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The Metals Research Laboratory

Brown University

Ultrasonic Attenuation In Vacuum
Annealed and Internally Oxidized
Single Crystals of Dilute Copper
Alloys

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by

Chung F. Ying and Rohn Truell

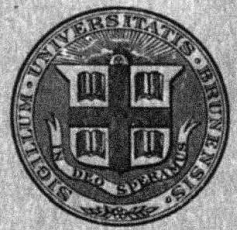
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Technical Report No. 2

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Prepared for

Office of Ordnance Research, U.S. Army
under Contract DA-19-020-ORD-1512



July, 1954

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PROVIDENCE 12, RHODE ISLAND

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FROM: Metals Research Laboratory
Division of Applied Mathematics
Brown University
Providence 12, Rhode Island

SUBJECT: Addition to Technical Report #2, July, 1954
Office of Ordnance Research, U. S. Army
Contract #DA-19-020-ORD-1512
"Ultrasonic Attenuation In Vacuum Annealed
and Internally Oxidised Single Crystals
of Dilute Copper Alloys"
Chung F. Ying and Rohn Truell

The attached Letter Report Number 10 contains technical information which was not available at the time Technical Report #2 was written. The information really belongs in said Technical Report and for this reason the attached Letter Report is sent to you to be included with the Technical Report.

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August 30, 1954

Contractor's Letter Report Number 10 for the period May 25, 1954
to August 24, 1954

From: Division of Applied Mathematics
Brown University, Providence 12, Rhode Island

To: Commanding Officer
Watertown Arsenal
Watertown 72, Massachusetts

Contract No.: DA-19-020-ORD-1512

Title: Examination of Solid Materials by Ultrasonic Methods

This report covers the period extending approximately from
May 25, 1954 to August 24, 1954.

Study of the effect of internal oxidation on the ultrasonic attenuation was continued. (Earlier results were described in Technical Report # 2, July 1954.) A Cu- $\frac{1}{2}$ % Al single crystal, which was discussed in the above mentioned technical report and which had been heated, was again heated in the presence of oxygen at 980°C for additional 326 hours. After this heating, the ultrasonic attenuation of both longitudinal and transverse waves in the specimen was found to be much higher than before the heating. Data for the longitudinal wave are plotted in Figure 1 in which earlier results presented in Technical Report # 2 are also shown for comparison. The velocities of propagation of the waves in the specimen were found to be slightly smaller than before the heating. A small piece was cut off from the specimen so that the cross-section of the specimen could be examined. Only an oval core* remained apparently unchanged; the rest of the specimen was internally oxidized. Under a microscope long needles running generally in directions perpendicular to the surfaces of the specimen were observed in the oxidized region**.

In connection with the effect of internal oxidation during which precipitates are formed in an originally homogeneous specimen, theoretical computation has been completed on scattering of wave energy by an elastic, isotropic solid sphere in an elastic, isotropic solid medium material. It will be presented in a forthcoming technical report.

Experiments were also carried out to determine the effect of

* The specimen was disk-shaped before cutting.

** J. L. Meijering and M. J. Druyvestorijn (Philips Res. Rep., 2, (1947) 81) reported a similar structure.

directions of propagation and vibration on the ultrasonic attenuation (Quarterly Report # 9). Two Cu- $\frac{1}{2}$ % Al samples were so oriented that a shear wave could propagate in the direction of $[111]$ while vibrating in a plane parallel to the direction of $[10\bar{1}]$, (111) and $[10\bar{1}]$ being the slip plane and the slip direction in copper at room temperature. The echo patterns in the measurements of attenuation were found to be, however, generally irregular. There was only rough indication that the attenuation was higher than the measured attenuation of a shear wave propagating in specimens of the same material in the direction of $[110]$ with its plane of vibration parallel to the direction of either $[110]$ or $[001]$. Some preliminary results are shown in Figure 2.

Ultrasonic measurements were extended to frequencies higher than those so far employed. Frequencies up to about 200 mc/sec were used as against the earlier highest frequency of about 75 mc/sec. Results on two of the studied single crystals are given in Figure 3 which shows attenuation-frequency plots on log-log scale.

Some ultrasonic measurements were taken on a Fe-Si single crystal and a Al-Ag single crystal.

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**ULTRASONIC ATTENUATION IN VACUUM ANNEALED AND
INTERNALLY OXIDIZED SINGLE CRYSTALS
OF DILUTE COPPER ALLOYS •**

12) 37

By

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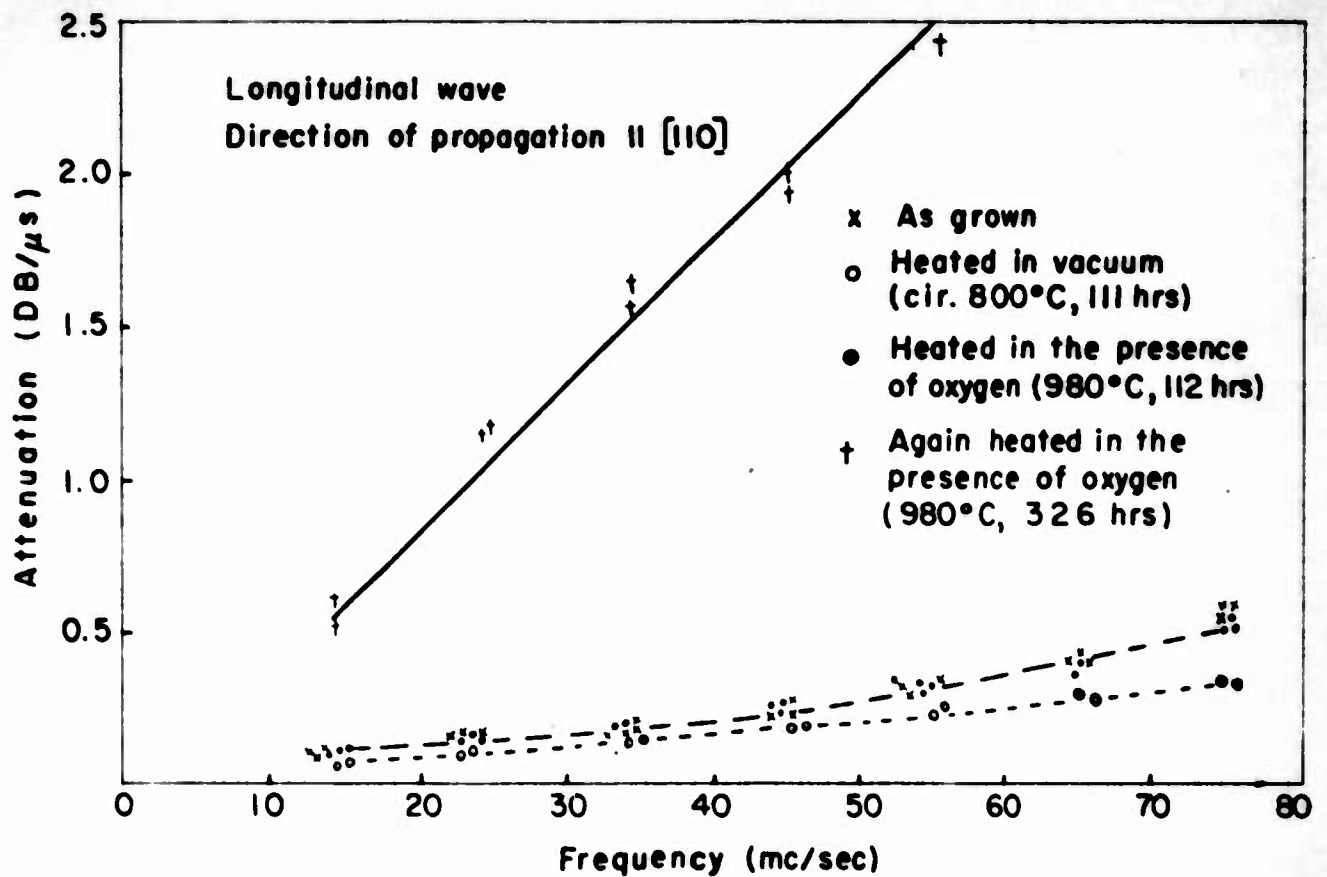


Fig. 1. Attenuation - Frequency Plot of Cu 320 (Single crystal of copper alloyed with 1/2 % aluminum)

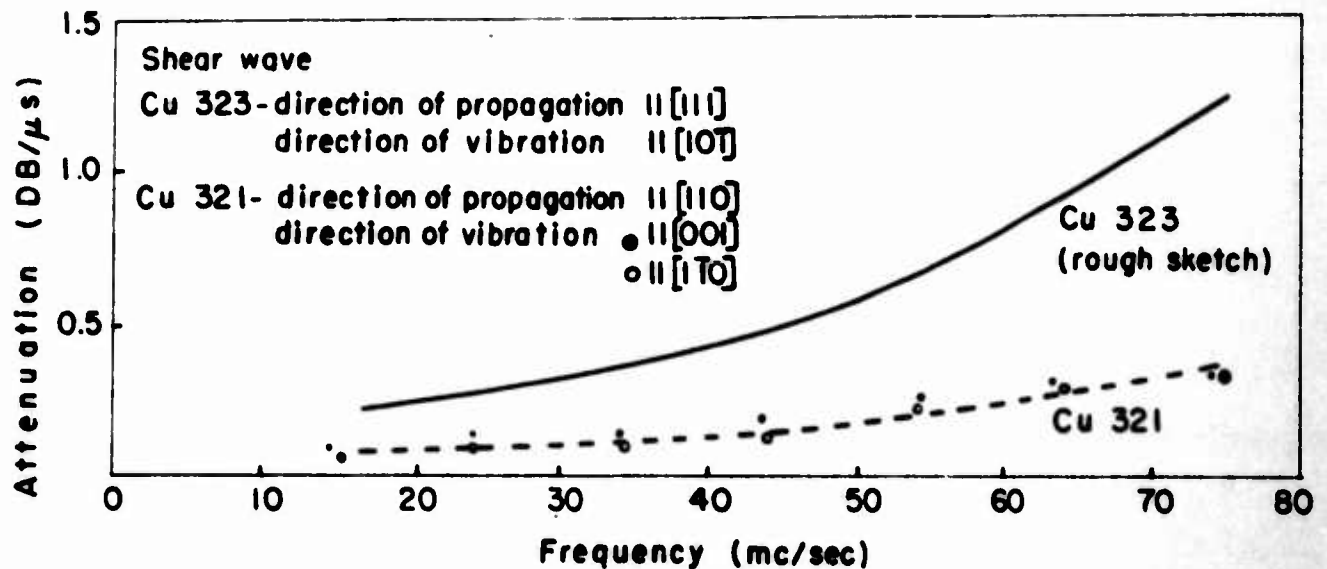


Fig. 2. Frequency - Attenuation Plot of Cu 323 and Cu 321 (Single crystals of copper alloyed with 1/2 % aluminum)

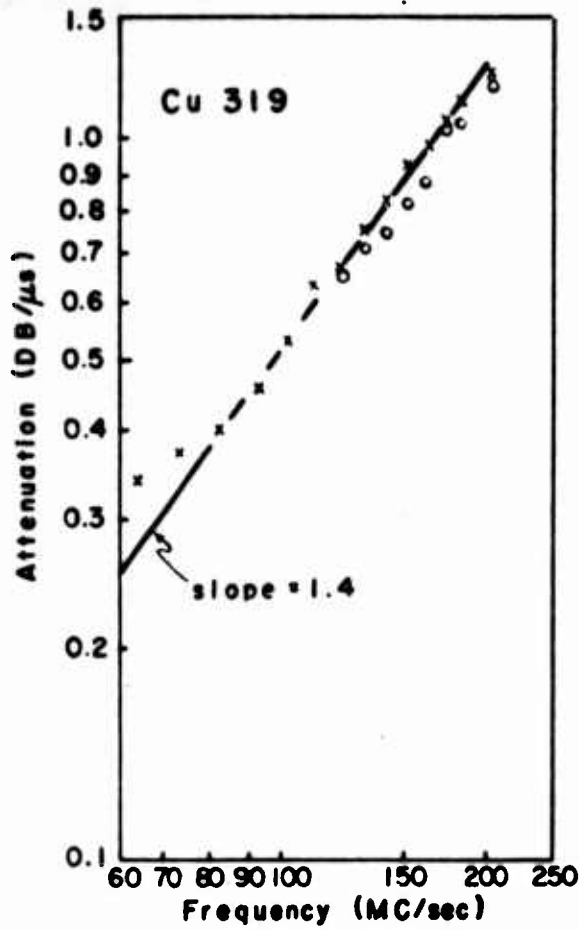


Fig. 3. Attenuation-Frequency Plot of Cu 319 and Cu 321 (Single crystals of copper alloyed with 1/2 % aluminum) Longitudinal Wave Direction of Propagation \parallel [110]

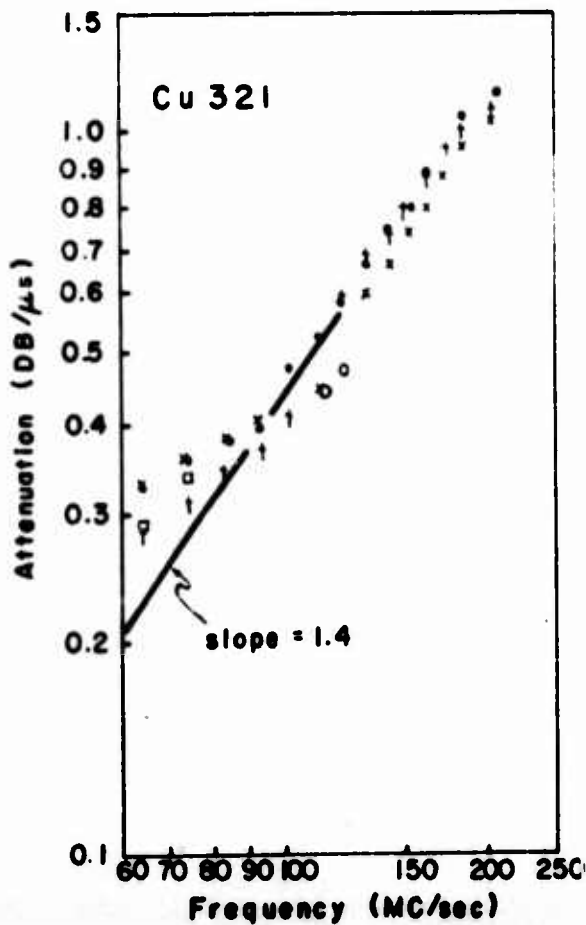


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ABSTRACT

Single crystals of copper alloyed with 1.00% aluminum and 0.50% aluminum respectively were heated at about 800°C in vacuum for over 100 hours. The attenuation of both longitudinal and transverse ultrasonic waves (10 - 75 mc/sec) in the specimens decreased from that before heating. The specimens were then heated at about 1,000°C in the presence of oxygen for over 100 hours also so that they were internally oxidized extensively. The values of attenuation were higher than those after the heating in vacuum. A single crystal of copper alloyed with 0.13% beryllium was similarly heated in the presence of oxygen. The attenuation first decreased and then increased through heating. This last specimen was studied metallographically.

Possible mechanisms responsible for the decrease in attenuation on annealing and for the increase on internal oxidation are discussed. Anchoring of dislocations by impurity atoms and scattering of wave energy by precipitates are probably the respective main causes.

Ultrasonic Attenuation In Vacuum Annealed And Internally
Oxidized Single Crystals Of Dilute Copper Alloys

I. INTRODUCTION

On dissolving a small amount of foreign element into a metal, precipitates can be formed inside the metal by the process of internal oxidation if all conditions are favorable. The alloy must be heated in the presence of oxygen such that the gas diffuses into the alloy and oxidizes the alloying element within the alloy, but not the host metal itself. In order that the oxidation be internal, two main requirements evidently have to be fulfilled. First, the affinity of oxygen for the alloying element must be considerably greater than that for the host metal. Second, oxygen must be able to diffuse into the alloy more rapidly than the alloying element diffuses out. An additional requirement for the appearance of the precipitates is that the solubility of the oxide thus formed must be relatively small in the metal.

Rhines and his colleagues^{1,2,3} tested a very large number of dilute alloys of copper, of silver, and of some white metals. They observed metallographically zones of internal oxidation, or subscales, in many of the alloys studied. Meijering and Druyvesteyn^{4,5,6} independently examined the penetration of the oxidation front into dilute alloys of silver, of copper, and of nickel. In addition, they found that in many cases, the ductile host metals hardened* on internal oxidation as might be expected from the creation of minute oxide particles which are able to block the glide planes if their sizes are correct.

* Earlier Rhines had reported that the scratch hardness of the alloys does not change on internal oxidation. The hardness referred to by Meijering and Druyvesteyn was that measured with an indentation tester. For discussion of this point, see Ref. 7.

In our study of solids through measurements of their ultrasonic attenuation, it was believed that it would be interesting to investigate how the minute particles of internal oxidation within a metal would affect the attenuation in the metal. Alloys were accordingly internally oxidized and the attenuation was measured before and after the oxidation. The process is not as simple as it might seem because internal oxidation at the same time reduces or removes the dissolved alloying atoms which probably play a role in attenuating ultrasonic waves. The first major question to be answered, however, is whether the total influence of these mechanisms is large enough to be detectable by our present methods of attenuation measurements.

To facilitate internal oxidation, the alloys have to be heated at elevated temperatures. Since heating alone may affect the attenuative property, it is necessary to sort out this component effect if present. Some of the alloys were therefore heated in vacuum. On studying their attenuative properties both before and after the heating, the effect of the heat treatment can be determined.

II. EXPERIMENTAL ARRANGEMENTS

A. Materials and Samples

Silver as well as copper was used in the preliminary tests. A single crystal of silver alloyed with zinc was grown in this laboratory. Later work was, however, confined to copper, mainly because this metal is harder than silver and this introduces less complication in the preparation of the material for ultrasonic measurements. All the samples to be reported in the following are alpha solid solutions of copper. Aluminum and beryllium were somewhat arbitrarily chosen as alloying elements.

To eliminate the diversion of acoustic path lengths of ultrasonic beams within grains* as well as reflection, refraction, and conversion of modes at the grain boundaries, and especially to avoid any change of grain sizes during heating, single crystals of the copper alloys were used. These single crystals were grown from the melt. Before melting, the copper used contained less than five thousandths of one per cent of total impurities while the aluminum used was 99.99% pure. Analysis of the beryllium used was not available. Copper and aluminum or copper and beryllium were first melted together in vacuum by induction heating which also stirred the solution. These alloys were then grown (by Horizons Incorporated) into single crystals in a helium atmosphere. All the ingots were one and one-half inches in diameter and a few inches in length.

The orientations of the ingots were determined by studying their back reflection Laue patterns. Sections with approximately correct orientation were cut off from these ingots and then further oriented so that after grinding, their opposite faces were closely parallel to some chosen crystallographic plane. The faces were later carefully lapped to the extent that opposite faces of each sample were parallel to each other and flat to within 1.3×10^{-4} cm over an area generally not less than 7 sq. cm. Parallelism within these limits is necessary to insure reliable ultrasonic measurements in the frequency range studied. The samples were usually over 1 cm in thickness before any heat treatment.

* The anisotropy factor of copper is large = $\frac{c_{44}}{(c_{11} - c_{12})/2} = 3.3$

B. Ultrasonic Measurements

The method of measuring the ultrasonic attenuation has been reported elsewhere^{8,9}. Briefly, the decrease with distance in the amplitude of a pulse of ultrasonic wave was measured as the pulse traveled back and forth within a sample between its parallel faces. The pulse of mechanical waves was produced by applying for a short duration a sinusoidal voltage to a quartz transducer cemented onto one of the opposite faces. Both longitudinal and transverse waves were used. The frequency range used was 10 to 75 megacycles per second.

C. Heat Treatment

For the study of the effect of heating alone, samples were heated in a large closed metal system evacuated by an oil diffusion pump backed by a mechanical pump. The pressure of the system was reduced to not more than a few microns of mercury during heating. A heating element inside the closed system was capable of raising the temperature inside the chamber to a maximum of about 810°C. This was the temperature at which all the samples were heated in vacuum.

For inducing internal oxidation, the general scheme used by Rhines,¹ of heating samples in an oxygen partial pressure, was followed. The sample was laid in an alundum crucible with a perforated flat bottom. The crucible was enclosed together with cuprous oxide and fine copper shavings in an iron pipe. The iron pipe was placed vertically in a muffle furnace with one end of the pipe extending outside the furnace. The top part of the pipe was then at a relatively low temperature during heating and consequently did not rust excessively so that the top cover, lined with copper foils, could be opened. A thermocouple was placed close to

the alundum crucible so that the electrically controlled temperature was nearly that of the sample. In some cases, samples after being heated had bright surfaces, but in others, they had thin black crusts. The cause of this difference was apparently the degree of tightness of the iron pipe system. During heating for internal oxidation, the temperature was generally maintained at 980°C.

Before any heating, either in vacuum or in oxygen, samples were deeply etched in order to avoid recrystallization on the surface during heating. The temperature was always raised or lowered very slowly. After heating, the samples had to be ground and lapped again for ultrasonic measurements.

III. EXPERIMENTAL RESULTS.

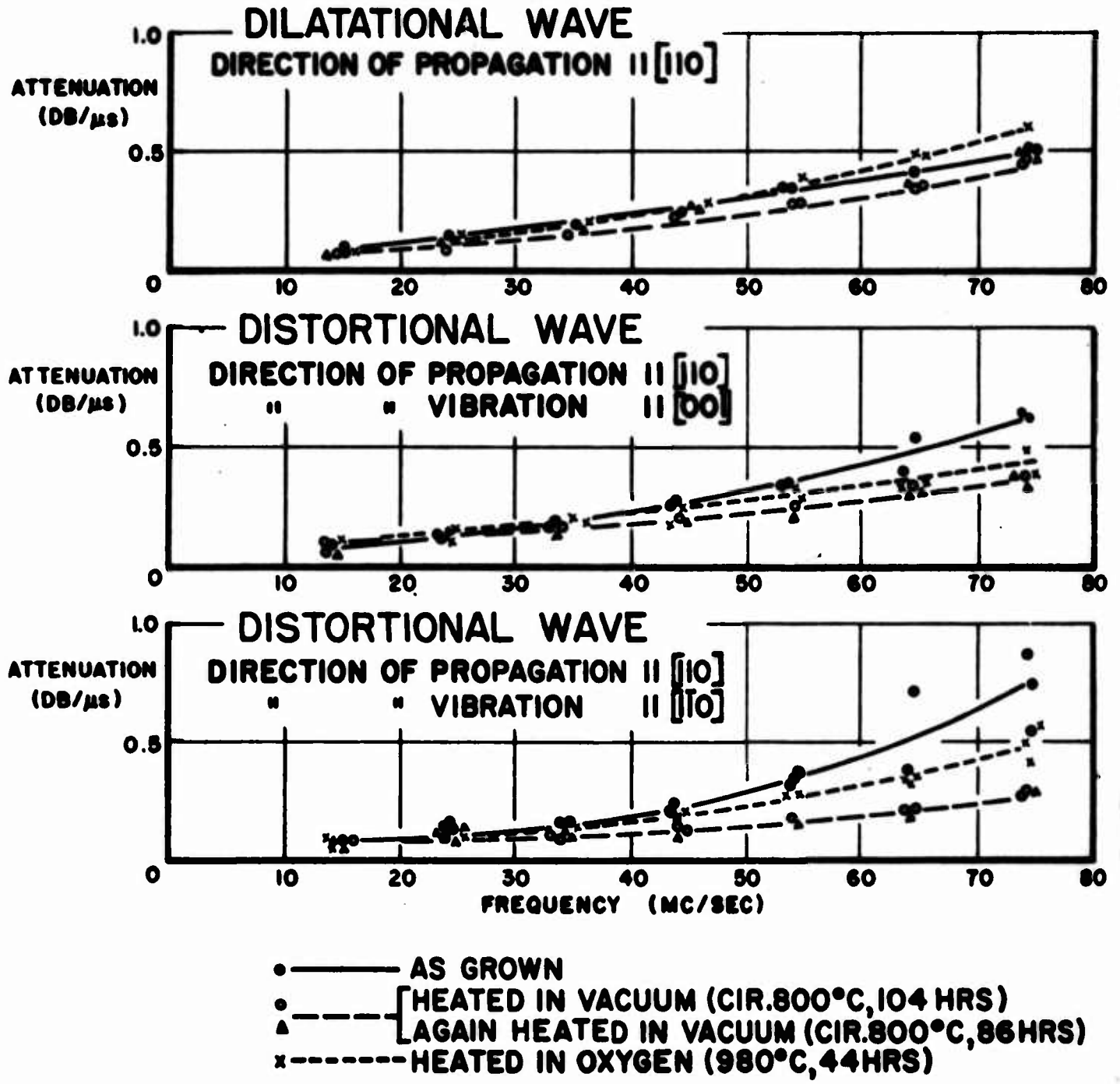
In addition to a few examined in preliminary runs, three single crystal samples were carefully studied. Two of these samples were copper-aluminum alloys; one contained 1.00% aluminum by weight while the other contained 0.50% aluminum by weight. The faces of these samples were parallel to (110) plane. The third sample was a copper-beryllium alloy, containing 0.13% beryllium by weight. Its faces were parallel to the (111) plane .

The sample containing 1.00% of aluminum, coded Cu 314, was heated for long periods twice in vacuum at about 800°C, and later heated at 980°C in the oxygen atmosphere as described earlier. The attenuation of the sample was measured before any heating and after each heating. The results and heating details are presented in Figs. 1 and 3. The sample was later heated in the oxygen partial pressure at 980°C for over fifty hours at the end of which the controlling thermocouple broke down,

the temperature of the furnace went up, and the sample partially melted. The remainder of the sample, which was over half of its original size, was still a single crystal although its orientation seemed to have shifted by about 10° from its direction before melting. The attenuation for longitudinal waves was measured after the remainder was oriented, ground, and lapped. The attenuation was found to be very high; at about 15, 25, and 35 mc/sec, the values were approximately 1.3, 1.6, and 1.8 db/ μ s respectively as against approximately 0.07, 0.14, and 0.19 db/ μ s after the first heating in the presence of oxygen.

The sample containing 0.50% of aluminum, coded Cu 320, was heated once in vacuum and once in the presence of oxygen. Its ultrasonic data and data on heat treatment are presented in Figs. 2 and 3. Corresponding data on the third sample, Cu 317, which contained 0.13% of beryllium, are presented in Fig. 4. The sample was not heated in vacuum, but its heating in the presence of oxygen was interrupted once to enable measurements of its attenuation after a relatively brief heating the effect of which will later be interpreted as close to the effect of heating alone. As will be noticed from Fig. 4 the ultrasonic measurements of this sample were less reproducible than those of Cu 314 and Cu 320.

The values of attenuation given in all the figures are expressed in terms of db/ μ s. By measuring the velocity of propagation of the pulse, it is possible to convert db/ μ sec to db/cm or neper/cm and to compute the internal friction. The related formulae are shown in Appendix 1. Computed values for one case of transverse waves travelling in Cu 320 are also shown there. An estimate of the strain amplitude of the waves used has been made and is presented in Appendix 2. This estimate is incomplete,



**FIG. I ATTENUATION-FREQUENCY PLOT OF Cu 314
(SINGLE CRYSTAL OF COPPER ALLOYED WITH
1% OF ALUMINUM)**

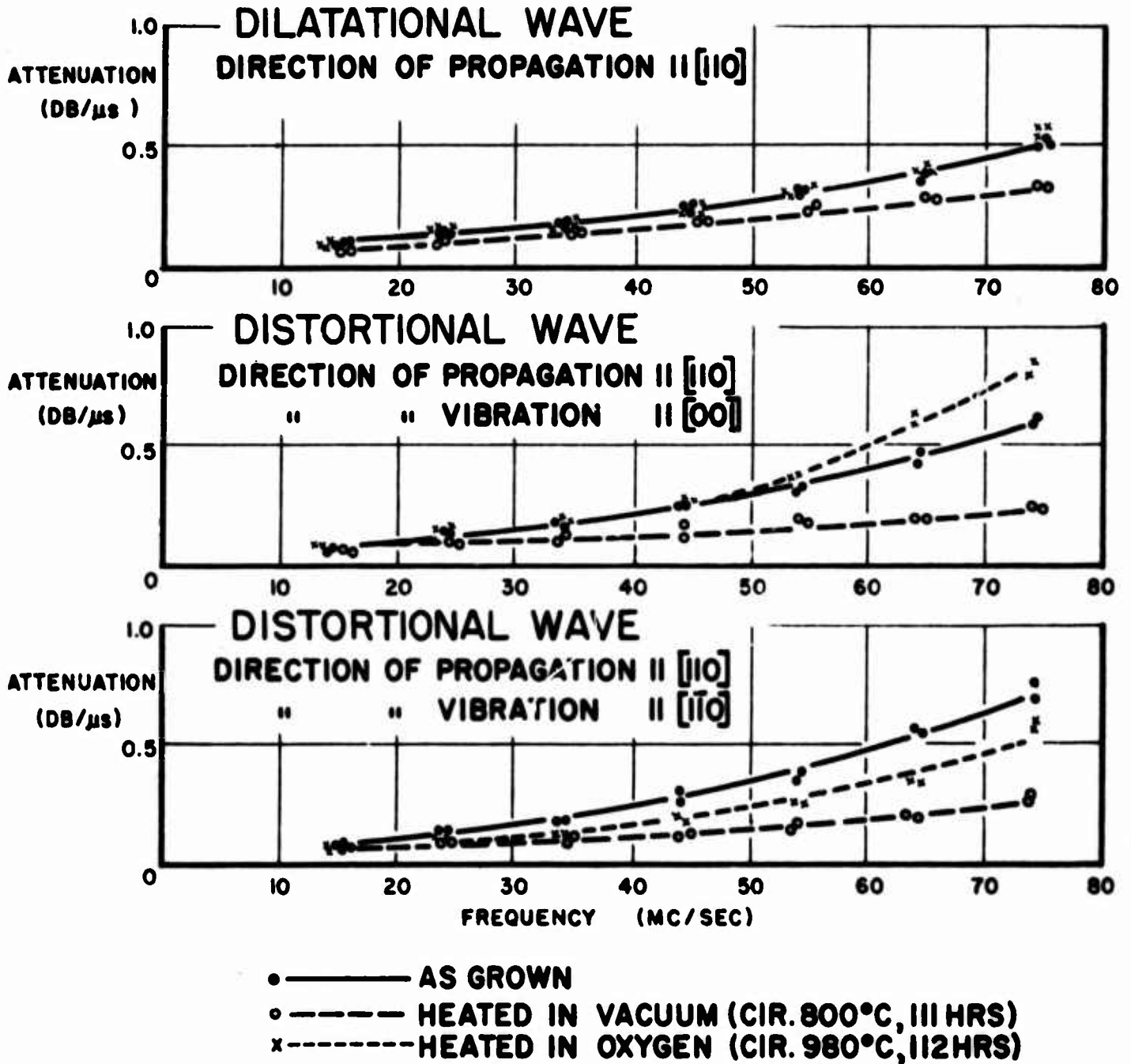


FIG.2 ATTENUATION-FREQUENCY PLOT OF Cu 320
(SINGLE CRYSTAL OF COPPER ALLOYED WITH
1/2% OF ALUMINUM)

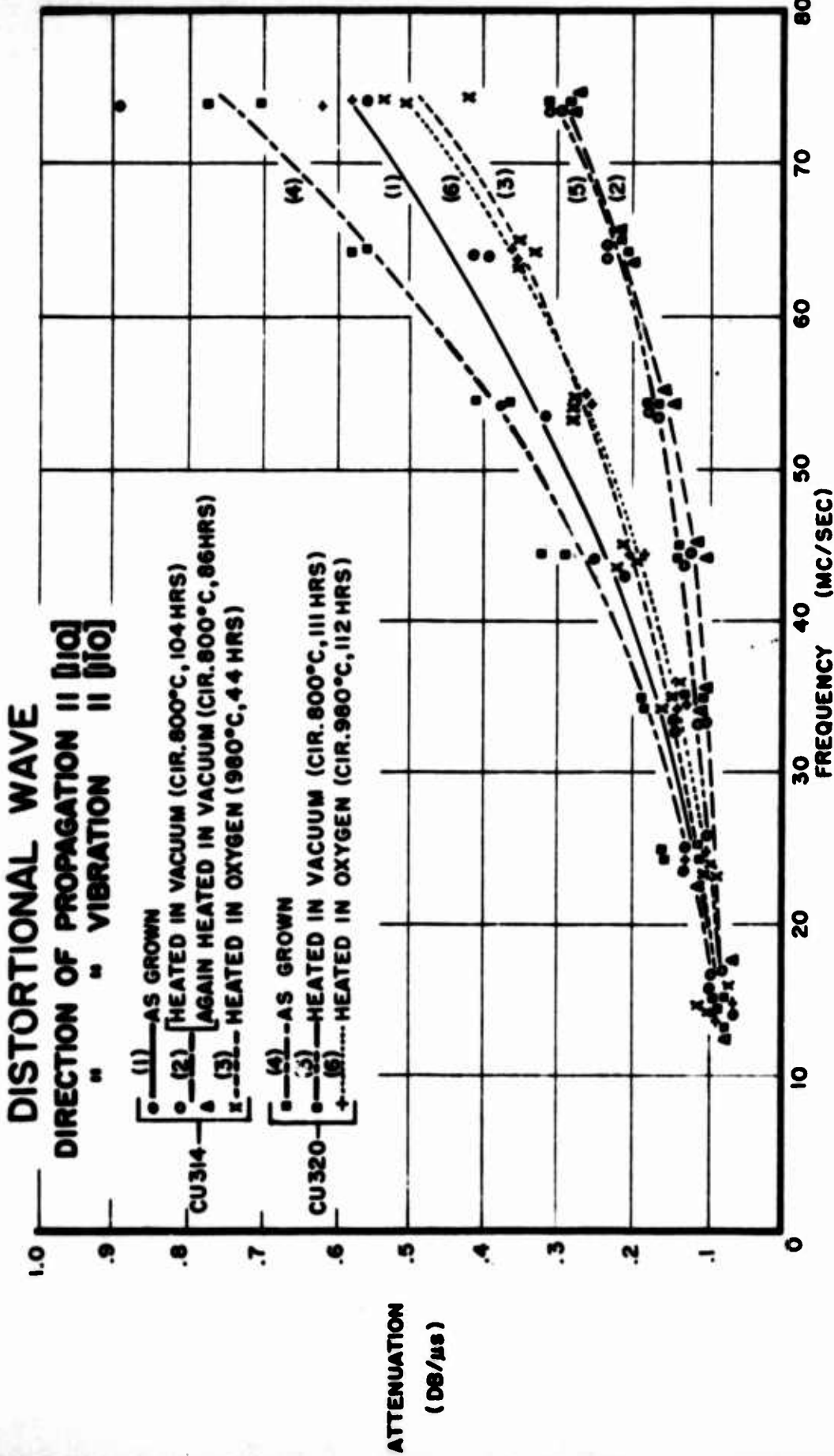
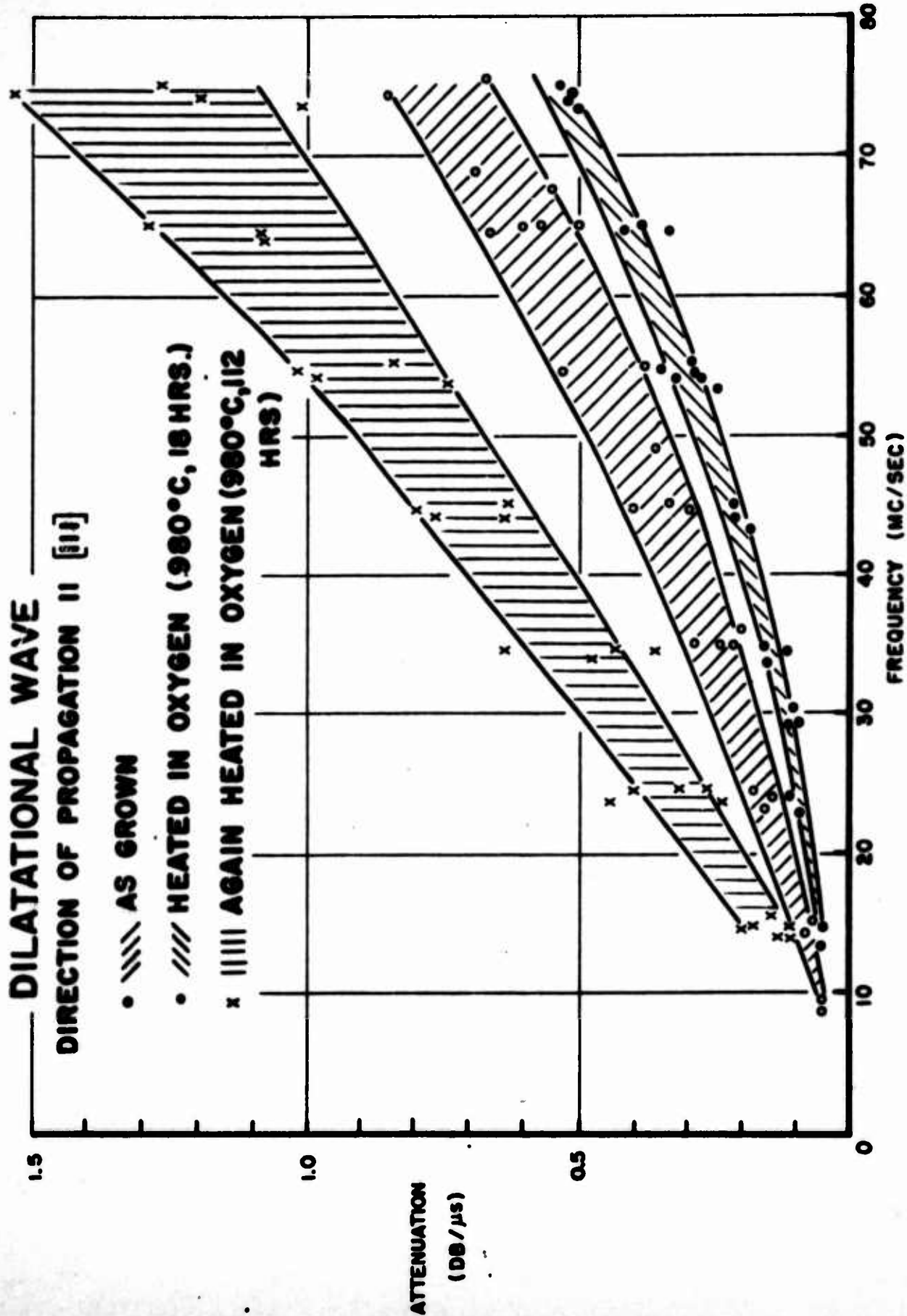
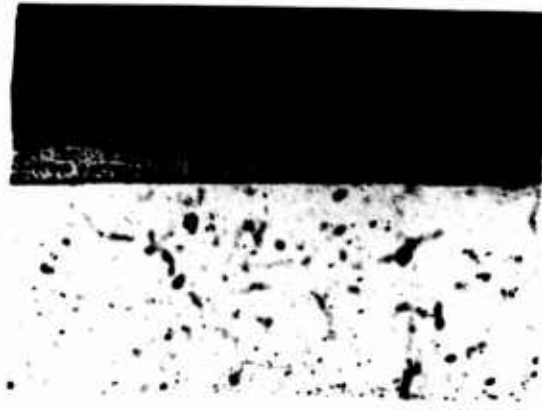


FIG. 3 ATTENUATION-FREQUENCY PLOT OF CU314 AND CU320
(ENLARGED PLOT OF THE LOWEST SETS OF CURVES IN FIGS. 1 & 2)



**FIG. 4 ATTENUATION-FREQUENCY PLOT OF Cu 317
(SINGLE CRYSTAL OF COPPER ALLOYED WITH .13% OF BERYLLIUM)**

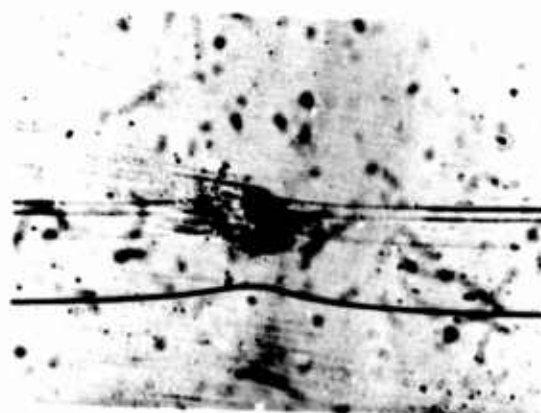
Oxygen



Oxygen



Oxygen



but it yields for the strain amplitude a definite upper limit which is about 2×10^{-6} in the present study.

Metallographic study was done on one of the three samples, Cu 317, although in preliminary runs quite a few samples of both copper-aluminum and copper-beryllium were examined microscopically. A subscale was observed after the first heating in oxygen by cutting a small piece off the sample. Its photomicrograph is shown in Fig. 5. After the second heating, another small piece was cut off, and its cross-section examined. Only one rim about as narrow as the rim appearing after the first heating was seen. Probably oxygen has penetrated through the whole piece during the second heating and the observed rim was one corresponding to the first heating⁵. (Another sample of similar composition heated several times showed several lines, some of which are shown in Fig. 6.) However, there is difficulty with this interpretation; this point will be discussed later.

There were interesting incidental observations in connection with the penetration of the reaction front. One such observation was the retardation of part of the front by an inclusion as shown by the photomicrographs in Fig. 6. The inclusion was probably a concentration of beryllium. Another finding was that in the case of copper alloyed with one per cent of aluminum, under certain conditions of heating in oxygen (presumably when the oxygen pressure was very low), an appreciable amount of slightly grayish powder was found on the bright surfaces of heated samples. The index of refraction of this powder was found* to be the

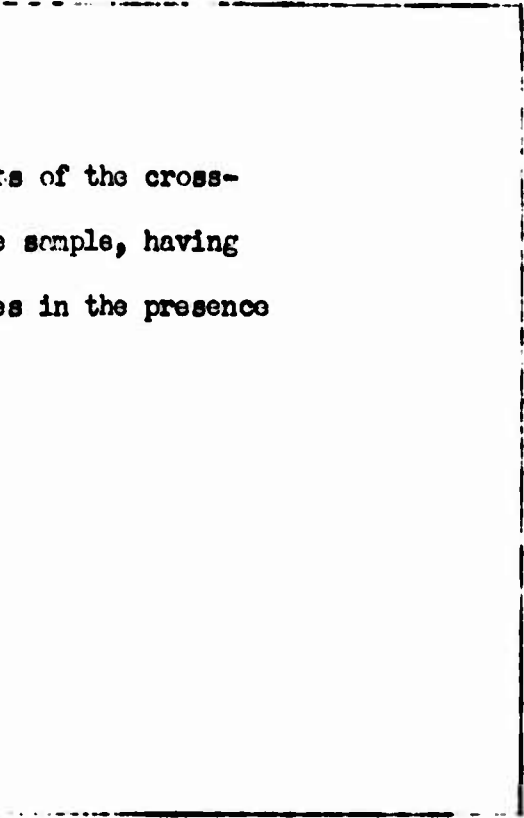
* by Prof. A. W. Quinn, Department of Geology, Brown University.

FIGURE 5

Photomicrograph of part of the cross-section of Cu 317 (Cu-0.13% Be) after the first heating in the presence of oxygen (130x).

FIGURE 6

Photomicrographs of parts of the cross-section of a Cu-0.11% Be sample, having been heated several times in the presence of oxygen (130x).



same as that of gel of aluminum oxide.

IV. DISCUSSION

Figs. 1 and 2 show that when Cu 314 (1.00% Al) and Cu 320 (0.50% Al) were heated in vacuum at about 800°C for over 100 hours (104 and 111 respectively), the attenuation in these samples for both longitudinal and transverse waves decreases at all the measured frequencies. Even though Cu 317 (0.13% Be) was not heated in vacuum, but was heated in a partial oxygen pressure, its attenuation coefficient decreased at first before it finally increased. (This sample was heated for a shorter period of time (18 hours), but at a higher temperature (980°C).) Therefore, it is concluded that in all three samples, the attenuation of both types of waves decreased at all measured frequencies, on heating at an elevated temperature for a long period of time.

As pointed out earlier, Cu 314 was heated in vacuum for a second time for another 86 hours. The attenuation coefficient did not further decrease* from its value after the first heating (Fig. 3), and this fact seems to indicate that in this alloy at least, a limit of the effect of heating has been reached during the first heating of 104 hours at 800°C or closely approached. If such a limit were also reached with Cu 320, it might be expected that the attenuation coefficients of Cu 314 and Cu 320 would perhaps be the same after vacuum annealing. A comparison of data shows that this was so in the case of transverse waves vibrating in the $[1\bar{1}0]$ direction (Fig. 3), but not in other cases. It may or may

* Close examination of Fig. 3 will show that the attenuation after the second heating was very slightly lower than the attenuation after the first heating.

not be coincidental that $[11\bar{0}]$ is a slip direction in copper.

Any explanation for the decrease in attenuation through annealing probably has to be based on the assumption that the internal state of the single crystal samples in their as-grown form were not in complete equilibrium. One possible consequence of vacuum annealing was that the alloying elements in heated samples became more evenly distributed because the as-grown single crystals may not have been homogeneous. Since inhomogeneity causes scattering of a transversing wave, the attenuation coefficient of a more homogeneous specimen should be smaller than that of a lesser one. The diffusion coefficients at 800°C of one per cent or less aluminum in copper was reported¹⁰ to be approximately $3.7 \times 10^{-10} \text{ cm}^2/\text{sec}$ or $1.3 \times 10^{-6} \text{ cm}^2/\text{hr}$ and that of one tenth of one per cent or less beryllium close to $4.2 \times 10^{-10} \text{ cm}^2/\text{sec}$ or $1.5 \times 10^{-6} \text{ cm}^2/\text{hr}$. Samples Cu 314 and Cu 320 were heated in vacuum for over 100 hours, during which the alloyed aluminum could migrate in appreciable amount, say one tenth of a millimeter. The samples might therefore be expected to be more homogeneous than before heating and decrease in their attenuation could be expected. In this connection it seems significant that for all three samples the reproducibility of the attenuation measurements improved after vacuum annealing or after a brief heating in the presence of oxygen (Figs. 1, 2, 3, and 4). However, since the amounts of elements alloyed in the samples were rather small (2.3 at. % of Al in Cu 314, 1.2 at. % of Al in Cu 320, and 0.9 at. % of Be in Cu 317), it is doubtful whether the decrease in attenuation due to homogenization and consequent decrease in scattering could be as large as those observed.

On the other hand, the migration of foreign atoms may affect the

attenuation in some other way than by changing the macroscopic property of the specimen, Koehler¹¹ proposed that an acoustic wave loses energy in a single crystal by exciting oscillation of sections of dislocation lines anchored by impurity atoms or other mechanisms. Koehler's investigation showed that the ratio of the energy loss per cycle to the total vibrational energy varies approximately with the inverse of the fourth power of¹² the concentration of solute atoms along a dislocation line. Cottrell showed that solute atoms differing in size from those of the solvent will migrate to the vicinity of dislocations where they can relieve stresses. Now the radii of copper, aluminum, and beryllium atoms are respectively 1.27, 1.43, and 1.11 Å. It probably can reasonably be assumed that the alloyed copper single crystals were not in complete equilibrium in their as-grown form. Additional solute atoms in the samples might have migrated during vacuum annealing toward the dislocations under the Cottrell force, increased the concentration of anchoring atoms along dislocation lines, and caused less attenuation of passing waves. This migration would eventually approach or reach its limit since there is, as Cottrell has shown, a saturation value of the concentration. This might explain the fact that the attenuation coefficients of Cu 314 did not alter during the second vacuum annealing.

It is obvious that the above interpretation is speculative. Even if the mechanism is correct, it may not be the only one responsible for the decrease in attenuation. For example the number of dislocations could have been reduced during vacuum annealing. For these reasons it seems that more quantitative analysis is needed and additional data is required for a really satisfactory interpretation. The relation between

dislocation motion and attenuation is under critical study in this laboratory. Further information is expected from a thorough study of the differences in attenuation values when longitudinal or transverse waves are used. Such differences should among other things depend on the direction of propogations in the crystal, the direction of vibration, and the slip direction.

On heating the three samples in the presence of oxygen, the attenuation increased for both types of waves at all measured frequencies (Figs. 1, 2, 3, and 4). As in the case of heating alone, no obvious regularity can be attributed to the magnitudes of changes in attenuation. Yet the general trend of increasing attenuation is unmistakable. Because of the diversity in the composition of the samples, in the orientation of samples, and probably in the condition of heat treatment (which will be further discussed below), it is not surprising that the observed magnitudes of changes in attenuation do not suggest any simple relation among them.

Copper alloys with 0.6 to 1.0% of aluminum were studied by Meijering⁶ and were reported to be hardened by heating at 950°C in air although when 1% of aluminum was alloyed with silver, it was found that there was no deep penetration of oxygen into the alloy. Rhines¹ examined microscopically copper containing from 0.01 to 0.91% of aluminum and reported that zones of internal oxidation were found in all cases. Rhines and his collaborators² identified by x-ray diffraction method the oxide as Al₂O₃. For the copper-beryllium alloy, Meijering⁶ reported that 0.2 to 0.35% of beryllium hardened copper most compared with the other alloying elements he studied. Rhines¹ observed subscales in copper alloyed with

0.018 to 0.101% of beryllium after heating at 1000°C. The oxide was supposed to be BeO.

On the strength of these findings and of the observations made in this study during preliminary runs in which rims were seen when the alloys were heated in the presence of oxygen relatively briefly, it is certain that Cu 314, Cu 320, and Cu 317 were internally oxidized. Some of these samples have not been cut and examined either because the sample has been damaged or because the sample is being preserved for further study.

From the empirical formulae obtained by Rhines and his collaborators², it can be estimated roughly how far oxygen penetrated into these samples. The estimate will be approximate because the experimental conditions in this study were not exactly the same as in their experiment. According to Rhines when an external scale of cuprous oxide was not formed, but a subscale alone was formed, the depth of penetration in centimeters, X, was given by

$$\log \frac{X^2}{t} = \frac{a}{T} + b$$

where t is the time of heating in seconds, T the absolute temperature, and a and b are constants for a particular alloy. On the other hand, if an external scale is formed simultaneously with the subscale, the thickness of the subscale, S, in centimeters is given by

$$\log \frac{S^2}{t} = \frac{c}{T} + d$$

where again c and d are constants for individual alloys. For a solid

solution of 0.45% Al in Cu, the constants are²

$$a = -11970 \quad b = 2.983 \quad c = -10800 \quad d = 1.215$$

Then at $T = 1000^{\circ}\text{C} = 1273^{\circ}\text{K}$,

$$X(\text{cm}) = 6.16 \times 10^{-4} \sqrt{t(\text{sec})} = 3.70 \times 10^{-2} \sqrt{t(\text{hr})}$$

$$S(\text{cm}) = 2.27 \times 10^{-4} \sqrt{t(\text{sec})} = 1.36 \times 10^{-2} \sqrt{t(\text{hr})}$$

For a solid solution of 0.101% of Be in Cu,

$$a = -11980 \quad b = 2.652 \quad c = -11980 \quad d = 2.572$$

and therefore at $T = 1000^{\circ}\text{C}$,

$$X(\text{cm}) = 4.17 \times 10^{-4} \sqrt{t(\text{sec})} = 2.50 \times 10^{-2} \sqrt{t(\text{hr})}$$

$$S(\text{cm}) = 3.80 \times 10^{-4} \sqrt{t(\text{sec})} = 2.28 \times 10^{-2} \sqrt{t(\text{hr})}$$

In the last case X and S do not differ much from each other.

The composition of Cu 320 and its temperature of heating are close to the first case discussed above while those of Cu 317 close to the second. The conditions of heating, i.e., of formation of external scale, etc., of these samples were somewhere between the condition under which the equation for X applies and that under which that for S is valid. Cu 320 was heated for 112 hours in the presence of oxygen. Therefore approximately for this sample

$$X = 0.39 \text{ cm}, \quad S = 0.14 \text{ cm}$$

The thickness of the sample during heating was 1.43 cm. Hence it is possible that half of the sample was internally oxidised after heating. The sample Cu 317 was heated twice for a total of 130 hours, and between

heatings was ground and lapped. Although thus not very definite, its thickness was in the neighborhood of 0.9 cm. For this sample X and S are approximately 0.3 cm. Therefore a possible two thirds of the sample was internally oxidized after the second heating. If for any reason, the oxygen did penetrate slightly deeper, there is the possibility that the sample was internally oxidized throughout. Then the earlier mentioned metallographic finding, that no second rim was seen after the second heating, is explained.

As to Cu 314 which contained 1.00% of Al, the closest alloy tabulated by Rhines is Cu-0.72% Al. For the later,

$$a = -12140 \quad b = 2.753 \quad c = -12140 \quad d = 2.015$$

from which it follows, at $T = 1000^{\circ}\text{C}$,

$$X(\text{cm}) = 4.06 \times 10^{-4} \sqrt{t(\text{sec})} = 2.44 \times 10^{-2} \sqrt{t(\text{hr})}$$

$$S(\text{cm}) = 1.73 \times 10^{-4} \sqrt{t(\text{sec})} = 1.04 \times 10^{-2} \sqrt{t(\text{hr})}$$

The length of time during which Cu 314 was heated the first time in the presence of oxygen was 44 hours. Then approximately

$$X = 0.16 \text{ cm} \quad S = 0.07 \text{ cm}$$

The thickness of Cu 314 during heating was 1.57 cm. Therefore, no more than one-fifth of its thickness was internally oxidized after the first heating in oxygen.

For the explanation of the increase of attenuation with internal oxidation, it will be noticed that the existence of oxidation boundaries within a sample can cause some energy loss to the progressing pulse of wave,

no matter how far within the boundaries are from the surfaces. A wave is partially reflected at the boundary of two media and the energy of the transmitted wave is always less than that of the incident wave. It is generally true that the oxidation front is reasonably parallel to the surface of the specimen (Figs. 5 and 6). Then it can be assumed in the samples the travelling wave impinged on the boundaries normally and therefore only a longitudinal wave was reflected from an incident longitudinal wave and a transverse from an incident transverse wave. If A_1 is the amplitude of an incident longitudinal wave, and A_2 that of the reflected, ρ_a the density of the medium in which the wave travels before meeting the boundary, ρ_b that of the second medium, and c_1 and c_2 the velocities of the longitudinal wave in the first and second media respectively, then

$$A_2 = A_1 \frac{\rho_b c_2 - \rho_a c_1}{\rho_b c_2 + \rho_a c_1}$$

Similarly, for the transverse wave,

$$B_2 = B_1 \frac{\rho_b c_4 - \rho_a c_2}{\rho_b c_4 + \rho_a c_2}$$

Of the samples studied, the differences in the acoustic impedances of the internally oxidized parts and the parts which have not been oxidized are not known, and it is only possible to say that while some energy was definitely lost by the travelling pulse of wave due to the existence of oxidation boundaries, the amount of the loss was probably small compared to the loss observed experimentally. The reason for this conclusion is simply that the impedance change determines the reflection coefficient,

but the measured velocities c_1, c_2, c_3, c_4 before and after oxidation do not differ by a measurable amount. Changes in the impedance from unoxidized to oxidized regions then depend only on density changes which are small in the present case.

The increase in the attenuation on internal oxidation appears to be caused by the scattering of the wave by the precipitated oxides. Meijering and Druyvesteyn⁵ reported that the copper alloys they studied have in the oxidized state a lattice spacing that was almost equal to that of pure copper. This indicated that Al_2O_3 and BeO were not dissolved, but existed in the form of precipitates. Rhinos¹ metallographically observed oxide particles in all copper alloys studied (although the picture he presented¹ of the alloy containing 0.17% of aluminum did not show the distinct individual particles evident in other alloys, including Cu-0.054%Be). It is reasonable to assume, therefore, that the precipitated oxides scattered energy from the travelling pulse and increased the attenuation. The scatterers might also be aggregates other than individual oxide molecules; for example, some oxide lamellae have been observed¹ inside Cu-Al and Cu-Be alloys.

Here again any attempt to further elaborate this interpretation must rely on a quantitative analysis of scattering* as well as more systematic experimental results. In addition other possible mechanisms may be involved. For example, as the solute atoms formed precipitates, the motion of dislocations and consequently the attenuation would be affected.

* in progress.

In closing, a rather interesting experimental finding may be mentioned. On several occasions during preliminary runs, the attenuation in some samples which had just been heated, was found to decrease consistently when the attenuation was repeatedly measured after each time remounting the transducer. This decrease in attenuation continued until a certain low value of the attenuation was reached, and after this point was reached further remounting of crystal and measurement produced no change within the experimental error. The cause of this effect has not been determined with certainty. One possible cause was the pressure applied to the sample during the mounting of a transducer, for this pressure, estimated conservatively, was about 100 g/mm^2 , or larger. Another possible cause was the passing of the acoustic wave through the sample. In one run, measurements were repeatedly taken with the same mounted transducer; some initial decrease in attenuation was noticed, but the decrease was not large enough to be really certain of the effect. It was not certain however that in this particular run the condition of treatment was exactly right for obtaining such initial decreases. This phenomenon remains to be studied further. Read's ¹³ work on single crystals of copper and zinc is interesting in this connection.

APPENDIX I

In the figures in the text the attenuation is measured in db/ μ s, a unit in which our measuring instrument is calibrated. Without measuring the velocity of propagation, the directly read values can indicate any change in the attenuation in the same sample or compare the attenuation in samples of the same nature as long as the velocity is known to remain unchanged. To evaluate the absolute value of attenuation, however, it is necessary to measure, in addition, the velocity of propagation of the wave. The attenuation constant α is defined by

$$u(x) = u(o) e^{-\alpha x}$$

or

$$\sigma(x) = \sigma(o) e^{-\alpha x}$$

where $u(x)$ and $\sigma(x)$ are respectively the maximum vibration amplitude and the maximum stress amplitude after the wave has travelled a distance x from the origin at which its amplitudes were respectively $u(o)$ and $\sigma(o)$. It can easily be shown that

$$\alpha(\text{db/in}) = 2.54 \times 10^6 \frac{\text{value of attenuation in db}/\mu\text{s}}{\text{velocity of propagation in cm/sec}}$$

$$\alpha(\text{neper/cm}) = 1.15 \times 10^5 \frac{\text{value of attenuation in db}/\mu\text{s}}{\text{velocity of propagation in cm/sec}}$$

one neper being 8.68 db.

The internal friction is defined as the ratio $\frac{\Delta W}{W}$ where ΔW is the energy dissipated in taking a specimen through a stress cycle and W is the energy stored up in the specimen when the stress is maximum. It can

be shown that approximately

$$\frac{\Delta W}{W} = \frac{2v}{f \lambda} \alpha$$

where v is the velocity of propagation and f the frequency. It may be pointed out that a term $\frac{I(0) - I(\frac{v}{f})}{I(0)}$ has been shown¹⁴ to be

$$\frac{I(0) - I(\frac{v}{f})}{I(0)} = 1 - e^{-\frac{2v}{f} \alpha}$$

$$\approx \frac{2v}{f} \alpha \quad \text{if } \frac{2v}{f} \alpha \ll 1$$

where $I(x)$ is the intensity of a travelling pulse of plane sinusoidal wave at distance x from the starting point. At $x = \frac{v}{f}$, the wave phase is the same as that at $x = 0$. This fraction gives some measure of the fraction of energy dissipated during one oscillation and seems to be a natural physical quantity for a travelling square wave pulse. As shown here it turns out to be numerically equal to $\frac{\Delta W}{W}$.

The velocities of propagation of longitudinal and transverse waves travelling in the three samples were measured and are listed in Table I*. The measured values were not corrected for the time spent by the pulse in the quartz and the salol which cemented the quartz onto the sample, but the errors thus introduced are likely not over one per cent¹⁵.

* The corresponding velocities in Cu-4\% Si as measured by Smith and Burns are approximately $\frac{12}{2.7}$, $\frac{12}{4.5}$, and $\frac{12}{8.5} \times 10^5$ cm/sec or approximately 4.5, 2.7 and 1.4 $\times 10^5$ cm/sec for waves travelling in the direction of $[110]$. These values differ by about 10% from values obtained in this study. The cause of these differences is under study.

TABLE I

VELOCITIES OF PROPAGATION

Sample	Type of Wave	Direction of Propagation	Direction of Vibration	VELOCITY OF PROPAGATION		
				Sample as Grown	Sample Heated in Vacuum	Sample Heated in the Presence of Oxygen
Cu 314 (1.00% Al)	Longitudinal Transverse Transverse	$\{110\}$ $\{110\}$ $\{110\}$	$\{110\}$ $\{001\}$ $\{110\}$	4.94	4.93	4.95
				2.90	2.90	2.91
				1.60	1.60	1.60
Cu 320 (0.050% Al)	Longitudinal Transverse Transverse	$\{110\}$ $\{110\}$ $\{110\}$	$\{110\}$ $\{001\}$ $\{110\}$	4.92	4.92	4.92
				2.89	2.89	2.88
				1.60	1.60	1.60
Cu 317 (0.13% Be)	Longitudinal	$\{111\}$	$\{111\}$	5.08	5.09	5.08

Also, within experimental error, no dispersion was observed in the measured frequency range, and therefore although the measured velocities were actually group velocities instead of phase velocities, values of the two velocities are not expected to be discrepant appreciably if at all.

The internal friction of Cu 320 when traversed by a transverse wave with its direction of vibration parallel to $[\bar{1}\bar{1}0]$ has been computed as an illustration for all the studied samples. It is plotted as a function of frequency in Fig. 7. The attenuation in db/in and neper/cm can easily be seen (Table I) to be

$$\alpha (\text{db/in}) = 15.9 \times \text{value of attenuation in db}/\mu \text{ s}$$

$$\alpha (\text{neper/cm}) = 0.719 \times \text{value of attenuation in db}/\mu \text{ s}.$$

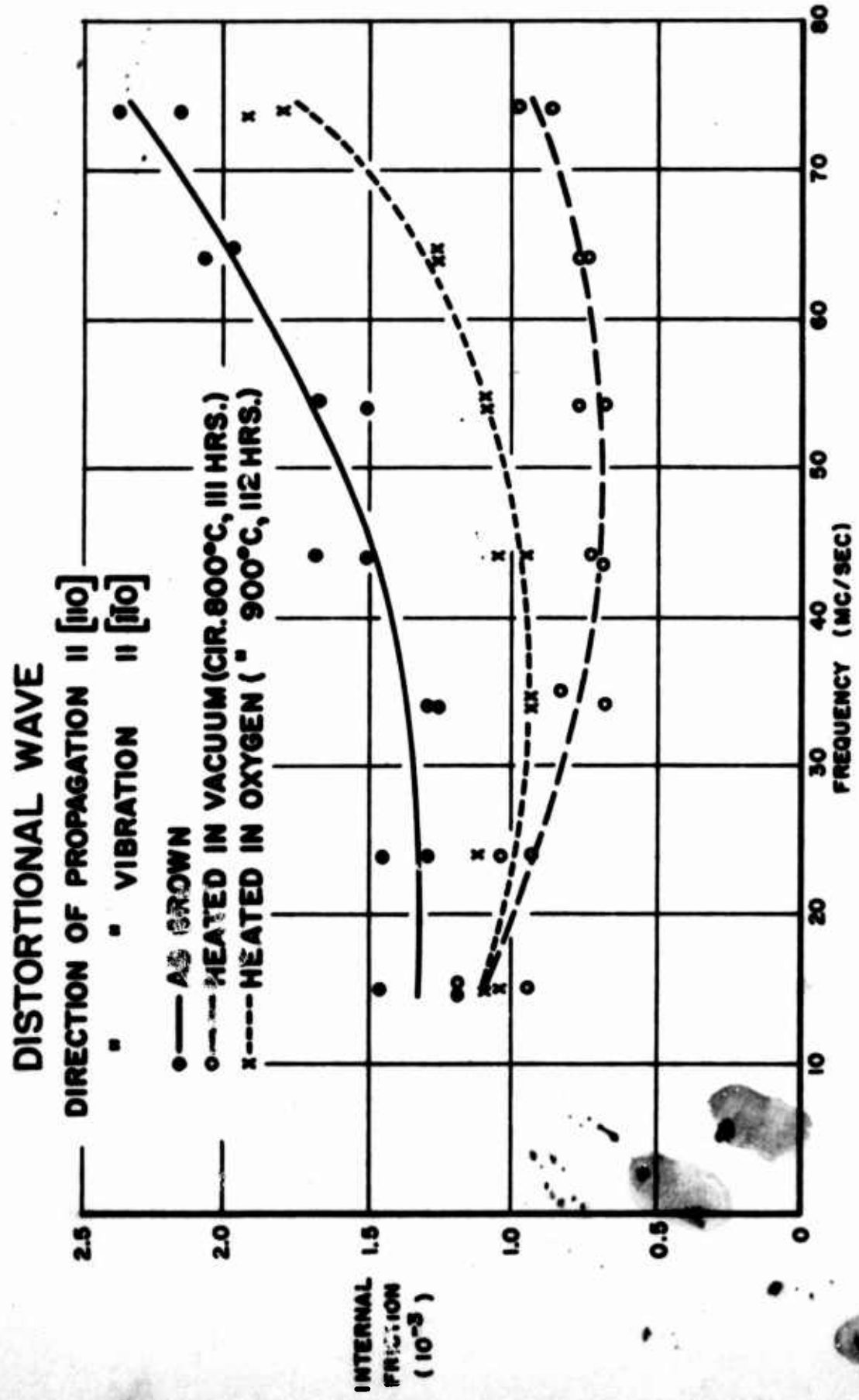


FIG. 7 INTERNAL FRICTION - FREQUENCY PLOT OF CU 320
(SINGLE CRYSTAL OF COPPER ALLOYED WITH 1/2% OF ALUMINUM.)

APPENDIX II

The strain amplitude of the acoustic wave generated by the use of a quartz transducer bonded onto a specimen is estimated by computing the strain of the cemented face of the transducer. The computation is based on the equation of motion and the piezoelectric equations of the quartz transducer and some circuital relations.

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is Consider an X-cut quartz transducer. Its equation of motion

$$\frac{\partial^2 \xi}{\partial t^2} = v^2 \frac{\partial^2 \xi}{\partial x^2} \quad (1)$$

while its piezoelectric equations are

$$-X = \frac{\partial \xi}{\partial x} X_0 + DQ \quad (2)$$

$$E = \frac{4\pi Q}{K} + D \frac{\partial \xi}{\partial x} \quad (3)$$

in which the x-axis is along the thickness of the crystal and

X_0 = Young's modulus along the thickness of the crystal

D = a piezoelectric constant relating the stress generated by the piezoelectric effect to the applied surface charge

= 13.85×10^4 c.g.s. for an X-cut quartz crystal

K = the longitudinally clamped dielectric constant

Q = the surface charge per unit cross-sectional area of the crystal

E = the electric field in the direction of the thickness of the crystal

X = the longitudinal stress in the direction of the thickness of the crystal

$$v = \sqrt{\frac{X_0 \left(1 - \frac{D^2 K}{4\pi X_0}\right)}{\rho}}$$

$$= \sqrt{\frac{c}{\rho}}$$

$$c = X_0 \left(1 - \frac{D^2 K}{4\pi X_0}\right)$$

= the elastic stiffness of the crystal

ρ = the density of the crystal

If

$$E = E_0 e^{j\omega t} \quad (4)$$

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then on the integrating Equation (1) with respect to time and on combining all the foregoing equations, one gets

$$\dot{\xi} = \dot{\xi}_1 \cos \frac{\omega X}{v} - j \frac{F_1 + \varphi V}{Z} \sin \frac{\omega X}{v} \quad (5)$$

$$i = -\varphi (\dot{\xi}_2 - \dot{\xi}_1) + j\omega \frac{\varphi V}{D} \quad (6)$$

$$F + \varphi V = (F_1 + \varphi V) \cos \frac{\omega X}{v} - j \dot{\xi}_1 Z \sin \frac{\omega X}{v} \quad (7)$$

where

A = the cross-sectional area of the crystal

F = the force on a cross-sectional area
= $X A$

$$\varphi = \frac{DKA}{4\pi l_t}$$

l_t = the thickness of the crystal

$$V = E l_t$$

= the electric potential difference across the thickness of the crystal

$$Z = \rho vA$$

$$i = \frac{\partial Q}{\partial t}$$

and the subscripts 1 and 2 indicate that the values be evaluated at the end faces of the crystal. The end faces are so located that their equilibrium positions are respectively $x = 0$ and $x = l_t$, the later position being that of the cemented face marked with the number "2".

In the experimental set-up in this study, the crystal is free at the end "1" while it drives the specimen at the end "2". Therefore

$$F_1 = 0$$

and Equations (5), (6), and (7) become

$$\dot{\xi} = \dot{\xi}_1 \cos \frac{\omega x}{v} - j \frac{\phi V}{Z} \sin \frac{\omega x}{v} \quad (8)$$

$$i = -\phi (\dot{\xi}_2 - \dot{\xi}_1) + j \omega \frac{\phi V}{D} \quad (9)$$

$$F + \phi V = \phi V \cos \frac{\omega x}{v} - j \dot{\xi}_1 Z \sin \frac{\omega x}{v} \quad (10)$$

This set of equations, together with appropriate conditions for the source of potential and the load, can be solved¹⁶ for $\dot{\xi}_2$ by using an equivalent electric network. On disregarding the bond between the crystal and the specimen, it can be shown that when the frequency of the applied potential is close to the resonance frequency of the quartz transducer,

$$\xi_2 = \frac{E}{\sqrt{\alpha^2 + \beta^2}} e^{-j \tan^{-1} \frac{\beta}{\alpha}} \quad (11)$$

where

$$\alpha = R_T + \frac{Z_S}{4\varphi^2} - \frac{R_T C_O}{4\varphi^2 C_M} \left(1 - \frac{\omega^2}{\omega_R^2}\right) \quad (12a)$$

$$\beta = \omega \frac{R_T C_O Z_S}{4\varphi^2} - \frac{1}{\omega} \frac{1}{4\varphi^2 C_M} \left(1 - \frac{\omega^2}{\omega_R^2}\right) \quad (12b)$$

in which

$$\omega_R = \pi \frac{v}{l_t} \quad (13)$$

is the resonance angular frequency and

R_T = the resistance of the transmitter which produces the potential difference V across the crystal

$$C_O = \frac{AK}{4\pi l_t}$$

$$C_M = \frac{2}{\pi^2} \frac{l_t}{\Lambda_c}$$

$$Z_S = \rho_S v_S A$$

ρ_S = the density of the sample the attenuation of which is being measured

v_S = the speed of the ultrasonic wave in the sample

The effect of the bond is negligible if the bond is very thin and stiff.

$\dot{\xi}_2$ being known, one can solve for $\dot{\xi}_1$, for from Equation (8)

$$\dot{\xi}_2 = \dot{\xi}_1 \cos \frac{\omega l_t}{v} - j \frac{\varphi V}{Z} \sin \frac{\omega l_t}{v}$$

and therefore

$$\dot{\xi}_1 = \left(\dot{\xi}_2 \sec \frac{\omega l_t}{v} + j \frac{\varphi V}{Z} \tan \frac{\omega l_t}{v} \right) \cos \frac{\omega X}{v} - j \frac{\varphi V}{Z} \sin \frac{\omega X}{v} \quad (14)$$

Substituting Equation (11) and the equation

$$v = v_0 e^{j\omega t} \quad (15)$$

into Equation (14) and integrating the later with respect to t, one gets

$$\xi = \frac{v}{\omega} \left[-\frac{\phi}{Z} \sin \frac{\omega x}{v} + \left(\frac{\phi}{Z} \tan \frac{\omega l_t}{v} - j \frac{1}{\sqrt{\alpha^2 + \beta^2}} e^{-j \tan^{-1} \frac{\beta}{\alpha} \sec \frac{\omega l_t}{v}} \right) \cos \frac{\omega x}{v} \right] + f(x)$$

The undetermined term f(x) does not vary with t and therefore has no significance to the generation of an acoustic wave. It will be taken as zero. Then

$$\xi = e^{j\omega t} \frac{v_0}{\omega} \left[-\frac{\phi}{Z} \sin \frac{\omega x}{v} + \left(\frac{\phi}{Z} \tan \frac{\omega l_t}{v} - j \frac{1}{\sqrt{\alpha^2 + \beta^2}} e^{-j \tan^{-1} \frac{\beta}{\alpha} \sec \frac{\omega l_t}{v}} \right) \cos \frac{\omega x}{v} \right] \quad (16)$$

It follows that

$$\frac{\partial \xi}{\partial x} = e^{j\omega t} \frac{v_0}{v} \left[-\frac{\phi}{Z} \cos \frac{\omega x}{v} - \left(\frac{\phi}{Z} \tan \frac{\omega l_t}{v} - j \frac{1}{\sqrt{\alpha^2 + \beta^2}} e^{-j \tan^{-1} \frac{\beta}{\alpha} \sec \frac{\omega l_t}{v}} \right) \sin \frac{\omega x}{v} \right] \quad (17)$$

which is the strain at position x.

At the cemented face of the quartz transducer,

$$\left(\frac{\partial \xi}{\partial x}\right)_2 = e^{j\omega t} \frac{V_0}{v} \left(-\frac{\phi}{Z} \sec \pi \frac{\omega}{\omega_R} + j \frac{1}{\sqrt{\alpha^2 + \beta^2}} e^{-j \tan^{-1} \frac{\beta}{\alpha}} \tan \pi \frac{\omega}{\omega_R} \right) \quad (18)$$

When $\omega = \omega_R$, the formula reduces to the simple form

$$\left(\frac{\partial \xi}{\partial x}\right)_{2, \omega = \omega_R} = \frac{\phi V_0}{v Z} e^{j\omega t} \quad (19)$$

The strain amplitude of the quartz transducer when the transducer is operated at its resonance frequency is then

$$\left| \left(\frac{\partial \xi}{\partial x}\right)_2 \right|_{\omega = \omega_R} = \frac{V_0 \phi}{v Z} \quad (20)$$

This is also the strain amplitude of the cemented end of the specimen if the bond is very stiff and thin. This is the quantity sought.

In the case of a 10 mc, X-cut quartz transducer,

$$\omega_R = 6.18 \times 10^7 / \text{sec}$$

Since

$$c = 4.05 \times 10^{11} \text{ g/cm sec}^2$$

$$\rho = 2.65 \text{ g/cm}^3$$

$$v = \sqrt{\frac{c}{\rho}} = 5.60 \times 10^5 \text{ cm/sec}$$

$$K = 4.55$$

one has

$$l_t = 2.80 \times 10^{-2} \text{ cm}$$

and

$$\left| \left(\frac{\partial \xi}{\partial x} \right) \right|_2 \omega = \omega_R = 6.18 \times 10^7 = 1.08 \times 10^{-6} V_0$$

In this study, approximately

$$V_0 = 500 \text{ volts} = 1.67 \text{ e.s.u.}$$

Then

$$\left| \left(\frac{\partial \xi}{\partial x} \right) \right|_2 \omega = \omega_R = 6.18 \times 10^7 = 1.80 \times 10^{-6}$$

For the computation of the strain amplitude at frequencies other than (but close to) the resonance frequency, other quantities must be known as shown in Equation (18).

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