Residual Strain Gradient Determination in Metal Matrix Composites by Synchrotron X-ray Energy Dispersive Diffraction

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An X-ray technique for the measurement of internal residual strain gradients near the continuous reinforcements of metal matrix composites has been investigated. The technique utilizes high intensity white X-ray radiation from a synchrotron radiation source to obtain energy spectra from small \((10^{-5} \text{ mm})^3\) volumes deep within composite samples. The energy peak positions satisfy Bragg’s law and allow determination of the lattice parameter. As the probe volume is translated, the peaks of the spectra shift and are used to infer lattice spacing changes and thus strain with a precision of \(10^{-5}\) to \(10^{-4}\) (depending on the sample grain size/probe volume ratio). The viability of the technique has first been tested using a model system with 800 \(\mu\text{m}\) \(\text{Al}_2\text{O}_3\) fibers and a commercial purity titanium matrix. For this system (which remained elastic on cooling), good agreement was observed between the measured residual radial and hoop strain gradients and those estimated from a simple elastic concentric cylinders model. The technique was then used to assess the strains near (SCS-6) silicon carbide fibers in a Ti-14Al-21Nb matrix after consolidation processing. Reasonable agreement between measured and calculated strains was seen provided the probe volume was located 50 \(\mu\text{m}\) or more from the fiber/matrix interface. Close to the interface, the measured elastic strains were smaller than anticipated, due to relaxation of the residual stress by plasticity and radial cracking during sample cooling.

I. INTRODUCTION

Low-density titanium-based metal and intermetallic matrix composites reinforced with either silicon carbide or aluminum oxide fibers are attracting interest for high-temperature aerospace applications.\(^1\) In all the systems of interest, the fibers have a smaller coefficient of thermal expansion than the matrix, and thus, residual stress gradients are created in the matrix during cooling from the high temperatures used for fabrication.\(^2\) It is found that the radial stress component in the matrix is compressive and has its greatest magnitude at the fiber/matrix interface. The hoop stress in the matrix is tensile and is also of greatest magnitude at the interface. The stresses are frequently sufficient to cause matrix plastic deformation\(^3,4\) or even radial cracking in low-ductility systems.\(^5\)

These stresses play a very important role in the mechanical properties of composites. For instance, the radial compressive stress effects both the transverse tensile properties (resulting in bilinear behavior) of ductile matrix composites\(^6\) and the longitudinal toughness of brittle matrix systems by affecting the fiber pullout stress.\(^7,8\) The stresses also add to those imposed during loading and result in premature deformation and fracture.\(^9,10,11\) It is thus important to develop ways to measure these stresses (or strains) and to test the validity of the many models that seek to predict them.\(^12,13,14\) This is of increasing importance as researchers seek to use the models to optimize the interface of fiber-reinforced composites in order to reduce the residual stress.\(^15,16\)

For many years, the state of residual stress (actually strains) at the surfaces of a body\(^17,18,19\) has been measured by the sin \(2\theta\) X-ray diffraction method. However, this technique is not useful for measuring the strains inside a composite sample, particularly the rapidly varying strain fields close to a fiber. This is because conventionally generated X-rays are strongly absorbed by most engineering materials, penetrating only a few microns. Efforts to overcome this have included surface X-ray measurements, followed by the mechanical or electrochemical removal of a thin layer of the surface material, after which another measurement is made.\(^20\) In this way, insight into the strains as a function of depth can be obtained. Unfortunately, the internal strains are altered by the destructive removal of surface layers, and the validity of the compensation methods for this effect are unclear. Neutron diffraction has been used for residual stress measurement, taking advantage of the high penetration of neutrons in engineering materials.\(^21,22,23\) While an internal strain is indeed measured by this approach, large diffracting volumes are required (because available neutron sources provide relatively low intensities) and only bulk average stresses are determined over a much larger volume than the reinforcement of many of today’s composite materials. Thus, the method is unable to resolve the radial changes in stress close to the fibers.

By utilizing high-intensity white synchrotron radiation, energy dispersive diffractometry offers the promise of both good penetration (through several millimeters of titanium, for example) and a potentially high spatial resolution of residual strain gradients.\(^24\) The work reported here explores the feasibility of using this technique for...
residual strain measurement in a metal matrix composite. The intent has been to measure the diffraction from volumes smaller than the reinforcing fiber, to determine the average lattice parameter in the probe volume, and to then scan the probe away from the fiber. The strain (or stress) profile thus measured can be compared with concentric cylinder elastic\cite{14} and recently developed elastic-plastic models\cite{16} of residual stress development upon cooling from the high temperatures used for fabrication.

II. MEASUREMENT PRINCIPLE

Energy dispersive diffractometry, based on Bragg diffraction, utilizes a solid-state detector to analyze the distribution of diffracted X-ray energies from a polychromatic (white radiation) incident beam (Figure 1). An intrinsic germanium detector is positioned at a fixed scattering angle $2\theta$ so that diffraction is detected from a volume defined by the incident and scattered beams. The energy of the diffracted peaks satisfies Bragg's law:

$$E_{hkl} = \frac{hc}{\lambda} = \frac{hc}{2 \sin \theta} \cdot \frac{1}{d_{hkl}} \tag{1}$$

where $E_{hkl}$ is the energy of an $\{hkl\}$ reflection, $h$ is Planck's constant, $\lambda$ is the wavelength, $d_{hkl}$ is the $\{hkl\}$ lattice spacing, and $c$ is the speed of light. For $E$ given in keV and $d$ in Å, the above equation becomes:

$$E_{hkl} = \frac{6.22}{d_{hkl} \sin \theta} \tag{2}$$

Thus, for a known experimentally fixed, scattering angle $2\theta$, each crystallographic plane with a lattice spacing $d_{hkl}$ diffracts at a particular energy $E_{hkl}$. Measurement of a peak energy at the fixed angle $2\theta$ allows the calculation of lattice spacing. Shifts in peak energy allow the strain, $\varepsilon$, be determined:

$$\varepsilon = -\left(\frac{\Delta d}{d}\right)_{hkl} = \left(\frac{\Delta E}{E}\right)_{hkl} \tag{3}$$

where $\Delta d$ refers to the change in the lattice spacing and $\Delta E$ the resultant peak shift.

Two factors determine the strain measurement capability of the energy dispersive approach: resolution and detectability/sensitivity. The resolution is obtained by differentiation of Eq. [1]:

$$\left(\frac{\Delta d}{d}\right)_{hkl} = \left(\frac{\Delta E}{E}\right)_{hkl} + \cot \theta \cdot \Delta \theta \tag{4}$$

where $\Delta E$ is the energy resolution of the solid-state detector and $\Delta \theta$ the angular divergence (determined by the collimation of the incident/diffracted beams). The energy resolution of an intrinsic germanium detector at 122 keV is $\Delta E/E = 4 \times 10^{-5}$, and for a typical setup, $\Delta \theta = 2$ mrad and $\theta \sim 2$ deg. Thus, the resolution apparently is only $\sim 1$ pct, insufficient for our purpose (we ideally need $10^{-2}$ pct strain resolution). However, it is important to realize that Eq. [4] is an expression for the ability to resolve two peaks in a single spectrum resulting from nearly identical lattice spacings. The actual strain resolution is determined by the ability to measure the shift in a single peak between two different spectra. This resolution is given in Eq. [3]:

$$\varepsilon = -\left(\frac{\Delta d}{d}\right)_{hkl} = \left(\frac{\Delta E}{E}\right)_{hkl} \tag{5}$$

Therefore, the strain resolution is determined only by the smallest resolvable shift in peak energy. To increase the sensitivity to peak shifts, one can fit the diffraction to a Gaussian plus linear profile. This theoretically sound practice\cite{27-30} has been shown to allow peak shifts of a few electron volts to be resolved and, depending on $E_{hkl}$, a strain sensitivity of $\sim 10^{-4}$\cite{27}.

The intersection of the incident and diffracted beams defines the X-ray probe volume. It is controlled by collimating the two beams (Figure 1). In this region, diffraction is measured only from lattice planes which are perpendicular to the diffraction vector $\mathbf{k}$, which is in the direction of the bisector of the angle formed by the incident and diffracted beams. These planes alone satisfy the Bragg condition for diffraction at the particular scattering angle being used. In this way, the hoop and radial strains can be measured independently, depending on the orientation of the fiber relative to the incident beam, as shown in Figure 2.

A system of slits was employed to collimate both the incident and diffracted beams, allowing precise control of the incident beam cross section, the scattering angle, the dimensions of the X-ray probe, and the angular divergence. For the experiments reported here, the probe volume was $50 \times 50 \times 1000 \mu m^3$ with the long dimension arranged parallel to the fiber axis (the direction in which the stress field does not change). These parameters control peak position, peak breadth, count rate, and resolution in the strain-sensitive direction, all of which were optimized for a particular experiment.

III. EXPERIMENTAL PROCEDURE

A. Test Samples

Three model single-fiber samples were fabricated by hot isostatic pressing (HIP) of either commercially pure titanium powder or an intermetallic Ti-14Al-21Nb (wt pct) alloy with either a 800-μm polycrystalline alumina
fiber or a Textron silicon carbide (SCS-6) fiber of 142 µm diameter. Titanium powder was provided by Johnson Mathey Inc., with an average particle size of 150 µm. The Ti-14Al-21Nb intermetallic alloy powder also had a 150 µm particle size. It was made by the plasma rotating electrode process by Nuclear Metals Inc. Samples were hot isostatic pressed in stainless steel cans in an ABB Minihipper under the conditions shown in Table I. Controlled cooling was done at least at 2 °C/min from the hold temperature to 500 °C and then cooled to ambient at around 20 °C/min. The resulting sample geometry was a 5- to 7-mm-thick flat plate with a single fiber embedded in the plane of the plate. The embedded fiber was at least 2.5 mm from any free surface.

B. X-ray Measurement Methodology

All energy dispersive experiments were performed using the NIST materials science beamline, X23A3, at the National Synchrotron Light Source, Brookhaven National Laboratory, Long Island, NY. Usable X-ray energies range from 5 to 60 keV, with the critical energy at 8 keV. The uncollimated beam cross section at the sample is roughly 50 × 5 mm.

A nominal scattering angle of ~5 deg was chosen to insure good energy separation between diffraction peaks.

| Table I. Composite Test Samples for X-ray Study of Internal Strain Gradients |
|--------------------------|-----------------|----------------|----------------|
| Sample | Matrix/Fiber Combination | HIP Conditions | |
| | | Temperature (°C) | Pressure (MPa) | Time (Hours) |
| HIP0 | CP Ti/800 µm Al₂O₃ | 850 | 100 | 4.0 |
| HIP1 | PREP Ti-14Al-21Nb/SCS-6 | 1050 | 100 | 4.0 |
| HIP2 | PREP Ti-14Al-21Nb/SCS-6 | 950 | 205 | 2.0 |

in the range between 20 and 60 keV. An EG&G Ortec high-purity germanium solid-state detector, with a resolution of 190 eV at 5.9 keV, was used to measure the diffracted energy spectrum. An Ortec 92X Spectrum Master provided high bias, amplification, and analog to digital conversion. Data acquisition, storage, and analysis were performed by Ortec Maestro II software operating on a COMPAQ* 386s Deskpro personal computer.

All spectra for a particular geometry, hoop, or radial were acquired during a single fill of the electron storage ring to eliminate peak shifting as a result of source position changes, as discussed subsequently. The sample was translated across the probe in steps as small as 50 µm in the region close to the interface. The step size was increased to as large as 750 µm far from the interface where the strain was expected to be almost constant.

IV. RESULTS AND DISCUSSION

A. CP Titanium/Al₂O₃ System

A typical sequence of X-ray intensity spectra for sample HIP0 is shown in Figure 3. The first (Figure 3(a)) corresponds to an X-ray probe centered on the fiber matrix interface, and both Al₂O₃ and the (hexagonal) titanium peaks are clearly resolvable. In Figure 3(b), the probe volume was radially translated 40 µm from the first location. An abrupt drop in the Al₂O₃ signal is observed for the 50 × 50 µm² probe area used here (though it had not completely disappeared). Figure 3(c) shows the spectrum after translating a further 40 µm. Also shown on the spectra are MnKα and Kβ obtained from an Fe³⁺ radioactive source. These had energies of 5.909 and 6.502 keV, respectively, and were used to calibrate the energy (channel number) axis. The sequence shown in Figure 3 was continued until the probe volume was 2500 µm away from the fiber. This was sufficiently far from the fiber that the stresses due to the thermal mismatch would have fallen to a small value, and the spectra at this location was used as a reference from which to calculate peak shifts. The peak shifts of individual Bragg reflections were found to have quite significant random errors; an average peak shift was determined from the six to eight strongest Bragg peaks.

Figures 4 and 5 show the hoop and radial strain profiles as a function of distance from the fiber/matrix interface for the HIP0 sample. Stress values are given on the secondary vertical axis (stresses and strains being related by one-dimensional Hooke's law). Also shown is a solid line that represents the predictions of a simple concentric cylinders elastic model for the residual stress gradient created on cooling. The general forms of the thermal stresses are given by:

\[
\sigma_{\text{hoop}} = A \left(1 + \frac{b^2}{r^2}\right) \quad \sigma_{\text{radial}} = A \left(1 - \frac{b^2}{r^2}\right)
\]

where \(b\) is the radius of the matrix sleeve, \(r\) is the distance in the radial direction, and \(A\) is a constant determined by the fiber and matrix elastic moduli and thermal
expansion coefficients, fiber radius, change in temperature, and Poisson’s ratio for the composite. The thermophysical data used for the elastic calculations are given in Table II.

Overall, quite good agreement is seen between the measured and predicted values, although there is point-to-point scatter which we will discuss subsequently.

As mentioned earlier, each data point shown in Figures 4 and 5 represents an average of all the intense matrix peak shifts of each spectrum. Eight peaks were used for the hoop strain and six for the radial strain measurements. The average standard deviation for the peak shift was $9.5 \times 10^{-4}$ for the hoop strain and $9.9 \times 10^{-4}$ for the radial strain. It should be noted that averaging is strictly valid only for an isotropic material, since in an anisotropic material, a constant stress will produce different strains depending on orientation. However, since the anisotropy factor for titanium is only 1.34, averaging
was considered to introduce less error than random fluctuation of only a single peak.

Two factors contribute to the random scatter in the individual data points of Figures 4 and 5, i.e., to the averaged peak shifts. In principle, given sufficient counts, a peak shift can be resolved to a strain of $10^{-4}$ using the Gaussian curve fitting technique.\[27,28,29\] In practice, we were unable to always gather enough counts at each measurement location to give ideal counting statistics because of a combination of our small ($\sim 10^{-3}$ mm$^2$) probe volume and time constraints associated with the Synchrotron. These time constraints arise from the need for periodic (roughly every 24 hours) reinjection of electrons into the accelerator ring. The electrons may be injected into a different orbit which causes a shift in the X-ray beam position which leads to unacceptable scattering angle and probe volume location shifts. A tradeoff between the number of measurement points and counting statistics, therefore, was made during data collection. The typical peak height that resulted had 1000 counts.

More serious contributors to the error were “single grain” effects. They are believed to be the primary contributing factors to the random fluctuations in the data. A schematic diagram illustrating how this effect can occur is shown in Figure 6. A basic assumption of the technique is that all of the grains in the probe are scattering only at a single angle, $2\theta_B$. However, suitably oriented grains at extremes (corners) within the probe volume scatter at angles either slightly greater or less than the nominal angle $2\theta_B$. The Bragg scattering contributions from these grains tend to shift the peak to either higher or lower energies according to Eq. [1]. We estimate the range of scattering angles between $2\theta_B \pm \Delta$ is large enough to shift a peak by an amount equal to a strain of 0.001.\[30\] Thus, if a suitably oriented large grain is located at the edge of the probe, its diffraction will skew the peak position (even with no strain present), resulting in an anomalous peak shift. Only if many randomly oriented grains are present in the probe will enough of them be properly oriented for diffraction so that this divergence contributes only to a peak broadening and not to a shift in peak position. Using typical probe dimensions of $50 \times 50 \times 1000 \ \mu m^3$ and a matrix grain size of 10 to 20 $\mu m$, on the order of 1000 grains are expected in a typical probe. Using solid angles, the probability that diffraction will be observed from any orientation in a single randomly oriented grain is calculated to be roughly $10^{-6}$. Thus, it is likely that only a few grains are contributing to any single peak, and there is a substantial probability that they diffract at some angle slightly larger or smaller than the nominal scattering angle. Further evidence for this was observed experimentally by the fact that the intensity of a particular peak varied greatly at different points in the sample.

We notice that the experimentally determined stresses near the fiber-matrix interfaces in Figures 4 and 5 always tend to lie below the prediction of the elastic model. For example, the radial stress components around 100 $\mu m$ from the interface reached a high of $\sim 130$ MPa, whereas the predicted values were $\sim 180$ MPa. Likewise, with the exception of the measurement immediately adjacent to the interface, the hoop stress components out to $\sim 150 \mu m$ were $\sim 50$ MPa less than the model prediction. Since the residual stresses are below the matrix yield stress throughout cooling,\[26\] it is unlikely these effects are due to plastic relaxation. Figure 7 shows a micrograph of this region. Although an interfacial reaction had occurred, it is not believed to be directly responsible for this, as it

![Table II. Thermophysical Data Used for Elastic Concentric Cylinders Model](image1)

![Diagram](image2)

**Fig. 6** - X-ray probe volume schematic diagram showing the range of scattering angles sampled.

**Fig. 7** - Scanning electron micrograph of the interface of the CP titanium/Al$_2$O$_3$ sample.
was confined to a 10 \, \mu m \, region \, near \, the \, fiber. \, We \, believe \, the \, difference \, to \, have \, arisen, \, in \, part, \, from \, small \, misorientation \, errors \, of \, the \, probe \, volume.

Figure 8 shows schematically the intended alignment of the fiber and probe volume. Recall that the axial dimension of the probe volume was 1000 \, \mu m \, for \, these \, tests, \, and \, therefore, \, a \, misorientation \, in \, either \, the \, \theta \, or \, \psi \, directions \, would \, rotate \, the \, probe \, and \, change \, the \, radial \, distances \, it \, sampled. \, As \, an \, example, \, suppose \, the \, probe \, is \, positioned \, correctly \, 40 \, \mu m \, from \, the \, interface; \, the \, average \, radial \, stress \, then \, sampled, \, \sigma_r, \, is

\[
\sigma_r = \frac{A}{(r_0 - r_1)} \int_{r_1}^{r_0} \left(1 - \frac{b^2}{r^2}\right) \, dr \\
= 189 \, \text{MPa}
\]

where \( r_0 \) and \( r_1 \) are the radial distances to the outer and inner edges of the probe volume (465 and 415 \, \mu m), respectively, and are almost the same as the value at \( r = 440 \, \mu m \) because of the weak variation in \( \sigma_r \) with \( r \). Suppose, however, the probe were rotated 10 deg in the \( \theta \) direction; the central longitudinal axis of the probe volume would then penetrate into the fiber (accounting for the fiber diffraction observed in the tests for probes close to the interface) and shorten the volume of the probe from which matrix diffraction would be sampled (from 1000 to 730 \, \mu m). The range of radial distances sampled then changes, ranging from \( r = 400 \, \mu m \) (where the probe enters the fiber) to \( r = 527 \, \mu m \). The average radial stress sampled in this situation falls from 189 to 173 \, \text{MPa}. Rotations of up to 10 deg in the \( \psi \) direction can also reduce the radial stress by a further 10 \, \text{MPa} or so.

The remaining discrepancies between the model prediction and the data could be due to a number of effects ignored in modeling, including the difference in modulus and \( \alpha \) for the reaction products and chemical gradients near the fiber. Further work is needed to investigate this.

B. Ti-14Al-21Nb SCS-6/System

Two SCS-6/Ti-14Al-21Nb samples containing very widely (several millimeter) spaced fibers were also examined. Figure 9 shows the residual hoop strain (stress) profile for sample HIP1, and Figure 10 shows the radial strain (stress) profile for sample HIP2. In the figures, the square points correspond to the experimentally measured data and the curve is the prediction of the elastic
concentric cylinders model. Using the same probe volume as before, it was found that because of the much smaller grain size of the samples, the scatter in peak shift data was much less and the local strains could be obtained from the analysis of a single diffraction peak rather than the average of 6 to 8 peaks as before.

It can be seen that the residual stresses measured 50 to 150 μm and beyond from the interface are in reasonable agreement with the residual stresses calculated from the elastic model. However, closer to the interfaces, the experiments indicate the stresses are significantly less than those of the elastic model. Errors associated with the finite cross section of the probe (50 × 50 μm) and up to a 10 deg misalignment of the probe volume (when nominally located 40 μm from the interface) can account for only 30 MPa of this difference. Using the data of Lukasak and Koss, Pindera has found from elastic-plastic calculations that, on cooling, the stresses exceed the matrix yield strength and that significant plastic deformation occurs. The analysis predicted plastic strains of ~4 pct close to the interface. These resulted in radial stresses of ~380 MPa and hoop stresses of only ~190 MPa at the interface, a substantial reduction from the predictions of the elastic model but still greater than those observed in the experiment.

To gain further insight into possible causes of the discrepancy, each sample was sectioned, polished, lightly etched, and examined by scanning electron microscopy (Figures 11 and 12). Sample HIP1 had transformed to the familiar α + β structure of these alloys. A 2 to 3 μm reaction product had formed at the interface during consolidation (1050 °C, 4-hour), and a β-depleted zone extended about 15 μm from the interface. About 10 relatively short (5 to 10 μm) radial cracks had formed in the β-depleted zone. Sample HIP2 had been deliberately consolidated at a lower temperature (950 °C, 2-hour) to avoid and minimize this interfacial damage. Only a 1 to 2-μm reaction zone and a few short (<5 μm) radial cracks were present. The matrix in this case had transformed to a combination of α, β, and orthorhombic phases.

These micrographs suggest several possible explanations for the lower than expected stresses. The radial cracking is probably the most important, since the crack face separation would allow relaxation of the elastic stress. However, other effects, such as volume changes accompanying the silicide/carbide reaction at the interface and impurity profiles near the fiber, could contribute. Again, this seems to be an area suited to further study.

V. SUMMARY

Synchrotron X-ray energy dispersive diffractometry has been used to measure thermal residual strains around Al2O3 and SCS-6 fibers embedded in HIP-consolidated titanium and Ti-14Al-21Nb matrix composites. For the first time, a measurement of the thermal residual strain gradients around ceramic fibers embedded several millimeters within thick metal matrix composites has been accomplished. Using the high-intensity white radiation available at the National Synchrotron Light Source, Brookhaven National Laboratory, the measurement of strain to a (grain size limited) precision of 10⁻³ or better from diffracting volumes of the order 10⁻⁶ mm³ has been demonstrated. The spatial resolution within the the sample was controlled by the probe dimensions and positioning errors. Typically it was ±20 μm, though further improvement is feasible. For the model 800 μm diameter Al2O3 fiber-titanium matrix system, reasonable agreement between measured and elastic predictions was observed. The agreement between measurement and elastic model predictions for the SCS 6/Ti-14Al-21Nb system was not as good. In particular, the measured stresses near the fiber were substantially less than those predicted by a simple elastic concentric model. Elastic-plastic models of the problem indicate that the SCS-6/Ti-14Al-21Nb system, significant plastic strains (~4 pct) occur on cooling and these relax the residual strains. However, the most important effect appears to be the radial cracking of the matrix near the fiber.

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Disclaimer: The names of material suppliers and equipment vendors are given in the text to aid the reader’s evaluation of the experiments. These should not be considered as product endorsements by either the National Institutes of Standards and Technology or the University of Virginia.

REFERENCES