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EVALUATION OF MICROPOROSITY BY MHZ-ATTENUATION MEASUREMENTS

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Abstract - Attenuation due to the scattering of ultrasound by micropores has been measured in Mn, S and Be doped copper single crystals grown by the Czochralski- and Bridgeman-techniques. After suppression of dislocation damping by γ-irradiation the attenuation \( \alpha_p \) due to pore scattering has been determined quantitatively in the frequency range 10 to 300 MHz. By fitting the theoretical \( \alpha_p(f) \)-dependence for spherical holes to the measured \( \alpha_p(f) \)-data we obtain the porosity \( P \) and the mean pore-diameter \( d_p \).

Pulsed ultrasonic techniques have found widespread use mainly as time-of-flight measurements e.g. for location of faults and as thickness gauges. There is current interest for measurements of back scattered sound for grain size measurements and for sound velocity effects to measure internal stresses /1/. The main problem for the evaluation of attenuation (and sound velocity) data is that a number of different physical phenomena simultaneously contribute to these sound transport properties /2/.

For the purpose of the present paper the measured total attenuation \( \alpha \) is given by

\[
\alpha = \alpha_G + \alpha_p + \alpha_D + \alpha_B
\]

where \( \alpha_G, \alpha_p \) are scattering contributions due to the presence of internal "surfaces" (grains \( \alpha_G \), pores \( \alpha_p \)); \( \alpha_D \) is due to absorption caused by dislocations and \( \alpha_B = \ell \alpha_B \) is the "background" attenuation due to all other scattering- and absorption- and phase-effects /2/.

The present paper is concerned with ultrasonic measurements on single crystals \( \alpha_G = 0 \) containing micropores (porosity \( P, \alpha_p \neq 0 \)) as well as mobile dislocations (dislocation density \( \lambda, \alpha_D \neq 0 \)); i.e.

\[
\alpha = \alpha_p + \alpha_D + \alpha_B
\]

By γ-irradiation the dislocation contribution can be suppressed \( \alpha_D = 0 \), i.e.

\[
\alpha_\gamma = \alpha_p + \alpha_B
\]

Furthermore the attenuation of a pore free \( (P = 0, \alpha_p = 0) \) Cu-crystal of identical orientation and identical sample condition (surface flatness, roughness, planparallelity) after complete dislocation pinning \( \alpha_D = 0 \) is given by \( \alpha_\gamma, P=0 = \alpha_B, P=0 \). Thus the pore scattering is given by

\[
\alpha_p = \alpha_\gamma - \alpha_\gamma, P=0
\]
under the valid assumption $a_B = a_B P = 0$, i.e. that the background values of porous and porefree specimens are identical.

To our knowledge the present paper presents the first experimental scattering data over a broad frequency range for a well defined scattering process (spherical holes in single crystalline matrix). By comparison with scattering theory the pore diameter $d_p$, the pore concentration $n_p$ (number/cm$^3$) and the porosity $P = 4\pi r^3 P/3$ can be evaluated.

EXPERIMENTAL

Ultrasonic samples were spark-erosion-cut from Bridgeman single crystals grown of high purity (Elmore) Cu, Cu+5ppmS, Cu+440ppmBe and from a Czochralski crystal of (ASARCO) Cu+200ppmMn. After grinding off the highly disturbed surfaces (0.2 mm) the samples were lapped flat and planparallel (0.5μm/cm) to a final orientation accuracy of better than 0.5° from <111>. The attenuation was measured with standard MATEC-equipment between 10 and 300 MHz using 0.25"Ø X-cut quartz transducers (VALPEY) and NONAQ-bond. For dislocation pinning 3 MeV-γ-Bremsstrahlung was used /3/. After RT-irradiation the samples were annealed 1 h at 100°C for maximum pinning /4/. A 3 MeV-γ-dose of $\Phi = 2.500 \mu$Ah results in about $1.2 \cdot 10^{14}$ Frenkel defects/cm$^3$ /3/.

RESULTS

Fig.1 shows the $a(f)$-data. The pure (Bridgeman) Cu-sample (curve 1, $a_1 = a_0 + a_\gamma$) exhibits the highest attenuation due to strong dislocation resonance damping contributions ($a_\gamma$). This is seen by comparison with curve 2 which is measured after strong γ-irradiation of the above sample ($a_2 = a_\gamma$). Curve 3 is measured on the Cu200ppmMn (Czochralski) sample after very strong γ-irradiation ($a_3 = a_\gamma + a_B$). The dose was chosen 4 times higher than for the pure sample because the initial dislocation loop length in the doped crystal is smaller and a higher Frenkel defect concentration is needed in order to completely pin the dislocations. It is seen that after complete dislocation pinning $a_3 > a_2$ at all frequencies. This excess attenuation is attributed to pore scattering. Curve 4 shows the frequency dependence of the pore scattering attenuation ($a_4 = a_3 - a_2 = a_B$).

DISCUSSION

Sound scattering by pores: In the case of independent scattering centers the sound intensity $dI$ scattered out of the sound wave of intensity $I$ over the sound path length $dx$ is given by

$$dI = -n_p \gamma I dx$$

where in the present case $n_p$ is the concentration of pores (number/cm$^3$) and $\gamma = \gamma(kr)$ is the frequency- and sizedependent scattering cross section of a single pore ($k = 2\pi/\lambda = 2\pi f/v$, $v$ = sound velocity, $r$ = pore radius). Since $a = -0.5 d\ln I/dx$ we obtain

$$a_p = n_p \gamma/2$$

Assuming a uniform pore size (delta function distribution) and using the normalized cross section $\gamma_0(kr) = \gamma/\pi r^2$ and the porosity $P = n_p 4\pi r^3/3 (= \text{total pore volume/cm}^3$) we obtain
In Fig. 2 we have plotted the theoretical $\gamma_N(kr)$-calculations by True et al. /5/ on log/log scales as $\gamma_N(kr)/kr$ versus $kr$. Such a plot is considered to be best suited for comparison with experimental data. In the range $kr<<1$ Rayleigh scattering, in the range $kr>>1$ stochastic scattering dominates.

Comparison with experiments: According to equ. (8) the theoretical mastercurve given in Fig. 2 is to be compared with a log/log plot of $\alpha_p/f$ versus $f$. Fig. 3 shows such a plot of the $\alpha_p/f$-data for Cu200ppmMn (cf. curve 4 in Fig. 1). The fit by the master curve of Fig. 2 is extremely good indicating that in this sample the pores are of uniform size. This is not the case for the doped Cu-samples shown in Fig. 4, which exhibit a less narrow $\alpha_p/f$ vs $f$ dependence and where the delta function master curve (Fig. 2) can only be used as an approximate description of the data. The discussion of pore size distributions needed to fit the $\alpha_p$-data for Cu5ppmS and Cu440ppmBe is postponed to another paper. Microscopic examinations of the electrolytically polished samples as function of depth below the (111)-surface indeed show very homogeneous pore diameters in the 10 $\mu$m range for Cu200ppmMn but rather inhomogeneous pore sizes for the samples of Fig. 4 (e.g. in Cu5ppmS relatively very large pores with most pores however in the 20 to 40 $\mu$m diameter range).

Evaluation of pore diameter and porosity: The coordinates of the maximum in Fig. 2 are given by

\[ (kr)_{\text{MAX}} = 0.9 \]
\[ (\gamma_N/kr)_{\text{MAX}} = 3.9 \]

In the experimental data plot the maximum is observed at $f_{\text{MAX}}$, $(\alpha_p/f)_{\text{MAX}}$ and we obtain from equ. (9a,b) and (8)

\[ r = 0.14 \frac{v}{f_{\text{MAX}}} \]
\[ P = 0.11 \frac{v(\alpha_p/f)_{\text{MAX}}}{\alpha_{[\text{Np/cm}]}} \]
\[ = 0.025 \frac{v(\alpha_p/f)_{\text{MAX}}}{\alpha_{[\text{dB/\mu sec}]}} \]

With these relations and the fits in Fig. 3 and 4 resp. we derive the porosity data given in

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pore Radius $r$ [\mu m]</th>
<th>Porosity $P$ [Vol %]</th>
<th>Pore Concentration $n_p$ [pores/cm$^3$]</th>
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<tbody>
<tr>
<td>Cu200ppmMn</td>
<td>6</td>
<td>$6 \cdot 10^{-3}$</td>
<td>$6.6 \cdot 10^4$</td>
</tr>
<tr>
<td>Cu5ppmS</td>
<td>17 *)</td>
<td>$10^{-2}$</td>
<td>$4.9 \cdot 10^3$</td>
</tr>
<tr>
<td>Cu440ppmBe</td>
<td>11 *)</td>
<td>$9 \cdot 10^{-3}$</td>
<td>$1.6 \cdot 10^4$</td>
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*) effective pore radius
Origin of Porosity: High purity Cu-crystals grown by the Czochralski technique are known to be highly perfect with respect to dislocation structure (low dislocation density $10^2-10^4\text{cm}^{-2}$, no small angle grain boundaries /6/). However, these crystals contain pores which have been attributed to vacancy condensation possibly assisted by simultaneous precipitation of the residual gaseous impurities (oxygen and/or hydrogen /7/). In Mn-doped Czochralski crystals the pore concentration is increased and the pore size distribution is narrower. These effects are attributed to enhanced pore nucleation due to Mn/vacancy trapping.

In contrast pure Bridgeman crystals are known to have comparatively high dislocation densities ($10^2-10^6\text{cm}^{-2}$) caused by contact with the hard crucible and additional small-angle grain boundaries /8/, however these crystals show negligible porosity. The latter is attributed to the increased vacancy sink density (dislocations) which favours annihilation of vacancies by dislocation climb. However, doped Bridgeman crystals also exhibit considerable microporosity which we attribute to impurity-vacancy trapping as in the doped Czochralski crystals.

Experimental limits for ultrasonic pore measurements: Fig.5 depicts the limiting ranges for ultrasonic measurements of porosity and pore diameter. It is seen that $P_{\text{MAX}}$ and $P_{\text{MIN}}$ both are functions of $d$. The limits for $d$ are derived from equation (10) under the assumption that the attenuation measurements cover the $f$-range from 2 to 300 MHz with the $(\alpha_f/f)$-maximum situated within the range 5 to 250 MHz; the latter range allows the proper observation of the maximum. According to Fig.5 the smallest observable pore diameter is about 6 $\mu$m whereas the maximum diameter is about 300 $\mu$m. The maximum porosity is determined by the highest total attenuation $\alpha_{\text{LIM}}$ which can be measured by the standard pulse echo technique ($\alpha_{\text{LIM}}$ = 6 dB/µsec corresponds to just two pulse echoes i.e. 4 passages of the pulse through a sample of about 1 cm length). Taking account of the $f$-dependent background attenuation $\alpha_{\text{B}}$ (cf. curve 2 in Fig.1) the limiting pore scattering attenuation is given by $\alpha_{\text{P}} = \alpha_{\text{LIM}} - \alpha_{\text{B}}$. With this value the upper limit $P_{\text{MAX}}(d)$ in Fig.5 is derived. On the other side the lower limit $P_{\text{MIN}}(d)$ is a consequence of the fact that $\alpha_{\text{P}}$ can only be measured with limited accuracy. Thus we have to assume that $\alpha_{\text{P}}$ must be at least 20% of the $\alpha_{\text{B}}$ value in order to make reasonable separation and $(\alpha_f/f)$ plots (cf. Fig.3) possible. As an example for the use of Fig.5 we find that pores with 50 $\mu$m diameter can be ultrasonically measured in the porosity range $5 \times 10^{-4}$ to $1.5 \times 10^{-3}$ Vol %.

It can be shown that attenuation measurements are much more sensitive for porosity detection than sound velocity measurements which yield $\Delta v/v = 8 \times 10^{-3}$ P; P[Vol %] /9/. We remind that Fig.5 only applies to the very special case of pores in a single-crystalline matrix. In polycrystals, however, sound scattering due to grain boundaries normally becomes very large ($\alpha_{\text{G}} > \alpha_{\text{LIM}}$) already at low frequencies (beyond 10 to 20 MHz) which makes the necessary broadband measurements of $\alpha_{\text{P}}(f)$ impossible. However, we believe that ultrasonic techniques can be used to evaluate porosity from measurements of backscattered sound instead of transmitted sound (pulse echo attenuation). These ultrasonic techniques would be of greatest interest for detection of voids and porosity e.g. in reactor materials.

ACKNOWLEDGEMENTS

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REFERENCES


/5/ in ref. /2/ pp. 391-405.


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<table>
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<tr>
<th>#</th>
<th>Material</th>
<th>RRR</th>
<th>$\Phi_j [\mu A h]</th>
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<td></td>
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<tr>
<td>2</td>
<td>--</td>
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<td>$2500$</td>
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<tr>
<td>3</td>
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<td>11400</td>
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<td>4</td>
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<td>$\approx$</td>
<td>$a_j$</td>
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</table>

Fig. 1: Frequency dependence of attenuation $a$ for 3 different sample states (c.f. inserted table).
**Fig. 2:** Normalized sound scattering cross section for a spherical hole (radius $r$) in Cu versus $k \cdot r$ ($k=2\pi f/v$; $f=\text{frequency}$, $v=\text{sound velocity}$).

**Fig. 3:** Measured $\alpha_p/f$-data for Cu200ppmMn (c.f. Curve 4 in Fig. 1) versus $f$ fitted by the theoretical scattering dependence (dashed curve, c.f. Fig. 2).

**Fig. 4:** $\alpha_p/f$-data for Cu5ppmS and Cu440ppmBe.

**Fig. 5:** Range of porosity $P$ as function of pore diameter $d_p$ (shaded area) which is accessible by ultrasonic attenuation measurements in Cu in the f-range 2-300 MHz.