ, of copper was the investigation in 1906 by Addicks[26]. He noted that 0.05% oxygen gave a maximum in conductivity of 101.5% for pure copper while all other impurities caused a uniform decrease. It is not clear whether Addicks was using the IACS value or not. Later Antiselle[27], surprisingly, showed σ for copper of unstated purity decreasing uniformly with increasing oxygen content from 0.015 to 0.20%. Heuer's[28] experiments on dilute alloys of iron in copper led him to suggest that the oxygen removed the iron from solution by formation of ferrous oxide, FeO.

In a series of three papers covering the period 1941—1943, Smart and Smith[29–31] described the development and characterization of high-purity copper. Their techniques are very nearly those used today in the production of pure copper. While all three papers contain some discussion of the effect of oxidation on the copper, both in the cast state and with the addition of various elements, one[30] is most relevant to our interests. In that experiment, very dilute alloys ($\sim 10^{-3}$ wt.%) of iron, nickel and cobalt were prepared and oxygen annealed. The authors concluded that the iron and cobalt were completely oxidized since the stock copper conductivity was restored on oxidation of the alloys. Very little oxidation of the nickel was observed. They also concluded, on the basis of magnetic measurements on a 2% alloy, that the iron oxide was Fe_3O_4 (magnetite), a result obtained earlier by Rhines[12] in an X-ray diffraction experiment. These authors make the very valid point that one should not expect oxidation to restore the conductivity to exactly its "pure" copper value since there is a small resistivity contribution due to oxide particles and also some small contribution from dissolved oxygen. Further, one should expect some electron scattering from the oxidized impurity, particularly if there is nonstoichiometry in the iron—oxygen complexes. Pawlek *et al.*[24] presented studies similar to those of Smart and Smith and extending to a number of ternary alloys but with little data on the conductivity of the iron binary.

Two papers by MacDonald and Pearson[32,33] appeared in 1955 in which low temperature (20K) resistivity was used to characterize dilute copper alloys. While no iron alloys were made, the stock copper used varied from oxygen-free (or reduced) to copper probably saturated with oxygen, the latter being observed to have a residual resistance ratio higher by a factor of three than the others. They also noted a low temperature minimum in the resistance *versus* temperature curves for the reduced specimens and its absence in those containing oxygen. This phenomenon is now termed the Kondo effect after the theorist who, in 1966, explained the magnetic interactions which give rise to the minimum. The existence of the minimum requires the presence of a transition element impurity such as iron.

B. The period 1959 to 1965

Most of the basic information on resistivity changes accompanying oxygen annealing of copper was developed during this period. The change from measurement of room temperature resistivity to measurement of the residual resistivity, usually at 4.2K, gave much greater sensitivity since it measures only the impurity contribution to the resistivity without the large thermal (phonon) contribution found in the room temperature measurements. Also, a number of these experiments used single crystals as opposed to the polycrystalline specimens of the previous era.

An important point to keep in mind about these experiments is that we are now often talking about quite high RRR values — of the order of 10,000. At this level the electronic mean free path is around 0.4 mm at 4K and the size effect resistivity (that due to surface scattering of the electrons) in wires of quite respectable size may be a significant fraction of the bulk resistivity. The size effect contribution to ρ at 4K of a 1.5 mm wire with bulk RRR = 10,000 is about 30% of the bulk resistivity. It is not always mentioned whether such a correction has been applied to quoted RRR values or not, and in small wires it is essential information. For example, the three specimens measured by Pawlek and Rogalla[34] actually seem to have about the same bulk resistivity.

The purity of the copper which became available in this period was such that standard analytical techniques could no longer always provide analyses of any great value, a situation which is not much changed to this day. Typical impurity levels in very pure copper dropped to the 0.1—0.01 p.p.m. range even for elements such as iron which tend to be in the 1—10 p.p.m. range for pure commercial copper. Note, however, that the low temperature residual resistivity is still significant, even at these low levels. Consider that 0.1 p.p.m. of iron contributes around 0.1 nΩ. cm to the residual resistivity (assuming a specific resistivity of ~ 10 μΩ.cm/at.%[35]) and compare this with the total residual resistivity of a RRR = 10,000 specimen which is 0.15 nΩ . cm.

Most of the work in this period occurred during 1959—1960. The most prolific group was that at Oak Ridge National Laboratory with some five papers[36–40]. Their general approach was to measure variations in the residual resistance of pure (99.999%) copper, and of alloys containing around 0.1 at.% ferromagnetic impurities (Fe, Ni, Co), as a function of anneal time in oxygen. Typical pressures were in the $1\text{—}3 \times 10^{-2}$ Torr (air) range and temperatures around 800°C. In all instances, except that of a nickel alloy[38], a significant decrease in the residual resistivity was noted after a sufficient anneal time. Their observed times are consistent with the discussion in the last section on the rate of diffusion of oxygen into copper. Several of the experiments[36,40] specifically considered the removal by oxidation, and restoration by reduction, of the Kondo minimum in the alloy resistivity. One experiment[37] measured the magnetic susceptibility of pure copper, both in the oxidized and reduced state, and concluded that the natural impurity iron, which was in a paramagnetic state in the reduced metal, precipitated as ferromagnetic particles (ferrite?) on oxidation. They also measured a 0.1% (at.?) Fe alloy in which the same behavior was observed on a much larger scale — to the point that the oxidized copper was attracted to a small bar magnet. The latest of these papers[39] reports two other experiments of interest. In the first, specimens were annealed under pure nitrogen and no change was noted in the resistivity, indicating that oxygen was, in fact, responsible for the reduced resistivity. Second, an oxidized specimen with some surface scale, due to the relatively high gas pressures used for the anneal, was measured, etched and then reduced. The resistivity returned to its former value indicating that the oxidation is really internal — no impurities are lost by oxidation at the surface.

Resistivity experiments on copper of high purity were also reported early in the period by Lange and Haussler[41] and by Dolecek and Schultz[42] with quite different results although the anneal times and pressures were nearly the same and the specimen sizes not greatly different. The former group finds a continuous increase of RRR with anneal temperature in oxygen (5×10^{-2} Torr) to 800°C while the latter sees a decrease after a peak at ~ 400°C. One should mention in passing that Dolecek[43] has also noted a significant effect of oxygen annealing on the resistance of pure copper measured in a magnetic field. In the orientation where the field is parallel to the current the normal increase with field is doubled for the oxidized specimen. No effect is seen in the case where the field is normal to the current.

The final paper from the early part of this period is the study by Domenicali and Christenson[44] of CuFe and CuCo alloys containing 0.1—0.3 at.% solute. They made no resistivity measurements below 76K but found measurements at that temperature to be sufficient to determine the effect of oxidation. They found the critical pressure for oxidation at ~ 1000°C to be between 0.5×10^{-3} and 0.5×10^{-4} Torr of pure oxygen, with reduction occurring below this range. Restoration of the unoxidized state was possible with both alloys, although it was observed to proceed much more slowly than the oxidation. Magnetic measurements on the CuFe rods again showed the ferromagnetism typical of the oxide magnetite. One should note, in regard to these magnetic measurements, that no simple relationship exists between resistivity and magnetization. This is because the magnetic behavior depends on the size of the oxide particles which, in turn, is determined by the kinetics of the process. The resistivity change depends only on how much of the impurity is oxidized.

Two brief papers at the end of the period discuss the oxidation of high purity copper single crystals, one at 1000°C[11] and one pulled from the melt[45] in the presence of oxygen. Dislocation counts were made in both instances and gave densities of 10^7—10^8 cm^{-2} for the oxidized crystals and values roughly an order of magnitude lower for annealed, unoxidized specimens. Both of these densities can be lowered by one order of magnitude by slow cooling at 50°C/h. (In unoxidized copper, densities of $\sim 10^2$ cm^{-2} can be attained with special anneal schedules[46] and single crystals with dislocation densities of ~ 5 cm^{-2} have been obtained by special growth methods[47].) It should be noted, however, that even the highest of these dislocation densities is not sufficient to affect the residual resistivity by more than a few percent. The dislocation resistivity contribution has been measured to be $\sim 10^{-19} N_D$ Ω.cm[48] (N_D is the dislocation density in cm^{-2}). While it seems that oxygen annealing increases the dislocation density [17,49], probably owing to mismatch of the precipitate particles, Young[50] has shown that existing dislocations play no role in the oxidation process.

Finally in this period we have the work of LeHericy, partly published in 1960[51], but later incorporated in a thesis[52]. The first two chapters of the thesis are of interest here and they were published separately in 1966[53]. This work is an exhaustive analysis of zone refined copper of various purities. It contains one of the few easily accessible descriptions of neutron activation analysis of copper. His work only briefly touches on oxidation but he does report a significant reduction in the 20K resistivity on annealing at 800°C and 7-8 × 10^{-2} Torr.

Gregory *et al.* [54] published a paper in 1965 which, while it contains no original data, presents an excellent evaluation of the types of copper available, ranging from tough pitch to "super-pure". Typical impurity analyses are presented, along with a chart showing the effect of the impurities on the electrical resistivity. The effect of oxygen on the resistivity is also considered in some detail.

C. The period 1966—1973

Essentially no new work was done on oxidation as a purification process *per se* until the last two years of this period. Most of the metal physics experiments mentioned earlier were done during this period but oxidation techniques described in earlier papers were used for specimen preparation. Three more papers detailing improvement of the RRR by oxidation were published. Two of these treat the oxidation of zone refined ingots[55,56] and one that of a number of wire specimens of varying size and purity[57].

Rumbo[58] measured the thermopower change which accompanies the RRR increase on oxidation. The specimen RRR increased from 1570 to 4900 and the thermopower dropped by a factor of 50, consistent with effective removal of transition element impurities. Basinski and Saimoto[59] looked at the effect of deformation processes on the resistivity of oxidized copper crystals. Studies on copper were reported by Westmacott[60] indicating a strong dependence of vacancy mobility and formation of visible defects on the residual oxygen concentration.

A very interesting experiment of this period[61] used the Mössbauer effect to study the kinetics of oxidation of iron in copper. The alloys contained rather large quantities of iron (0.6—3.5 at.%) and thus some processes were seen, such as the precipitation of paramagnetic metallic iron (γ), which would not be expected in dilute alloys. The oxidation studies were performed on a 2.2 at.% alloy specimen. Progressive two-hour anneals at 850°C of a thin (0.025 mm) foil at 3 × 10^{-4}, 3 × 10^{-3} and 3 × 10^{-2} Torr showed a progressive formation of FeO by the reaction

$$2\mathrm{Fe} + \mathrm{O}_2 \rightarrow 2\mathrm{FeO}\ . \qquad (3)$$

Some residual γ-Fe and Fe in solution were observed after the anneals. The oxide could be completely reduced by a 1.5 h anneal in hydrogen at 900°C. When the oxidized foil was further annealed at 0.2 Torr for 2 h at

850° C, the oxide apparently changed to Fe_3O_4 by the reaction

$$6\,FeO + O_2 \rightarrow 2Fe_3O_4\,. \qquad (4)$$

The identity of Fe_3O_4 was further confirmed by observation of a transition characteristic of this oxide at ~ 120K. An attempt to further oxidize to Fe_2O_3 was not successful.

Howling[62], in an NMR experiment, noticed a severe "loss" of Mn from a CuMn alloy powder as a function of anneal time at 400° C in a capsule sealed at 7.5×10^{-2} Torr. He concluded that oxidation of the solute was responsible. A typical loss curve is given in the paper showing a decrease from 0.7 to 0.1 wt.% Mn after 80 hours of annealing.

A number of papers on high purity copper have appeared in the last two years. Another review paper[19], similar to that of Gregory *et al.*[54], discussed the effect of oxygen and of other impurity elements on the electrical resistivity of commercial electrorefined copper. Blanie and LeHericy[63] reported the production by electrolytic techniques of a copper crystal with RRR ≈ 15000, without the use of oxidation. Analysis of their copper showed that the final iron level was down to 0.01 p.p.m. Reich[64] prepared a report for limited distribution which describes an OECD program in which oxygen and hydrogen annealed specimens of very pure copper were analyzed by several unindentified laboratories. The analysis was primarily chemical, but some RRR measurements are described. An interesting result of the analysis is that there seems to be a very large variation in the oxygen level measured on specimens cut from the same boule (1—5 p.p.m.). The variation does not correlate with depth into the boule and may well indicate the limits of the analysis technique rather than a basic inhomogeneity in the oxygen distribution.

In a report to the International Copper Research Association, the author[65] described the oxidation of polycrystalline copper wires with various purity levels ranging from oxygen-free copper (RRR = 100) to five nines stock (RRR = 1400). Oxidation increases the ratios by a factor of 6—7 in most cases. This same experiment looked at the effect of oxidation on the low temperature (4—35K) resistance measured in high (10*T*) transverse magnetic fields and concluded that the oxidation had no other effect on the magnetoresistance beyond the lower zero field resistivity due to the effective purification of the anneal. Later work on this experiment has concentrated on the magnetic properties of the impurities and their oxides[66]. Another experiment using polycrystalline wires was reported by Wilder *et al.*[67] in which a slight improvement in RRR was observed for some specimens on oxidation at a relatively low temperature (800° C). Finally, an experiment in which 1 h isochronal anneals of pure copper wires were made was reported by Carapella *et al.*[68]. The RRR is observed to increase with anneal temperatures to a peak at ~ 700° C and to drop thereafter, a result which is difficult to explain. While no oxidation should have occurred, the anneals were done in nitrogen gas which may have had some oxygen present. Grain sizes were measured and show a good correlation with RRR, increasing as the ratio increases.

IV. OTHER GASES AND OTHER METALS

The concept of diffusing a gas into a pure metal in order to further lower the residual resistivity has been applied to metals other than copper. In this section we review these experiments briefly and present some of the results. The reader should note that far and away the most common result of diffusing a gas into a pure metal is to *increase* the resistivity. This behavior is treated in some detail in the review by Aleksandrov[69]. Here we are concerned only with the "anomalous" case of a resistivity decrease.

A. Silver

Pearson[70] attempted an oxygen anneal (940°C, 1/2 atm O_2, 1/2 mm wire) of silver and found only a slight increase in RRR from 364 to 472. He observed little change in the thermoelectric power and concluded that unlike gold, the silver contained very few iron impurities. The actual process of diffusion of oxygen into silver was studied by Verfurth and Rapp[23] and values for the solubility and diffusivity were obtained which agreed well with previous work. Strom-Olsen[71], starting with crystals with RRR 150—200, increased the ratio to 800—1350 by 24 hour anneal at

850°C under 1 Torr oxygen followed by 24 more hours of annealing at 10^{-2} Torr. Adah and Gavenda[72] have achieved ratio increases by a factor of 10. Ehrlich[73], in a very recent paper, has reported ratios to 9500 for a single crystal annealed at 900°C at pressures of the order of 10^{-4} Torr of oxygen. This paper also contains an excellent detailed treatment of the oxidation process.

B. Gold

Pearson[70] found a significant improvement in the ratio of a gold wire (~ 0.25 mm diameter) from RRR = 330 to 1124 by annealing at $T \simeq 1040$°C in air followed by an anneal at $T = 520$°C in air (no times are given). The low temperature (1K) thermoelectric power was observed to decrease by two orders of magnitude, a further indication that iron impurities were oxidized by the anneal. At about the same time Sekula[38] reported an experiment in which specimens of 99.995% Au were annealed in oxygen at 900°C and 2×10^{-2}Torr for 2, 3 and 8 hours. The resistivity *versus* temperature curves all show a Kondo minimum which decreases and moves to lower temperatures with increasing anneal time. The ratios at the minima were 48, 70 and 85 respectively. The stock gold had a ratio of about 20. One specimen was annealed for 72 h at 1 atm of O_2 which raised the ratio to 140 and removed the Kondo minimum completely. Subsequent heating at 900°C and in 2.5×10^{-2} Torr of CO restored both the higher resistivity and the minimum. Andersen and Nielsen[74] report a ratio increase, measured on 40 μm foils, of from 32 to 607 between the vacuum annealed state and a 24 h oxygen anneal at 950°C in air. Siegel[75], in the course of a vacancy annealing experiment, used oxidation in air to achieve ratios as high as 5800 in gold foils. Adah and Gavenda[72] have increased the ratio of bulk gold by a factor of 2—3 by oxidation.

An ingenious technique for removing iron from gold was reported by Walker[76] in which chlorine gas is admitted to the anneal tube after the specimen temperature is raised to 850°C. Iron chloride compounds are formed and volatilized without any reaction with the gold occurring. Using this technique he has been able to reduce the iron content of a 0.08 mm diameter wire from 250 p.p.m. to < 1 p.p.m. in 6 h of annealing in 0.1—0.3 Torr of Cl. In another, high purity, wire the iron content was reduced from 2.2 p.p.m. to 0.07 p.p.m. after a three-day chlorine anneal. The ratio, measured following a slow cool, was 10,000.

C. Tantalum

Seraphim *et al.*[77] have shown that the RRR of tantalum can be raised from ~ 1000 to ~ 8000 by short term (15 min), high temperature (2693K) anneals at 2×10^{-5} Torr of oxygen. Their specimens were 0.25 mm wires. A different stock material gave improvement only from 750 to 1000 which is also the result reported by Fawcett *et al.*[78] for a similar experiment.

V. OTHER STUDIES OF OXIDATION

A. Oxidation of alloys as a hardening technique

Here we review a few representative experiments in which internal oxidation of a relatively high 0.1—1%) concentration of a purposely introduced solute is used as a means of hardening copper. The field of oxide dispersion hardening is large and our treatment is limited to papers representative of those which consider the oxidation process itself in some detail. The papers tend to concentrate on the morphology, composition and distribution of the particles formed by the oxidation process although, frequently, measurements are also reported on dislocation density and various mechanical properties.

The sources of oxygen for these experiments are mostly the same as those described in Section II B. An elaborate, two furnace, modification of the Rhines Pack method in which the Cu—Cu_2O powder is physically separated from the copper has had its merits debated in the literature at some length[79—81]. This technique seems to give better control over the oxidation process, but the exact mechanism is still uncertain.

The solute metals most often used for oxide dispersion hardening of copper are Al, Si, Be and, recently, Ti. Because of their high oxide stability, these elements tend to form small particles in dispersion[1]. Large particles give significantly less hardening of the metal[6]. An early investigation by Smart and Smith[31] does describe the oxidation of a number of other solute elements (Ag, Cd, Sn, Sb and Te) and the effect of the oxides on the softening temperature.

Typical morphology of the Al_2O_3 precipitate as determined by Ashby and Smith[82,83] is 30 mm triangular plates or tetrahedra showing precipitation along preferred planes in the matrix.

The silica dispersion in copper is probably the most studied. Bolsaitis and Kahlweit[84] have studied both the details of the oxygen diffusion and the formation of the SiO_2 precipitate. The precipitate is observed to first form as dendrites at the oxidation front; these later assume a spherical shape with diameters in the range of 10 − 100 mm. The authors also give curves of particle size distribution *versus* distance from the surface which show an increasing mean size with depth. Ashby and Smith[83] earlier showed that the precipitate particle size could be controlled to as large as 5000 nm, that the particles were amorphous and, when found in grain boundaries, tend to be lenticular in shape.

BeO precipitate particles tend to be larger, with a mean observed dimension of 300 nm, and consist of triangular plates lying on $\{ 111 \}$ planes of the matrix[21]. The particle size is observed to vary with depth. Meijering[85] reports a change in hardness with depth of a cylindrical copper single crystal, with a BeO precipitate, which decreased from the surface to a minimum and then rose to its maximum value at the axis. He suggests that this hardness change is determined by velocity changes of the oxidation boundary which, in turn, affect the dispersion of the oxide.

A very recent paper by Wood *et al.*[86] reports on studies of oxygen diffusion and particle morphology for the TiO_2 precipitate. They describe the particles formed in the matrix as "extremely small" and ellipsoidal in shape.

B. Surface studies

An increase in electrical resistance of the order of 20% is seen in thin copper films as oxygen is adsorbed on them over the liquid nitrogen (77K) to room temperature range. Furthermore, the temperature coefficient of the resistance for this temperature range is observed to decrease by about 10%. Most of this work seems to have been done by Murgulescu and Ionescu[87–90].

The experiments are typically performed on films 10 nm or less in thickness. The films are vacuum deposited and exposed to a reduced pressure of air at 273K or at 77K.

There is at present no good explanation for the observed resistance variations. Three possibilities are offered: (1) The chemisorption bond ties up some of the metallic conduction electrons either partially or totally; (2) The surface interactions form a gas—metal complex which causes loss of the metallic character of the boundary; (3) The type of surface scattering of electrons which gives rise to the normal size effect is changed by the changes in surface condition *i.e.*, some of the diffuse electron scattering is changed to specular[91].

The experiments to date seem to offer no way to choose among the mechanisms. They do seem to indicate that explanation of the observed effects will require a combination of the possibilities listed.

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