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Nuclear-Magnetic-Resonance and X-Ray Study of Solute Loss by Internal Oxidation in Comminuted and Vacuum-Annealed Cu-Mn Alloys

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It is shown that Cu-Mn alloys lose part of their solute Mn during comminution and vacuum annealing. X-ray measurements indicate that the solute loss occurs by the mechanism of internal oxidation, the dominant oxide formed being MnO (manganosite). NMR and x-ray measurements have been correlated in terms of loss of solute Mn from the Cu lattice. The results indicate that physical measurements on both annealed and unannealed samples of powdered Cu-Mn alloys can lead to errors in interpretation, if measured parameters are correlated with solute concentrations obtained directly from chemical analysis. Similar effects were observed with solutes of Ti, Fe, and Al in Cu.

I. INTRODUCTION

THE NMR parameters of Cu-based binary alloys are usually explained in terms of direct and indirect internuclear reactions and quadrupole perturbations.[1–6] For binary alloys containing sufficient solute to produce second-order quadrupole interactions throughout the Cu lattice, first-order quadrupole effects arising from cold work should not be observable. First-order perturbations affect only the satellite components of the NMR line, whereas second-order perturbations affect both the satellites and the central maximum.[5] For Cu alloys containing in excess of approximately 1 at.% of solute, therefore, the observed Cu^{63} linewidths, intensities, and Knight shifts, should not change with annealing heat treatment. The relative intensity of the central maximum in an alloy dominated by second-order quadrupole interactions should follow the probability relation $I(c)=I_0(1-c)^n$, where c is the solute concentration present in the host lattice and n is the number of resonant atoms whose contributions to the total observed intensity is wiped out by an isolated soluteatom.[7] For many solutes in Cu, the $(1-c)^n$ relation has been verified,[7,8] but usually only for unannealed materials.

For solute concentrations below approximately 1 at.%, both first- and second-order perturbations will be apparent, and the effects of cold work will be of significance. In this region, the change of NMR parameters with annealing heat treatment can be considerable.

Two authors in particular have examined the effects of heat treatment on the NMR of Cu-based alloys. Rowland[8] used samples that were generally not annealed. In a few unspecified instances, when filings were annealed, he found that the resonance intensities before and after annealing were unchanged. From second-order perturbation theory, this is what one should expect. Rowland, however, did not study the Cu-Mn system. Of the several authors who have studied Cu-Mn alloys,[9–16] all used unannealed material except Chapman and Seymour.[16] These authors used Cu-Mn filings and found wide differences between the NMR parameters of material as filed and material which had been vacuum-annealed for 4 h at 400°C. In particular, the annealed samples showed a narrowing of the linewidth, an increase in the intensity, and a reduction in the Knight shift: changes which, one may suggest, are typically associated with a loss of solute from the lattice. Chapman and Seymour observed that a second anneal had no further effect on the Cu^{63} resonance. They proposed that heat treatment produces a clustering of solute Mn ions and used the magnetic effects of such clusters to account for their NMR results. X-ray photographs of unannealed and heat treated samples of alloys were taken and no difference between the two patterns could be detected.

It is the purpose of this paper to establish that changes in the NMR parameters do indeed arise from loss of solute. The loss, however, is not due to clustering of Mn, but results from internal oxidation[17–23] of a portion

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of the solute during comminution and vacuum anneal of the powdered samples.

II. NMR INTENSITY MEASUREMENTS

Resonance parameters were measured with a conventional Pound-Knight-Watkins NMR spectrometer.[24] The magnetic field was maintained constant at 8000 G. Intensities of NMR lines were measured as peak-to-peak heights of the recorded derivative curves of the absorption line,[8] normalized by injection of a calibrating signal from a Watkins calibrator.[25] Modulation was constant at 500 cps and 2-G peak. Only the Cu^{63} line was examined. All measurements were made at room temperature.

Samples were prepared from bulk Cu-Mn alloys grown by the Czochralski method. Ingots were swaged to rods of 6 mm diam. Samples were also chill-cast in quartz tubes under argon. Chill-cast samples were also obtained from Johnson-Matthey. In all cases the Cu purity was said to be 99.999%. Mn content was determined by wet chemical analysis. Where possible, concentrations of Mn were also checked in the electron probe against a standard Mn sample. Alloy rods were sealed in evacuated quartz tubes and annealed at 400°C for 16 h. Metallographic sections of rod samples were examined for second-phase components. Where necessary, bulk alloys were sealed in evacuated quartz envelopes, homogenized at 900°C for 3 h, and quenched in water. Alloy rods were checked for homogeneity of Mn solute dispersion by electron-probe analysis. Measured variations in the radial homogeneity were usually better than 2%, this variation being the statistical error of the probe.

Alloy rods were comminuted by high-speed cutting with a tungsten carbide rotary cutter,[26] both in the dry state and under oil. Samples were also ground under oil[27] and occasionally hand-filed. Samples exposed to oil were rinsed in benzene and acetone, and air-dried. All powders were screened to <150 or <400 mesh (Tyler). Three-gram samples were then sealed in evacuated Pyrex or quartz tubes.

Alloys prepared by high-speed cutting or grinding had one dimension $<10\,\mu$, and no eddy current losses were encountered. The skin depth at 10 Mc and 20°C is $27\,\mu$ for Cu containing 0.30 weight % Mn, so hand-filed samples of particle size greater than 600 mesh required a correction for eddy current loss.

Typical changes in resonance intensity as a function of vacuum annealing time at 400°C are shown in Fig. 1. Results for several methods of sample comminution are given. Changes in the resonance intensity with vacuum-annealing time varied with the particle size and the method of comminution. High-speed cutting under oil or in liquid N_2 tended to reduce the extent of the intensity change on annealing, but did not necessarily prevent it. Similarly, exposing the sample to air between successive anneals did not significantly change the results, nor did cleaning the alloy particles with acids, nor did high-speed cutting of the alloys in atmospheres of N_2, H_2, NH_3, and Ar. In several instances, annealed samples were chemically analyzed. The total Mn content was found invariant. Annealing under flowing hydrogen also failed to prevent intensity changes from occurring, although this is to be expected from a consideration of the kinetics of Mn oxidation.[28] At 400°C, if the partial-pressures ratio p_{H_2}/p_{H_2O} is less than 10^{10}, oxidation of Mn will take place. Most laboratory hydrogen supplies have considerably more H_2O than 1 part in 10^{10}, hence oxidation of Mn will take place even during hydrogen anneal.

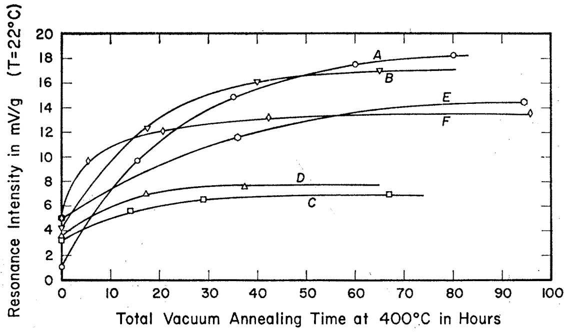

FIG. 1. Measured change of resonance intensity of comminuted Cu-Mn alloys as a function of vacuum-annealing time at 400°C. Sample A = <400-mesh particles, ground under oil in the method of Drain. Chemical concentration = 1.97 wt.% Mn. Sample B = <150-mesh, high-speed cut under flowing NH_3. Chemical concentration = 0.36 wt.% Mn. Sample C = <150-mesh, high-speed cut in air. Chemical concentration = 0.49 wt.% Mn. Sample D = <400-mesh, high-speed ground under kerosene. Chemical concentration = 0.97 wt.% Mn. Sample E = <150-mesh, hand filed in air. Chemical concentration = 0.30 wt.% Mn. Resonance intensity corrected for eddy current losses. Sample F = <150-mesh, high-speed cut under oil. Chemical concentration = 0.30 wt.% Mn. Reference intensity for annealed pure Cu = 38.5 mV/g.

One must pay attention to the possibility of the quartz and glass envelopes giving off O_2 and passing O_2 through the walls, resulting in the starting material being filled with O_2 to begin with. The permeation P of gaseous O_2 through vitreous silica at 900°C has been measured by Norton.[29] Using his value of $P = 9\times10^{-13}$ cm^3 gas (STP)/sec/mm thickness/cm^2 area/cm Hg difference of gas pressure, the weight of O_2 diffusing through the walls of a 1-mm-thick quartz tube of 30-cm^2 surface area is 2.1×10^{-9} g/h. The loss of Mn to MnO from this source is thus 7.2×10^{-9} g/h at 900°C, which is quite negligible.

Measurements of O_2 permeation through quartz or glass at 400°C are not available. According to Dr.

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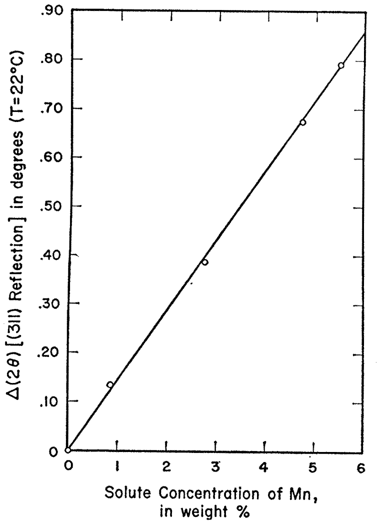

FIG. 2. Measured diffraction-angle differences $\Delta(2\theta)$ for the (311) reflections of annealed bulk Cu-Mn alloys, as a function of solute Mn concentration.

Altemose,[30] however, who studied the diffusion of helium through glass,[31] the results of Norton can be reliably extrapolated to 400°C. This yields a permeation P of 1.7×10^{-9} cm^3 (STP)/h/mm of wall thickness. The corresponding loss of Mn is 8.0×10^{-12} g/h and again may be discounted.

The solubility of O_2 in quartz at 950°C was derived by Norton[29] as 2.3×10^{-3} cm^3 (STP)/cm^2 solid for 76-cm gas pressure applied. Exposure to the atmosphere would result in a solubility of 5×10^{-4} cm^3/cm^3 of quartz. An envelope consisting of 5 cm^3 of solid quartz would, therefore, contain 3.5×10^{-7} g of O_2. Loss from this source would be 1.2×10^{-7} g of Mn, and again may be neglected. In a similar manner we can neglect loss of Mn at 400°C from this source of O_2. The residual vacuum of 7.5×10^{-2} Torr accounts for 6×10^{-7} g of O_2 in the gas phase and may also be neglected. There remains outgassing as a possible major source of O_2. Bulk samples heat treated at 900 and 400°C gave concentrations of Mn, determined by precision x-ray lattice measurements, which were in agreement with concentrations obtained from chemical analysis. This confirms the correctness of the analysis above and also indicates that significant loss of solute from outgassing O_2 does not occur.

III. X-RAY MEASUREMENTS

In order to use x-ray measurements for accurate determination of true solute concentrations of Mn, it was necessary to establish a calibration curve of diffraction angle, or lattice parameter, as a function of known solute concentration. Greater accuracy was required than could be obtained from published-lattice parameters for the Cu-Mn system.[32] Use of powdered samples directly was out of the question, since the solute concentration of powdered Cu-Mn samples was always uncertain. Initially a calibration curve for annealed bulk alloys was established. These alloys were prepared and heat-treated as described in Sec II. Mean-lattice constants for the bulk alloys were measured, using several reflecting planes for diffractometer scans.

Since many of the internally oxidized powder samples had low residual solute concentrations, it was necessary to improve the precision of x-ray determination of solute in the concentration range below 1 at.%. This was done by utilizing differences in the 2θ value for the diffraction angle of a single reflecting plane, as a function of the true solute concentration of Mn present in the Cu lattice. Using sectioned and polished samples cut from annealed bulk alloys, values of $\Delta(2\theta)$ for the (311) reflection (measured with respect to the 2θ value for a pure Cu sample) were measured as a function of Mn solute concentration. These results are given in Fig. 2. Solute concentrations determined from this curve are in agreement with those derived from the mean-lattice parameter calibration utilizing reflections from several lattice planes. The measurement is valid for bulk samples. With powders, variations in the mechanical packing of the alloy in the x-ray mound caused excessive errors in the measurement of $\Delta 2\theta$. These errors were eliminated by mounting powdered samples under Scotch cellophane tape on a glass slide. The diffraction angle was then reproducible to within 5 mdeg.

Annealed samples of <400 mesh Cu gave the same 2θ value for the (311) reflection as bulk Cu. A correction was necessary for particles of larger size. A direct transi-

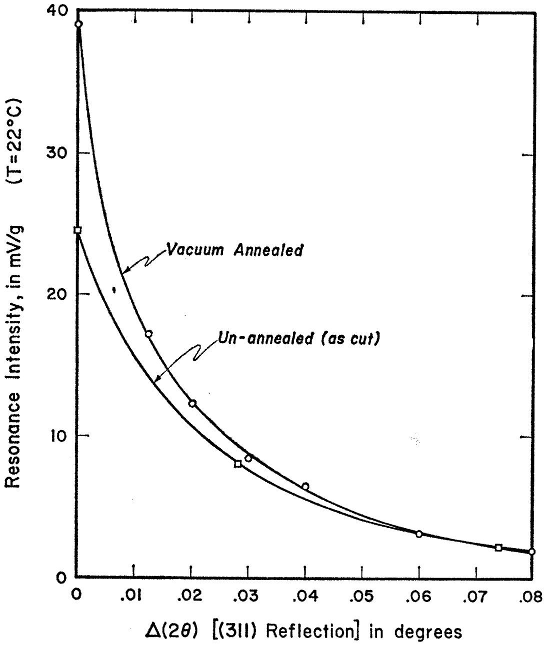

FIG. 3. Correlation between observed resonance intensities and measured $\Delta(2\theta)$ for the (311) reflections of comminuted Cu-Mn alloys of varying solute concentration of Mn.

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[30] V. O. Altemose, Corning Glass Research Laboratory (private communication).

[31] V. O. Altemose, J. Appl. Phys. 32, 1309 (1961).

[32] W. B. Pearson, *Handbook of Lattice Spacing and Structures of Metals* (Pergamon Press, Inc., New York, 1958), p. 587.

tion was then made from measured $\Delta(2\theta)$ values of annealed powdered samples to the calibration curve of Fig. 2 for annealed bulk alloys. Unannealed powders gave broader diffraction peaks than annealed samples, but at the higher solute concentrations $(>0.2$ weight $\%)$ $\Delta 2\theta$ could be determined with sufficient accuracy. The point at $\Delta 2\theta = 0$ for unannealed pure Cu was obtained with the accuracy of the resonance intensity measurement $(\sim 2\%)$. A reliable calibration curve for as-cut samples was therefore obtained. To first order, $\Delta 2\theta$ curves for annealed and unannealed samples, as a function of true solute concentration, can be considered the same. All $\Delta 2\theta$ measurements have therefore been referred to the calibration of Fig. 2. The correlation between resonance intensities of annealed and unannealed samples and measured values of $\Delta 2\theta$ is shown in Fig. 3. Final curves giving resonance intensities as a function of solute concentration, for both annealed and unannealed powdered samples, are shown in Fig. 4. Resonance analysis of these curves will be given elsewhere.

IV. CHANGE OF SOLUTE CONCENTRATION WITH VACUUM ANNEALING

The calibration curve of Fig. 4 applied to the intensity variations shown in Fig. 1 immediately yields the results given in Fig. 5. These curves show the true residual solute concentration of Mn remaining in the Cu lattice as a function of vacuum-annealing time. The starting concentrations of solute Mn, as determined from chemical and x-ray analysis, for the various samples are given in the legend. As vacuum annealing proceeds, equilibration of a solute oxide is achieved, the oxygen apparently being adsorbed on the particle surface or present as Cu_2O. Absolute loss of solute tends to be greater with alloys of greater initial solute concentration. This was especially apparent in the loss of solute during comminution. The change in mechanical properties of the alloy can probably account for this effect, but no simple correlation was evident. Sample B (comminuted under an atmosphere of NH_3) did not lose solute during comminution. The greatest loss occurred with Sample A, ground under oil in the method of Drain.[27] Solute loss on comminution is, presumably, also caused by internal oxidation.

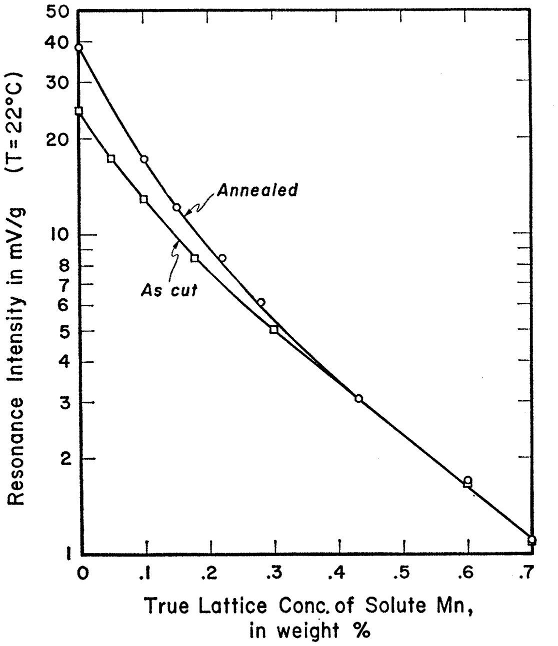

FIG. 4. Resonance intensity of comminuted Cu-Mn alloys as a function of true lattice concentration of solute Mn. Curves are given for vacuum-annealed and unannealed (as-cut) samples.

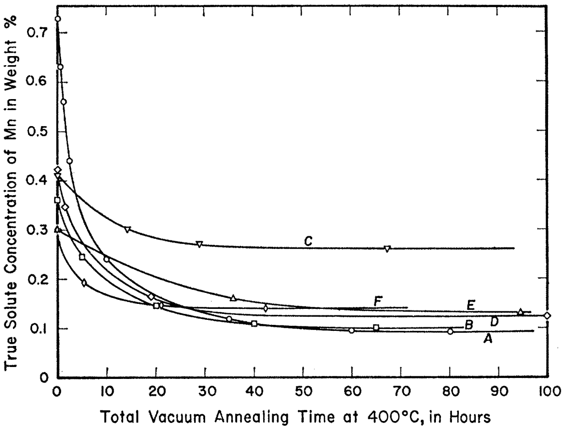

FIG. 5. True lattice concentration of solute Mn in comminuted Cu-Mn alloys, as a function of vacuum-annealing time at 400°C. Samples A, B, C, D, E, and F are those defined in Fig. 1.

No limit on concentration for this loss of solute can be set from these experiments. The limit would probably be set by a compromise between the increase of mechanical hardness and rate of surface oxidation with solute concentration. The percentage loss would then go through some form of maximum, probably at a concentration in the vicinity of 3 to 5%.

V. OXIDE IDENTIFICATION

A. X-Ray Analysis

Debye-Scherrer photographs repeatedly identified a second phase in vacuum-annealed powder alloys as cubic MnO (manganosite). A typical result is shown in Fig. 6. This photograph was obtained with Sample A of Figs. 1 and 5. The Mn-solute concentration of this sample had fallen from 1.97 to 0.09 wt.% by comminution and vacuum annealing. Confirmation of this identification of MnO was made using monochromatic $CuK\alpha_1$ radiation and a Guinier-type focusing diffraction camera. No evidence of free or clustered Mn was found in the x-ray studies. A complete indexing of Fig. 6 is given in Table I.

As far as I am aware, no previous x-ray study of the Cu-Mn system has identified the oxide specie of Mn produced by internal oxidation. Rhines[17] studied the

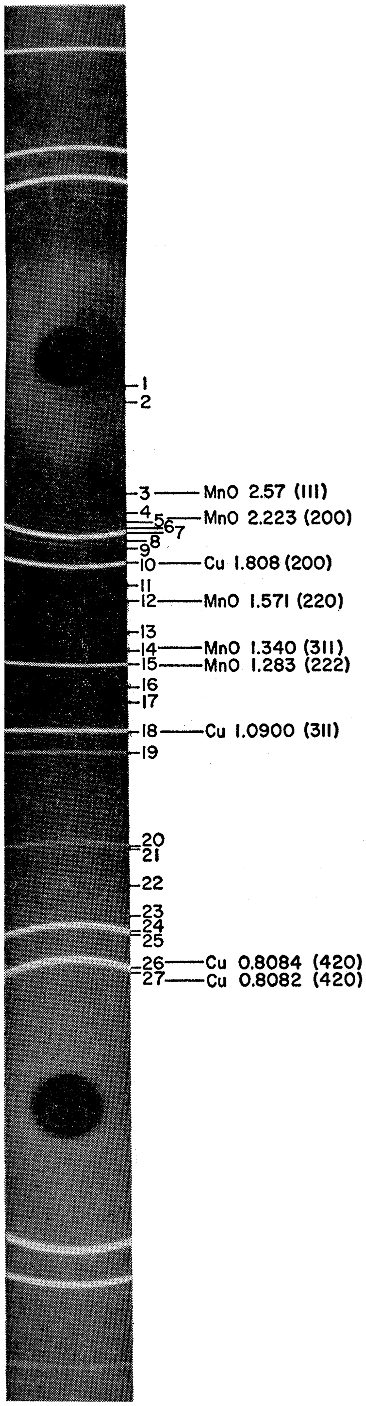

FIG. 6. X-ray powder photograph of a comminuted and vacuum-annealed Cu-Mn alloy (Sample A of Fig. 1 after 80-h anneal at 400°C). Each line has been indexed in terms of its associated lattice, the lattice spacing in Å, and the corresponding (*hkl*) value.

TABLE I. Indexed lines of x-ray powder photograph shown in Fig. 6. *d* values are in Å and *I* values are relative intensities taken from H. D. Swanson.[a] The second phase present is identified as MnO (manganosite).

Line No.	d_{Observed}	$(khl)_{\text{Cu}}$	I_{Observed}	d_{MnO}	$(hkl)_{\text{MnO}}$	I_{MnO}
1	6.982		2	Instrument line		
2	5.869		1	Instrument line		
3	2.6033		2	2.57	(111)	62
4	2.3077	$K\beta$ (111)	8			
5	2.2197		3	2.233	(200)	100
6	2.1479		2	Instrument line		
7	2.0881	(111)	100			
8	1.9958	$K\beta$ (200)	5			
9	1.9554		2	Instrument line		
10	1.808	(200)	90			
11	1.6643		1	Collodian reflection		
12	1.5727		2	1.571	(220)	58
13	1.4150	$K\beta$ (220)	3			
14	1.3433		2	1.340	(311)	21
15	1.2781	(220)	70	1.283	(222)	13
16	1.2058	$K\beta$ (311)	3			
17	1.1572	$K\beta$ (222)	1			
18	1.0900	(311)	70			
19	1.0440	(222)	20			
20	0.9041	(400)	12			
21	0.9035	(400)	4			
22	0.8644	$K\beta$ (331)	1			
23	0.8363	$K\beta$ (420)	1			
24	0.8294	(331)	30			
25	0.8292	(331)	10			
26	0.8084	(420)	30			
27	0.8082	(420)	10			

[a] H. E. Swanson, N. T. Gilfrich, and G. M. Ugrinic, Natl. Bur. Std. U. S. Circ. No. 539, V, 45 (1955).

Cu-Mn system, but attempts to identify the oxide species failed. Meijering and Druyvestyn[18] weighed an oxidized sample of Ag-Mn alloy and proposed an oxide $MnO_{1.88}$, midway between Mn_2O_3 and MnO_2. These authors also identified Al_2O_3, MgO, and SnO_2 in Ag alloys. Using x-ray diffraction methods, Rhines, Johnson, and Anderson[33] identified the following oxides in Cu alloys: Al_2O_3, SiO_2, Cr_2O_3, Fe_3O_4, TiO_2, ZrO_2, SnO_2, Pb_3O_4, ZnO, and CoO. Martin and Smith[34] identified SiO_2 in internally oxidized Cu-Si alloys, using a refractive-index method. Ashby and Smith[35] identified γ Al_2O_3 in internally oxidized Cu-Al alloys, by means of electron diffraction.

Apart from the measurement herein reported, no evidence concerning the type of Mn oxide formed appears to be available. Bulk samples of Cu-Mn alloys were therefore internally oxidized at 900° in an atmosphere of oxygen. X-ray measurements identified the presence of MnO in these samples. These results will be presented elsewhere.

In a recent paper, Gonser *et al.*[36] have made oxidation studies of the Cu-Fe system using the Mössbauer effect. Internal oxidation of Fe was observed when a 2.2 at.% Fe sample was annealed in a vacuum of 3×10^{-4} Torr at 850°C for 2 h. The observed spectra indicated the presence of FeO. This converted to Fe_3O_4 on further oxidation. Essentially, no evidence for Fe_2O_3 was found. Extending the present study to include several transition metal solutes showed that internal oxidation effects occurred with solutes of Ti and Fe in vacuum-annealed Cu alloys. Internal oxidation effects were also observed with Al in Cu.

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[33] F. N. Rhines, W. A. Johnson, and W. A. Anderson, Trans. AIME **147**, 205 (1942).

[34] J. W. Martin and G. C. Smith, J. Inst. Metals **83**, 153 (1954).

[35] M. F. Ashby and G. C. Smith, Phil. Mag. **5**, 298 (1960).

[36] U. Gonser, R. W. Grant, A. H. Muir, and A. Wiedersich, Acta Met. **14**, 259 (1966).

B. Electron Microscopy

Usually, direct-transmission microscopy of thin sections of internally oxidized alloys has failed to give an oxide diffraction pattern.[22,37] In such attempts only the dominant Cu lattice diffraction pattern is seen, even though metallography reveals an easily visible array of oxide particles.[21]

Attempts were made to examine internally oxidized Cu-Mn powder directly by sprinkling a portion of a vacuum-annealed powdered alloy on a supporting substrate of collodion. Transmission diffraction through the thin edges of the particle revealed only the Cu diffraction pattern. Thin disks of bulk Cu-Mn alloys were therefore oxidized internally using the method of Rhines.[17] The disks were then electropolished and studied in transmission. Carbon extraction replicas were also prepared. Single-crystal diffraction patterns of oxide inclusions were identified as cubic MnO (manganosite). The presence of γ Mn_2O_3 and $MnO \cdot Mn_2O_3$ (manganese spinel) were also identified. No electron-diffraction evidence for free or clustered Mn was observed. Details of the electron microscopy study and observations on the oxide particle morphology will be published elsehwere.[38]

VI. KINETICS

The results of Figs. 1 and 5 were obtained from internally oxidized samples which had been vacuum-annealed in glass tubes of some 30 ml volume. These tubes were flame-sealed at a residual pressure of 7.5×10^{-2} Torr, leaving 5.7×10^{-4} mg of available oxygen in the gas phase. A 3-g sample of Cu-Mn would lose only 3.9×10^{-5} wt.% of Mn solute from this source of oxygen. According to Phillips *et al.*,[39] the oxygen solubility limit in Cu at 550°C is 15 ppm. A bulk sample of Cu-(0.31 wt.% Mn) alloy, grown by the Czochralski method, showed a measured oxygen content of only 2.3 ppm. Any oxygen present as an oxide would have been included in the analysis.

A Cu alloy sample of <150 mesh particles, obtained by high-speed cutting in air, was oxidized to a uniform red color by heating in air. According to Constable,[40] the visible red stage of Cu oxidation corresponds to a layer of Cu_2O, some 1300 Å thick. The measured weight gain of the oxidized particles above was 1.4 mg of O_2 per g of alloy. This amount of O_2 could produce a loss of solute Mn of 0.52 wt.%. Assuming that all of the O_2 went to form a uniform layer of Cu_2O, the measured weight gain indicates a surface area for the alloy particles of 200 cm²/g. This agrees well with the value of 160 cm²/g calculated from the measured physical dimensions of the particles. Originally, the alloy sample contained 0.72 wt.% Mn. The observed loss of solute Mn after vacuum-annealing the oxidized sample was 0.56 wt.%. Agreement between the observed and anticipated loss of Mn provides support for the contention that an oxide layer of Cu_2O can account for the loss of solute observed in these experiments. To account for the measured total loss of solute for sample A (1.97−0.09 wt.% Mn) of Fig. 5, however, the uptake of oxygen must be very large. Some dependence of the loss of solute on particle size should be expected. This was verified experimentally.

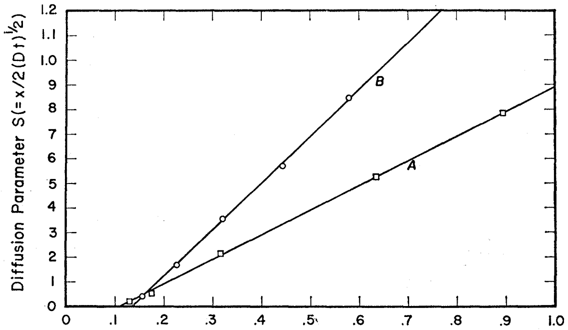

FIG. 7. Diffusion plot of $S[=x/2(Dt)^{1/2}]$, derived from observed solute concentrations of Mn, as a function of vacuum-annealing time t at 400°C. Samples A and B are those defined in Fig. 1.

Young *et al.*[41] have shown that the uptake of oxygen on the (100) face of Cu, at 178°C, saturates at 600 Å of Cu_2O. The formation time of this oxide layer is 10 min. Comminution must, therefore, result in extremely high temperatures, even under oil, if oxide thicknesses of the required magnitude are to form rapidly. To account for the loss of solute Mn (from 1.97 to 0.73 wt.%) on comminution of sample A of Fig. 5, extensive oxygen diffusion would also be required.

Rhines *et al.*[33] and Meijering and Druyvestyn[18] have derived complex expressions for the rate at which an internal oxide front advances. A simplified form of the kinetics reduces to a solution of Fick's law $\partial c/\partial t = D\partial^2 c/\partial x^2$, for a one-dimensional diffusion of oxygen of concentration c at time t and distance x. Since the particles were generally in the form of thin flakes,[26] we can assign boundary conditions as follows. At time $t=0$, the oxygen concentration is zero internally and finite at the surface. At $t=\infty$, the oxygen is uniformly distributed through the particle (in oxide form). More conveniently, we use the solute conctenration c of Mn as the variable, starting with a concentration c_0 at $t=0$ and equilibrating to a final concentration c_f at $t=\infty$.

A standard error function solution is

$$(c_0 - c)/(c_0 - c_f) = 1 - \operatorname{erf}(S),$$

where $S = x/2(Dt)^{1/2}$ and x and D define the half-thickness of the thin dimension of the particle and a diffusion constant for oxygen, respectively.

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[37] M. F. Ashby (private communication).

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The observed Mn solute concentrations obtained from Fig. 5 were used to evaluate the corresponding parameter S as a function of annealing time. A plot of S versus $t^{-1/2}$ should yield a straight line of slope $x/(2D^{1/2})$. Results for samples A and B are plotted in Fig. 7. Curve A for the <400-mesh particles gives the result $x/(2D^{1/2})=53$. Taking the average thickness of a thin flake as $4\,\mu$, we obtain a diffusion constant at 400°C of $D=3.3\times10^{-12}$. Similarly, curve B for <150-mesh particles gives the result $D=4.8\times10^{-12}$ at 400°C, if we take the mean particle thickness at $8\,\mu$. We can compare these values of the diffusion constant derived on the assumption of oxygen diffusion with a known value for the diffusion of oxygen in Cu. Extrapolating measured values from 600°C,[42] we obtain $D=3.3\times10^{-12}$ at 400°C. This agrees well with the values obtained from our analysis.

The corresponding value for Mn diffusion in Cu (taking $D_0=10^7$, $E_0=91$ kcal/mole)[43] gives $D=4\times10^{-21}$ at 400°C. The rate limiting process for the growth of MnO is thus the low-energy mechanism of oxygen diffusion at $E_0=46$ kcal/mole.

VII. CONCLUSION

X-ray and NMR measurements on powdered and vacuum-annealed Cu-Mn alloys have been interpreted in terms of loss of solute Mn from the Cu lattice.[44] X-ray and electron-diffraction data have confirmed the presence of a second phase identified as cubic MnO in the form of manganosite. Electron diffraction has also established that minor quantities of a second phase, identified as γ Mn_2O_3 and manganese spinel ($MnO\cdot Mn_2O_3$) were also present. Chemical analysis has established that the total Mn content of the sample remains constant during comminution and vacuum annealing. We conclude that internal oxidation is responsible for the observed loss of solute. No evidence for free or clustered Mn has been found. The low solid solubility of oxygen in Cu and the small oxygen component present in the evacuated and sealed envelopes, suggest that sufficient oxygen or oxide must accumulate during the act of comminution, or on exposure to the atmosphere, to account for the observed loss of solute. Observed changes of solute concentration with vacuum annealing time have been interpreted on the basis of diffusion of oxygen from the sufrace of a particle. Diffusion constants derived on the basis of this model are in agreement with known diffusion constants for oxygen diffusion through Cu.

The conditions for internal oxidation can be summarized as follows[17,45]:

I. Oxygen must *dissolve* and diffuse in the alloy.

II. The solute must form an oxide which is more stable than the oxide of the solvent.

III. The solute oxide must be insoluble in the alloy.

If these conditions exist, then some loss of solute will result from comminuting and vacuum-annealing alloy samples. Both annealed and unannealed samples of powdered alloys can therefore lead to errors in interpretation, if measured parameters are correlated directly to solute concentrations obtained from chemical analysis. The effects reported here are not restricted to powdered alloy samples. Drastic resistivity changes have also been observed in rods and wires of Cu-Mn, Cu-Fe, and Cu-Co alloys, heat-treated in rarefied atmospheres of O_2 by Domenicali and Christenson.[46] These authors correctly suggested that observed resistance changes arose from internal oxidation effects, but no study of the oxide or its kinetics was attempted.

Resonance results based on the true solute concentrations of annealed samples of Cu-Mn, Cu-Ti, and Cu-Fe and other alloys have been interpreted on the basis of internuclear reactions and quadrupole effects. These results will be presented elsewhere.

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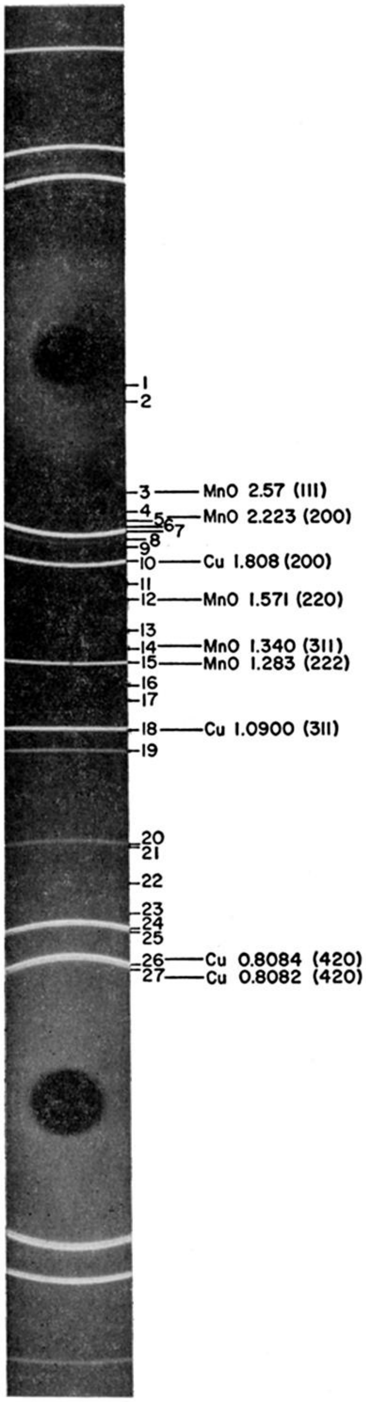

FIG. 6. X-ray powder photograph of a comminuted and vacuum-annealed Cu-Mn alloy (Sample A of Fig. 1 after 80-h anneal at 400°C). Each line has been indexed in terms of its associated lattice, the lattice spacing in Å, and the corresponding (*hkl*) value.