Photopyroelectric Measurement of the Thermal Diffusivity of Recrystallized High Purity Aluminum

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Abstract. Thermal diffusivity measurements on high purity (99.99% pure) aluminum samples are reported, using chirped and sinusoidally-modulated laser excitation and photopyroelectric detection of the thermal wave response. The results are found to be dependent on the degree of recrystallization of the specimen: for cold-rolled aluminum, the thermal diffusivity is measured to be $\alpha = 3.10 \times 10^{-5} \text{ m}^2/\text{s}$, which rises to $3.88 \times 10^{-5} \text{ m}^2/\text{s}$ for fully recrystallized samples, and then falls to $3.53 \times 10^{-5} \text{ m}^2/\text{s}$ for samples exhibiting the initial stages of grain growth.

Introduction

The measurement of laser-excited thermal wave phenomena through the use of pyroelectric detectors, known as the photopyroelectric (PPE) technique, has recently been demonstrated to be a simple and sensitive method for the thermal analysis of condensed matter [1–4]. Photothermal techniques, of which photopyroelectric methods form a subset, have already been shown to be applicable to nondestructive materials evaluation [5–7] and to the monitoring of industrial processes, measuring such things as doping levels in semiconductors [8–9], and metal oxide homogeneity in magnetic recording media [10–11]. Among the many alternative photothermal detection techniques, however, PPE methods combine high temporal resolution with high sensitivity and low cost [12]; consequently pyroelectric materials such as thin-film polyvinylidene fluoride (PVDF) show great potential for use as sensor elements in thermal and spectroscopic photothermal detection systems.

In previous reports the PPE technique was applied to the study of the thermal properties of quartz, aluminum and stainless steel [13–15], as well as to the high- T_c superconductors [16–20]. The present work reports PPE measurements for the thermal diffusivity of high purity aluminum in various stages of recrystallization, using a chirped laser excitation technique and a thin PVDF

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film as the detector element. A single-frequency modulation PPE technique, which yields relative values for the thermal diffusivity, is also applied, and is shown to give results that are in good qualitative agreement with the absolute chirped PPE measurements. The results show consistent differences in the specimen thermal diffusivity depending on the degree of recrystallization; this could indicate a possible crystallographic anisotropy of the thermal diffusivity in high purity aluminum.

Theoretical Background

Chirped Modulation PPE Detection

In the chirped modulation PPE technique, a cw laser is directed through an acousto-optic modulator which is driven by a fast frequency sweep waveform voltage x(t), or chirp. The resultant laser beam intensity is thus chirp-modulated, before being focussed on the sample. The thermal response y(t) is then detected at the back surface by a fast thin-film pyroelectric detector. The impulse response is then calculated from x(t) and y(t) through cross correlation and Fast Fourier Transform (FFT) analysis [21–22]. Chirped PPE detection has several advantages over conventional pulsed laser methods [23] for determining the thermal diffusivity of metals and oxides. The technique is characterized by the low incident power density and high source stability inherent in cw laser systems; it is thus suitable for samples with low optical damage threshold. Although this advantage is also present in single-frequency modulation/lock-in techniques, chirped modulation enables measurements that are directly interpretable in terms of thermal pulse propagation times through materials.

For a pyroelectric detector with thickness d, pyroelectric coefficient p and dielectric constant ε_0 in contact with the back surface of the sample, the current impulse response due to heat flow through a sample of thickness l may be obtained through a Green's function treatment [14], yielding

$$I(t) = \frac{p dA}{\varepsilon_0 t^{3/2}} \sum_{n=0}^{\infty} (-1)^n \beta_{32}^n \left[\tau_{1n}^{1/2} e^{-\tau_{1n}/4t} - 2\tau_{2n}^{1/2} e^{-\tau_{2n}/4t} + \tau_{3n}^{1/2} e^{-\tau_{3n}/4t} \right].$$
(1)

The coupling coefficients between adjacent layers i and j in the air-sampledetector-backing system (Fig. 1: layers 1 to 4, respectively) are given by $\beta_{ij} = (b_{ij} - 1)/(b_{ij} = 1)$, where $b_{ij} = \kappa_i \alpha_j^{1/2} / \kappa_j \alpha_i^{1/2}$. Here κ_n and α_n are the thermal conductivities and diffusivities of the *n*th layer, and we have defined

$$\tau_{1n}^{1/2} = \frac{2nd}{\alpha_{3}^{1/2}} + \frac{l}{\alpha_{2}^{1/2}},$$
 (2a)

$$\tau_{2n}^{1/2} = \frac{(2n+1)d}{\alpha_3^{1/2}} + \frac{l}{\alpha_2^{1/2}},$$
 (2b)

$$\tau_{3n}^{1/2} = \frac{2(n+1)d}{\alpha_3^{1/2}} + \frac{l}{\alpha_2^{1/2}}.$$
 (2c)



Fig. 1. Schematic of experimental arrangement for photopyroelectric experiment. Inset: geometry for theory of thermal response of a solid sample using laser excitation and thin-film photopyroelectric detection.

The parameter A is a constant incorporating the static thermal properties of the sample-pyroelectric system:

$$A = -\frac{(\alpha_3 \alpha_2)^{1/2}}{2\sqrt{\pi}\alpha_2(b_{32} + 1)}$$
(3)

Equation (1) describes a pulse peaked at time τ_p , and is valid under the following approximations: a large thermal mismatch at the sample front surface $(b_{12} << 1 \text{ or } \beta_{12} \simeq -1)$; a metal backing for the thin-film detector $(b_{43} \ge 1 \text{ or } \beta_{43} \simeq 1)$; and a sample that is thermally thick compared to the detector $(\tau_2 >> \tau_3$, where τ_n is the time for a unit heat impulse to travel through the *n*-th layer; equivalently, $l^2/\alpha_2 >> d^2/\alpha_3$). All these approximations are valid in this work.

Along with the dependence on the sample thermal parameters, the pulse shape is sensitive to the detector properties; for a PVDF detector, as in our case, $\alpha_3 = 8 \times 10^{-8} \text{ m}^2/\text{s}$ and $\kappa_3 = 0.19 \text{ W/m-K}$ for the detector thermal diffusivity and conductivity [24]. Inserting these values in Eq. (1), it may be shown [18–20] that τ_p varies linearly with the parameter l^2/α , where we have written $\alpha = \alpha_2$, with a slope $F_p = 0.08$, for PVDF detection, independent of the sample thermal conductivity $\kappa = \kappa_2$. This is a consequence of the fact that the current response at earlier times is a strong function of the thermal diffusivity, and is only weakly dependent on the thermal conductivity; furthermore, F_p is only dependent on the thermal and geometric properties of the detector. The absolute value of the sample thermal diffusivity may then be calculated from the relation

$$\alpha = F_p \left(\frac{l^2}{\tau_p}\right). \tag{4}$$

Single-Frequency Modulation PPE Detection

Estimates of the thermal diffusivity may also be obtained from the frequency response of the sample to sinusoidally-modulated excitation. The sample-detector geometry is the same as in Fig. 1, except for a thin-film blackbody reference deposited on the PVDF film, and that the excitation intensity I_0 is modulated at a single frequency f. If the film is optically opaque and thermally thick, and the sample surface reflectance R_2 is written in the form $A_2 = 1 - R_2$, the output voltage normalized by the PPE reference response is given by [25]

$$V_N(f) = 2\eta_2 A_2 \left(\frac{b_{32}}{b_{32}+1}\right) \exp(-\sigma_2 l), \tag{5}$$

where η_2 is the heat conversion efficiency. Furthermore $\sigma_2 = (1 + i) a_2$, and $a_2 = (\pi f/\alpha_2)^{1/2} = \mu_2^{-1}$, where μ_2 is the thermal diffusion length, and $b_{32} = k_3 a_3/k_2 a_2$. The amplitude and phase of the normalized PPE signal are given by

$$|V_N(f,\lambda)| = 2\eta_2(\lambda) A_2(\lambda) \left(\frac{b_{32}}{b_{32}+1}\right) \exp[-a_2(f)l],$$
 (6a)

$$\Phi_D(f) = a_2(f) \ l = \sqrt{\frac{\pi f}{\alpha_2}} \ l. \tag{6b}$$

A plot of $ln |V_N|$ against $f^{1/2}$ yields a straight line with slope $-(\pi f/\alpha_2)^{1/2}l$, from which the thermal diffusivity $\alpha = \alpha_2$ may be determined:

$$\alpha = l^2 \pi \left[\frac{\Delta(f^{1/2})}{\Delta(\ln|V_N|)} \right]^2.$$
(7)

It is important in this formulation to ensure that the sample satisfy the condition $\mu_2 \ll l$, that is, that the sample is thermally thick, in order to apply Eq. (10), otherwise the PVDF thermal properties will contribute significantly to the detected signal.

Experimental

This investigation was undertaken using specimens from 2 mm-thick sheets of high purity aluminum, with an elemental impurity specification of < 0.01% by weight. Laser excitation of the samples was normal to the rolling plane. Specimens for examination by optical micrography were cross-sectionally cut and etched, and examined at $32 \times$ magnification.

A conventional arrangement was used for the PPE experiments (Fig. 1). The detector consisted of 28 μ m-thick PVDF film, uniformly poled and vacuum-deposited with electrodes of NiAl. The NiAl electrodes are composed of a 0.015 μ m base of nickel and a 0.04 μ m film of aluminum, which give both high thermal and electrical conductivity as well as good adhesion of PVDF. The electroded 28 μ m PVDF film, which has a flat frequency response up to several MHz, is stretched and fixed to a stainless steel backing. This assembly is then enclosed in a gold-coated Inficon metal housing for electrical contact and to screen electromagnetic *rf* interference. The samples were affixed to PVDF detector through a thin layer of thermal compound, whose contribution to the sample PPE signal was negligible [16, 26].

For the chirped experiments the PPE responses were excited with 20 mW incident power from the 488 nm line of an Ar^+ laser. The *cw* beam was chirped by an acousto-optic modulator before being focussed on the sample front surface. The driver waveform to the modulator had an amplitude of 85 mV, and the modulator exhibited a flat power spectrum over the 0–1 kHz modulation band. The PVDF output was fed to a fast current amplifier and then to the system input of an FFT analyzer; the impulse response time window was 800 ms, digitized into 2048 points. The current impulse response was then recovered by correlation and FFT operations as discussed above.

For the single-frequency modulation PPE measurements, the illumination source consisted of a 1000 W xenon lamp-monochromator system, modulated from 3–16 Hz by a mechanical chopper [27–28]. The output signal was filtered and preamplified before connection to a digital lock-in analyzer, referenced to the chopping frequency. The spotsize at the sample for both the chirp and single-frequency modulated PPE experiments was approximately 10 μ m. Although this configuration falls within the regime of a three-dimensional theory, preliminary experiments with expanded beam diameters revealed no measurable difference in pulse time characteristics compared to the focussed beam arrangements. The one-dimensional model for excitation and heat flow in the sample, as outlined above, is thus adequate for our purposes.

Results and Discussion

Cross-sectional optical micrographs of the aluminum samples, perpendicular to the rolling direction, are shown in Figs. 2(A)-(E). In cold-rolled aluminum the crystallites are elongated in the rolling direction, as in Fig. 2(A). Figures 2(B) to 2(D) show samples with approximately 90% and 100% (two specimens I and II) recrystallization, respectively. In Fig. 2(E) grain growth is evident in the sample, with individual grains ranging up to 250 μ m in diameter.





Fig. 2. Optical micrographs of high purity aluminum samples, showing cross-section perpendicular to rolling direction: (A) cold-rolled, (B) 90% recrystallized, (C) 100% recrystallized I, (D) 100% recrystallized II, and (E) recrystallized aluminum showing grain growth. The cross-sectional sample thickness is approximately 2 mm; magnification is $32 \times$.

Figures 3(a)-(e) show the representative normalized impulse responses for the samples in Fig. 2 above, taken with chirped modulation and PPE detection. Although the responses are qualitatively similar—a peak followed by a gradual decline to slightly negative value, and then a slow recovery—the peak time appears to be a function of the degree of recrystallinity: for example, the impulse response for cold-rolled aluminum occurs at a later time than for fully recrystallized aluminum. Because of the diffusive nature of thermal-wave propagation through the sample, any increase in α leads to a narrowing of the pulse, and a faster arrival of the detected temperature change at the sample back surface. The narrowing of the impulse response is thus indicative of a corresponding increase in the thermal diffusivity. Qualitatively the data indicate an increase in thermal diffusivity from cold-rolled to fully recrystallized high purity aluminum, where it remains relatively constant. The value for α subsequently decreases on further annealing and grain growth.

Figure 4 shows the normalized frequency responses for recrystallized aluminum, taken with the single-frequency modulation PPE technique, in the form $ln |V_N| vs f^{1/2}$, showing the linear relationship predicted the theory. As in Eq. (7), the slopes are related to the thermal diffusivity and reflect the observations above: an increase in thermal diffusivity from cold-rolled to fully recrystallized aluminum and then a drop upon further processing. However, within the frequency range of this particular experiment, $\mu_2 \gg l$, and the condition for sample thermal thickness does not apply. Consequently it was impossible to retrieve absolute values for the thermal diffusivity from the single-frequency work.

Quantitative measurements of the thermal diffusivities are, however, available from the chirped PPE (impulse response) experiments, according to Eq.



Fig. 3



Fig. 3



Fig. 3a-e. Thermal impulse responses obtained for high purity aluminum, using chirped modulation PPE, for corresponding samples described in Fig. 2.



Fig. 4. Normalized frequency responses obtained for high purity aluminum, using single-frequency modulation PPE, for corresponding samples described in Fig. 2, in the form $ln |V_N|$ vs f^{1/2}, showing the predicted linear relationship.

Photopyroelectric Measurement of Recrystallized Aluminum

Aluminum Specimen	$ au_{p}$ (ms)	$\alpha \\ (\times 10^{-5} \\ m^{2}/s)$
Cold-rolled	8.925 ± 0.170	3.10 ± 0.02
90% recrystallized	7.125 ± 0.112	3.82 ± 0.05
100% recrystallized I	7.225 ± 0.050	3.75 ± 0.05
100% recrystallized II	6.750 ± 0.001	4.06 ± 0.01
Initial grain growth	7.725 ± 0.146	3.53 ± 0.02

Table 1. Summary of chirped photopyroelectric measurements of the impulse response peak time and thermal diffusivity for high purity aluminum.

(4), and the results are summarized in Table 1. These measurements are absolute values, and the standard deviations reflect the result of five separate experiments on each specimen, with each experiment consisting of 300 averages. The peak delay τ_p falls from 8.925 ms for cold-rolled aluminum to an average of 7.033 ms for fully recrystallized aluminum, and then exhibits a rise to about 7.725 ms for the final sample. The change in the thermal diffusivity is smaller but still measurable: For cold-rolled high purity aluminum, $\alpha = (3.10 \pm 0.02) \times 10^{-5} \text{ m}^2/\text{s}$, which rises to $(3.88 \pm 0.05) \times 10^{-5} \text{ m}^2/\text{s}$ for fully recrystallized samples, and then falls for to $(3.53 \pm 0.02) \times 0^{-5} \text{ m}^2/\text{s}$ for the sample exhibiting the largest grains. We should stress that this variational dependence with recrystallization is reproducible; all our experiments exhibited the same trend for the thermal diffusivity.

One possible explanation for the above results is based on the crystallographic anisotropy in the thermal diffusivity. The effective increase in the measured α values as shown in Figs. 2(b)-(d), could be ue to an average reorientation during the recrystallization process, normal to the rolling plane and parallel to the thermal diffusion direction. This mechanism does not account for the apparent decrease in α for the specimen in Fig. 2(e). However, in this sample a typical grain can have a dimension of 250 μ m, which is as much as 10– 100 times the laser spotsize. Consequently the measured thermal diffusivity for this case may be characteristic only of the local crystallographic orientation, rather than an average over all orientations.

Conclusions

The thermal diffusivity of high purity aluminum has been measured using a photopyroelectric technique. The thermal diffusivity is found to be dependent on the degree of recrystallization, and rises from $\alpha = 3.10 \times 10^{-5} \text{ m}^2/\text{s}$ for coldrolled aluminum to $3.88 \times 10^{-5} \text{ m}^2/\text{s}$ for the fully recrystallized material. The change may be due to a crystallographic reorientation and anisotropy in the metal. Further recrystallization results in a decrease of the diffusivity to $3.53 \times 10^{-5} \text{ m}^2/\text{s}$, and may be due to preferential sampling of grains with a specific

crystallographic orientation. However, the results may not necessarily relate to crystallographic orientation, but may be related to dislocation loops, especially in high purity alloys such as in this work. Further experiments are being undertaken with single crystalline samples, or large grain specimens, in order to clarify the mechanisms that first allow and finally suppress the enhancement of the thermal diffusivity during recrystallization.

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References

- 1. A. Mandelis. Chem. Phys. Lett. 108:388 (1984)
- 2. H. Coufal. Appl. Phys. Lett. 44:59 (1984)
- 3. H. Coufal. IEEE Trans. UFFC 33:507 (1986)
- 4. H. Coufal, R. Grygier, D. Home and J. Fromm. J. Vac. Sci. Technol. A5:2875 (1987)
- 5. A. Mandelis, ed. *Photoacoustic and Thermal Wave Phenomena in Semiconductors*, North-Holland, New York (1987)
- 6. G. Busse. Infrared Physics 20:419 (1980)
- 7. P. Cielo. J. Appl. Phys. 56:230 (1984)
- 8. B. Witowski, W.L. Smith and D.L. Willenborg. Appl. Phys. Lett. 52:640 (1988)
- 9. A. Rosencwaig, J. Opsal, W.L. Smith and D.L. Willenborg. Appl. Phys. Lett. 46:1013 (1985)
- 10. S.B. Peralta, H.H. Al-Khafaji and A.W. Williams. Nondestr. Testing and Eval., 6:17 (1991)
- 11. S.B. Peralta and A.W. Williams. Appl. Phys. Lett. 54:2405 (1989)
- 12. H. Coufal and A. Mandelis. Ferroelectrics, in press (1991)
- 13. J.F. Power and A. Mandelis. Rev. Sci. Instrum. 58:2018 (1987)
- 14. J.F. Power and A. Mandelis. Rev. Sci. Instrum. 58:2024 (1987)
- 15. J.F. Power and A. Mandelis. Rev. Sci. Instrum. 58:2033 (1987)
- I.A. Vitkin, S.B. Peralta, A. Mandelis, W. Sadowski and E. Walker. Meas. Sci. Technol. 1:184 (1990)
- S.B. Peralta, I.A. Vitkin, A. Mandelis, W. Sadowski and E. Walker. In *Photoacoustic and Photothermal Phenomena II*, ed. by J.C. Murphy, J.W. Maclachlan Spicer, L.C. Aamodt and B.S.H. Royce, pp. 211–213. Springer-Verlag, Berlin (1990)
- 18. S.B. Peralta. Bull. Am. Phys. Soc. 35:464 (1990)
- 19. S.B. Peralta, Z.H. Chen and A. Mandelis. Ferroelectrics, in press (1991)
- 20. S.B. Peralta, Z.H. Chen and A. Mandelis. Appl. Phys. A. in press (1991)
- 21. A. Mandelis, L.M.L. Borm and J. Tiessinga. Rev. Sci. Instrum. 57:622 (1986)
- 22. A. Mandelis, L.M.L. Borm and J. Tiessinga. Rev. Sci. Instrum. 57:630 (1986)
- 23. Y.S. Touloukian, R.W. Powell, C.Y. Ho and M.C. Nicolau. In *Thermal Diffusivity*, ed. by Y.S. Touloukian and C.Y. Ho, Vol. 10. Plenum, New York (1973)
- 24. KYNAR[™] Piezo Film Technical Manual, Pennwalt Corp., King of Prussia, PA (1983)
- 25. A. Mandelis and M.M. Zver. J. Appl. Phys. 57:4421 (1985)
- 26. M. Marinelli, F. Mercuri, U. Zammit and R. Pizzoferrato. Appl. Phys. A., in press (1991)
- 27. C. Christofides, A. Mandelis, K. Ghandi and R.E. Wagner. Rev. Sci. Instrum., 61:2360 (1991)
- 28. C. Christofides, K. Ghandi and A. Mandelis. Meas. Sci. Technol., 1:1363 (1991)