

DAMPING BEHAVIOR IN FERROELECTRIC REINFORCED METAL MATRIX COMPOSITES

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Damping Behavior in Ferroelectric Reinforced Metal Matrix Composites

Ben Poquette

(ABSTRACT)

Ferroelectric-reinforced metal matrix composites (FR-MMCs) show promise as high damping materials for structural applications. Most structural materials are valued based on their stiffness and strength; however, stiff materials typically have limited inherent ability to dampen mechanical or acoustic vibrations. The addition of ferroelectric ceramic particles may also augment the strength of the matrix, creating a multifunctional composite. In this work, the damping behavior of FR-MMCs created by the addition of barium titanate (BaTiO_3) discontinuous reinforcement in a bearing bronze ($\text{Cu-10w\%Sn}$) matrix has been studied. It has been shown that even when combined with other traditional composite mechanisms, added damping ability has been achieved due to the ferroelectric nature of the reinforcement. FR-MMCs currently represent a material system capable of exhibiting increased damping ability, as compared to the structural metal matrix alone.

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Chapter One- Project Introduction

Most structural metals are selected based on high stiffness and strength; however, stiff materials efficiently transmit vibrations, which are normally an unwanted side effect of mechanical motion. Because vibrations can cause mechanical failure via high cycle fatigue, induce physical discomfort, and compromise stealth, significant effort is made to eliminate them. Effective vibration suppression (damping) could be achieved by incorporating multifunctional composites, which can simultaneously improving passive damping, strength, and stiffness, into existing and planned structures.

Ferroelectric ceramics have been shown to have high damping behavior below their Curie temperatures (T_c),¹ and the damping ability of these ceramics can be extended to stiff structural materials through compositing. The addition of ferroelectric particles may not only improve damping capacity, but may also augment the load bearing capacity of the matrix, creating a multifunctional composite.

A multifunctional material is designed to simultaneously address two or more engineering functions.² The concept of multifunctionality can be applied to many applications, including structural materials that are at the same time self-interrogating, self-healing, stealth providing, or energy dissipating. In most applications, the implementation of multifunctional materials leads to improved system efficiency. In this work, barium titanate (BaTiO_3) particles are incorporated into a Cu- 10w%Sn (bearing

bronze) matrix, and the damping properties of the resulting ferroelectric reinforced metal matrix composite (FR-MMC) have been investigated above and below the Curie temperature of the ferroelectric reinforcement.

Previous work has shown limited success in this area.³⁻⁶ In these studies, FR-MMCs were fabricated by the consolidation of mixtures of metal and ferroelectric ceramic powders. These consolidation methods consisted of pressing or rolling of the powders into a green body followed by high temperature sintering. Consolidation in this manner though, has some severe implications. It can result in high levels of porosity in the matrix degrading its mechanical properties. This porosity tends to collect around the reinforcing particles degrading the matrix/reinforcement (M/R) interface, resulting in reduced M/R interaction which can greatly reduce the reinforcement's impact on composite behavior.

The purpose of this work is to understand new methods to improve the overall quality of FR-MMCs as compared to work previously done in this area, while at the same time further the understanding of the damping ability of this system and how volume fraction affects this. The new methods utilized to improve composite quality included: secondary pressing and sintering (to decrease porosity), and electroless copper plating of the ceramic particles (to improve the matrix/reinforcement interface). Decreasing overall porosity as well as improving the matrix/reinforcement interface can serve to improve the overall quality of the composites. This would lead to improved mechanical properties as well as increased activation of the damping mechanisms of the reinforcement

Chapter Two- Background

The focus of this work is the fabrication and characterization of ferroelectric reinforced metal matrix composites (FR-MMCs) for damping applications. This subject brings together several different areas of expertise. In order to address each of these areas, this chapter will be divided into four sections. The first section will focus on the concept of damping, the quantities used to represent it, and the methods used to measure damping ability in materials. Metal matrix composites (MMCs) and their strengthening mechanisms will be addressed in the second section, with the focus being on the predicted behavior of the bronze-BaTiO₃ system. The third section will address ferroelectric materials, what makes them unique, and the root of their high-damping capability. Finally, section four will address electroless plating, paying special attention to electroless plating of Cu onto nonconducting substrates.

1. Damping

In many practical applications, the rate at which elastic waves (periodically changing local strains) become attenuated in a structure is of considerable importance. For example, the use of components made from materials with a high damping ability, leads to reduced noise and vibration in machinery. Here, the amplitude of vibration is lowered, reducing noise volume and/or the danger of fatigue failure.

1.1 Types of Damping

Vibration is a form of simple harmonic motion. As with all motion, it will continue until a retarding force is applied. A retarding force is any force applied opposite that of the harmonic motion. The application of this retarding force is termed damping. During damping, mechanical energy is dissipated, often in the form of heat. Thus, damping can be thought of as the dissipation of energy with time.

Free Decay

Free decay involves the single excitation of a structure by an external source. Energy is transferred through elastic waves and the structure begins to vibrate. As this energy is depleted, the amplitude of vibrational motion in the object decays. This is shown graphically in Figure 1.

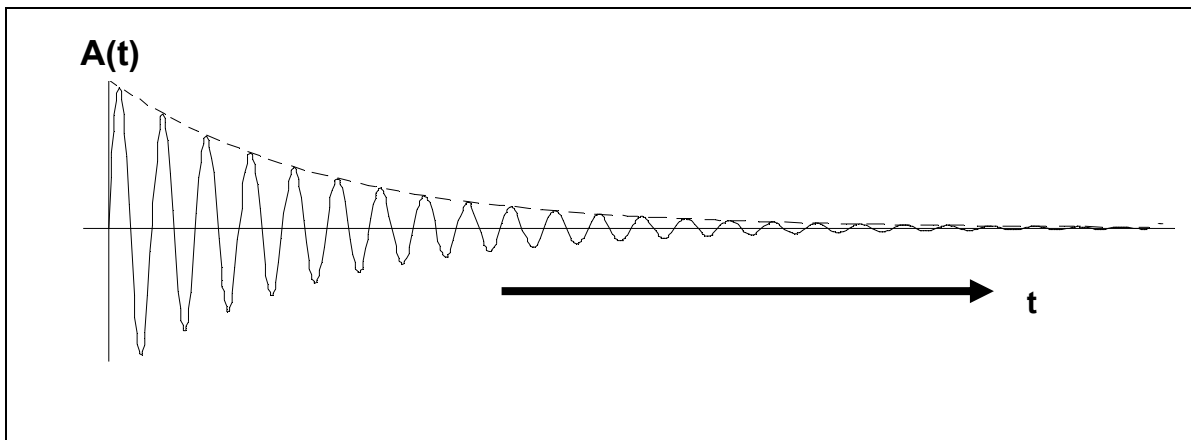


Figure 1. Free decay of vibration.

Here the sinusoidal wave of motion deteriorates in amplitude (A) as a function of time (t). When this kinetic energy is completely eliminated, the harmonic motion of the structure ceases. At this point it is said to be completely damped. In this case, damping can be quantified by the trend seen in the decay of the vibration amplitude.

Damping of an Oscillatory Force

Damping will also occur while a structure is continuously excited. This is based on stress/strain behavior and is essentially a manifestation of anelasticity. In any case, there

is a response time between when an object is stressed and when it responds to that stress. This response time results in a phase lag (δ), between the curves for stress and strain. This is shown in Figure 2. The phase lag will be zero degrees for purely elastic materials and 90 degrees for purely viscous ones.

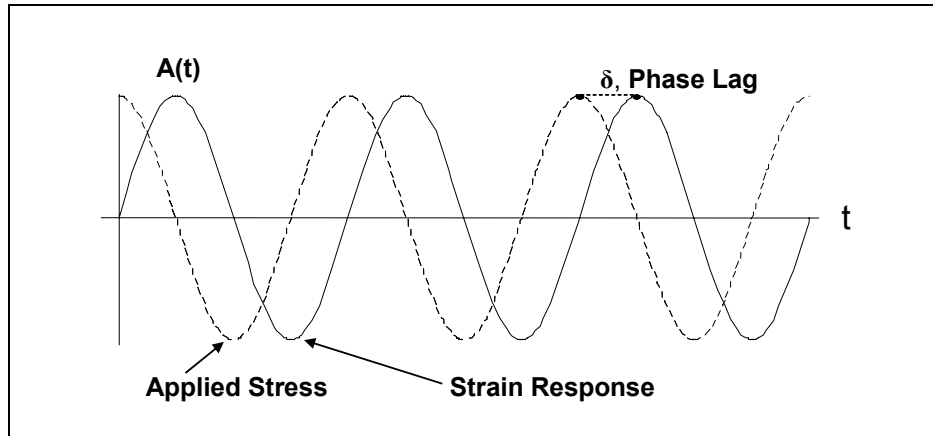


Figure 2. Stress-strain phase lag.

The tangent of the phase lag ($\tan \delta$) is known as the loss tangent. This value is commonly used to quantify damping ability. In reality, damping in a structure can be attained by active and/or passive methods. Active methods make use of both sensors and actuators to counter structural vibration in real time. Passive methods make use of the inherent ability of certain materials to absorb vibrational energy. Only passive methods will be addressed in this work.

1.2 Damping Mechanisms

Impact Damping

Impact damping is a simple concept, in which vibrations from one system are passed to another. In this case, a retarding force is applied when the non-vibrating object comes in contact with a vibrating one.⁷ Grasping the vibrating ends of a tuning fork is an example of this phenomenon. Vibrational energy is dissipated from the fork to your hand, causing a strong damping effect. In contrast, a tuning fork left in air will vibrate for quite a long time.

Friction Damping

Friction damping is based on restricting the movement of the vibrating object through contact friction. As the vibrating mass moves in contact with the damping object, there is a frictional force created at that interface. In this case, the frictional force becomes the retarding force responsible for decreasing the total energy of the vibrating object. On the large scale, friction damping is not very common, due to the material degradation associated with constant friction. On the smaller scale however, it can be very useful. One common example is the friction between matrix and reinforcement particles in composite materials.⁸

Viscoelastic and Microstructural Damping

Damping can also be inherent to the material in motion. Here the damping ability is dependent on the material's internal friction, which is its ability to dissipate strain energy. Traditionally materials for vibration damping have been primarily polymers due to their viscoelastic character caused by molecular movements. However, there are various mechanisms by which energy can be absorbed within a material. In crystalline specimens, various factors associated with features such as inclusions, porosity, dislocation motion, plastic zone creation, grain boundary sliding, other crystalline defects, phase changes, and magnetoelastic effects can cause internal friction.^{9,10} The essential requirement for each mechanism is that it can be activated by the current local stresses and within the timescale for which the external load is applied. Consequently, at any given temperature, each mechanism can only respond up to a certain maximum frequency (minimum response time) and down to a certain minimum strain amplitude (local stress level). Due to this, the damping properties of a material can vary greatly with loading conditions, such as the frequency and amplitude of the applied stress, as well as sample temperature.

Combinations of materials (composites) can also be effective at damping vibration. Composite structures combine the inherent damping abilities of two or more unique materials, while making use of the additional frictional damping arising at the matrix/reinforcement interfaces.

1.3 Mathematical Methods for Damping Measurement

Nomenclature

As previously mentioned, all of the energy-absorbing processes active in a material contribute to its internal friction. In this section, several commonly used quantities for describing internal friction will be discussed.¹¹

Loss Tangent	Loss Factor	Damping Ratio	Specific Damping Capacity, SDC	Logarithmic Decrement	Inverse Quality Factor	Ratio of Energy Loss to Elastic Stored Energy Per Cycle
$\tan \delta$	η	ζ	Ψ	Δ	Q^{-1}	$W_{\text{loss}}/W_{\text{stored}}$

Table 1. Commonly used measures for internal friction

The relationship between these quantities is outlined in Eq. 1.

$$\tan \delta = \eta = \zeta = \frac{\Psi}{2\pi} = \frac{\Delta}{\pi} = Q^{-1} = 2\pi \frac{W_{\text{loss}}}{W_{\text{stored}}} \quad [1]$$

Here $\tan \delta$ is referred to as the loss tangent. η is the loss factor. ζ is the damping ratio. Ψ represents the specific damping capacity. Δ is the logarithmic decrement. Q^{-1} is the inverse quality factor, and $W_{\text{loss}}/W_{\text{stored}}$ is the ratio of the energy loss (W_{loss}) to the energy stored (W_{stored}) per cycle.

Free Decay Method

The free decay method can be used to characterize damping of either resonant or subresonant vibrations. The basis for this model begins with Figure 3.

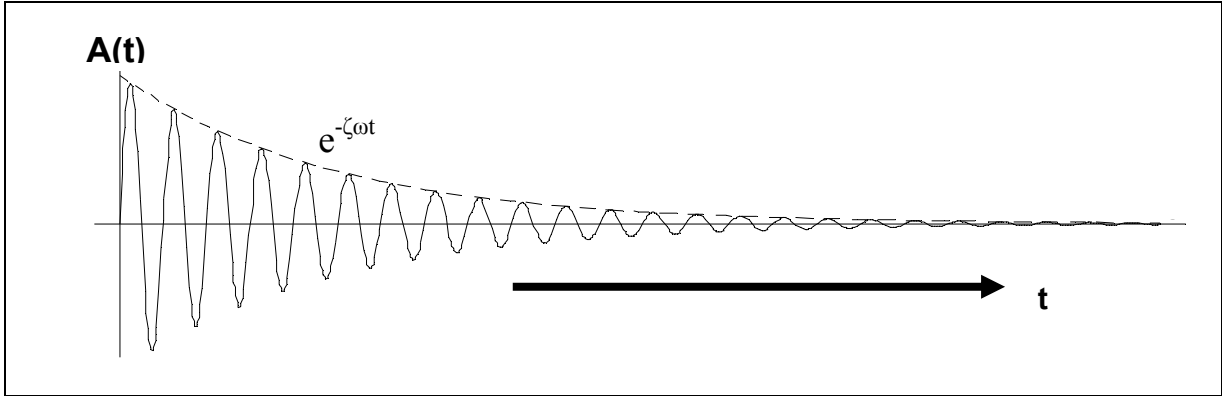


Figure 3. Free Decay

Here the solid line represents the function of amplitude with respect to time ($A(t)$). The dotted line connecting the amplitude peaks is the decay envelope and is described using the function $e^{-\zeta\omega t}$, with ω being the natural frequency of the material, and t is time. To find the damping ratio (ζ), this line is also curve fit to the function e^{-at} , where a is the fit determining constant. The two quantities are then set equal, and ζ is found using Eq. 2.⁸

$$a = \zeta\omega \quad [2]$$

Half-Power Bandwidth Method

The half-power bandwidth method involves plotting the magnitude of the frequency response function ($x(t)$) on a linear scale near the region of resonance. A curve of this nature can be seen in Figure 4.

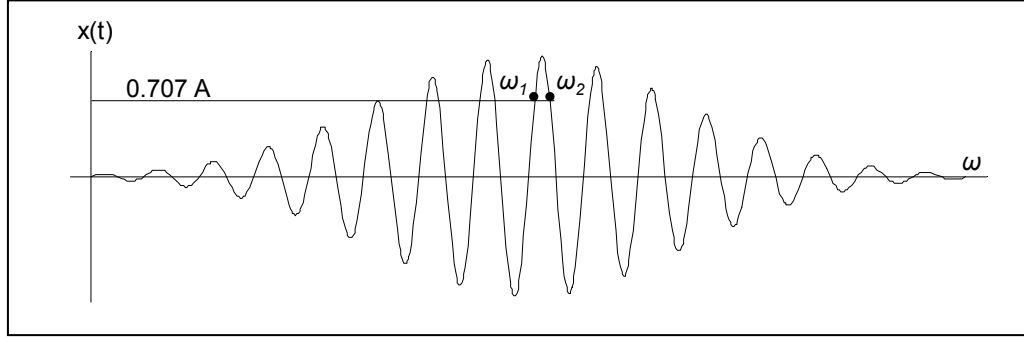


Figure 4. Magnitude of the frequency response function $x(t)$ on a linear scale.

If the damping is sufficiently small making the peak at resonance sharp, then the inverse quality factor (Q^{-1}) can be determined. This is done by first identifying the maximum amplitude value (A) and then measuring the frequencies at $1/\sqrt{2}$ or (≈ 0.707) of A (ω_1 and ω_2). Finally Q^{-1} can be determined using Eq. 3.^{12,13} In this equation, ω_d is the damped natural frequency of the material being examined.

$$Q^{-1} = \frac{0.5(\omega_2 - \omega_1)}{\omega_d} \quad [3]$$

Stress-Strain Hysteresis Method

This method is used to find the specific damping capacity (Ψ) using a stress-strain hysteresis curve like that seen in Figure 5.¹⁴

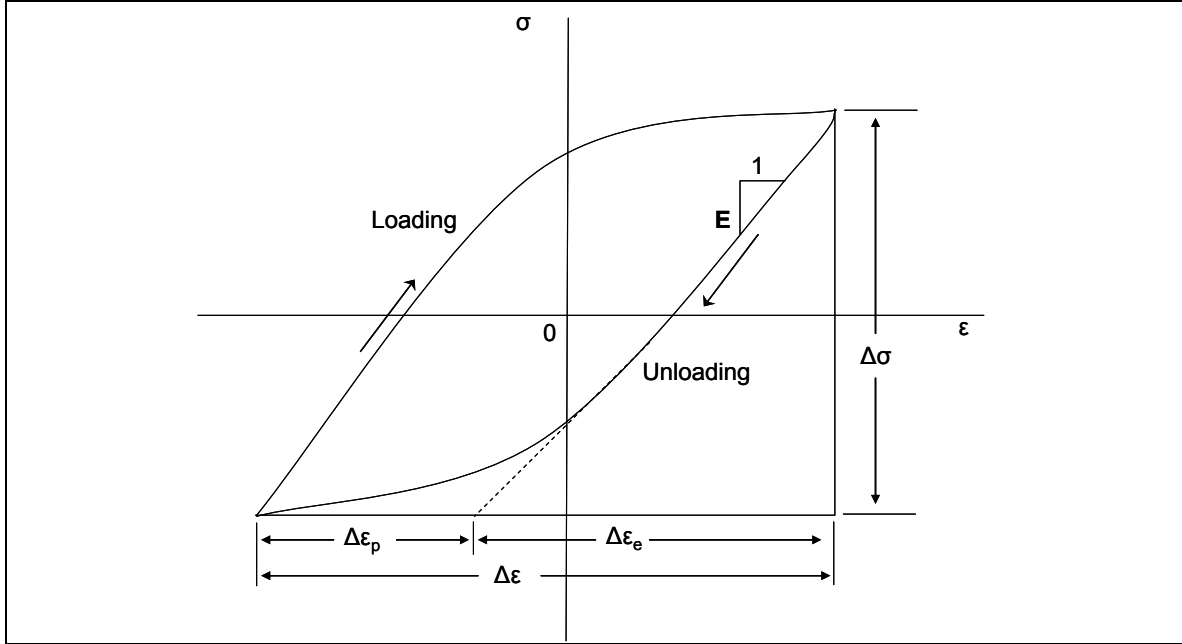


Figure 5. Stress-strain hysteresis curve.

Specific damping capacity is found using Eq. 4,⁸ where the energy dissipated (ΔW) is the area between the loading and unloading curve, and the energy stored (W) is the area under the loading curve in Figure 5.¹⁵

$$\psi = \frac{\Delta W}{W} \quad [4]$$

Phase Lag Method

In this method, the phase-lag (δ), between the sinusoidal curves of applied stress and resulting strain, can be found. An example of this can be seen in Figure 6.

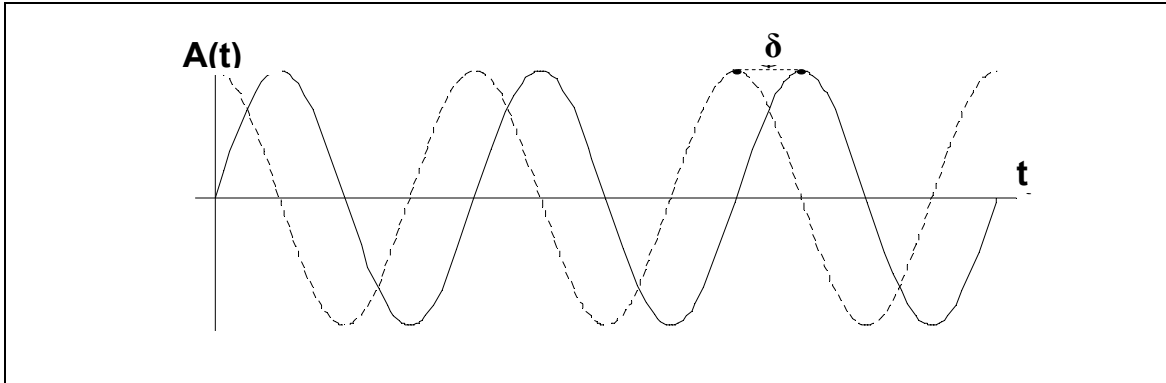


Figure 6. Sinusoidal stress and strain curves showing the phase-lag.

With δ being known, the loss tangent ($\tan \delta$) can be computed by taking the tangent of δ .¹⁴ This can then be converted to any of the other quantities for damping capacity using Eq. 1.

1.4 Damping Measurement Techniques

Torsion Pendulum

The torsion pendulum has been largely used as one of the principal experimental methods for measuring anelastic properties of materials. The torsion pendulum comes in three varieties: direct, inverted and Collette. The simplest of these is the direct torsion pendulum. It uses the free decay method to measure internal friction (Q^{-1}) from the torsional movement of the sample. The direct torsion pendulum consists of a wire-shaped specimen hanging vertically, with an inertial arm connected to the bottom, as in Figure 7.

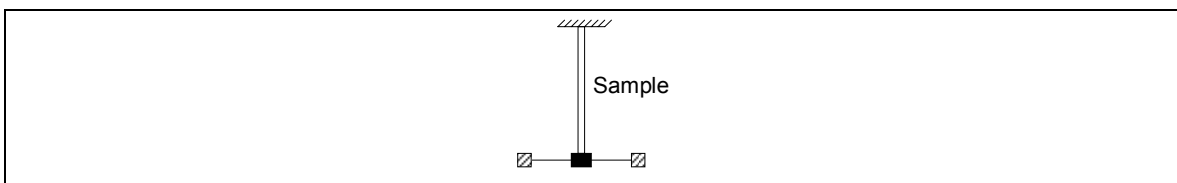


Figure 7. Diagram of a direct torsion pendulum

To keep external losses low, this apparatus is usually suspended in an evacuated chamber. This simple system does have some drawbacks. If the tensile load exerted on

the sample by the inertia arm is too great, creep deformation can occur in the sample at high temperatures. For this reason most torsion pendulum used today are inverted.¹⁶

With the inverted torsion pendulum, the specimen is situated below the inertial arm. Since only a small force is needed, a thin suspension wire made from a low damping material is used to keep the sample in place. The wire is made very thin so that its torsional rigidity can be neglected.¹⁶ This can be seen in Figure 8.

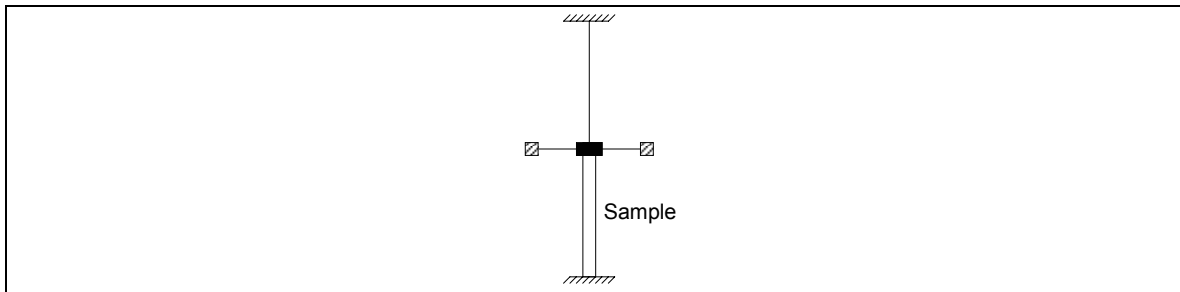


Figure 8. Diagram of an inverted torsion pendulum

The inverted pendulum also uses the free decay method to measure the internal friction (Q^{-1}) from the torsional oscillation of the sample. This technique has become such a standard method that the results are taken directly, neglecting any contribution by the thin suspension wire.¹⁶

The Collette pendulum was introduced to make damping measurements on samples with large cross section and to perform measurements at small strain amplitudes (10^{-7} - 10^{-6}), which are out of range for other types of pendulums.¹⁴ The Collette pendulum is obtained from the inverted pendulum by adding a second suspension wire between the inertia member and the specimen, as seen in Figure 9.

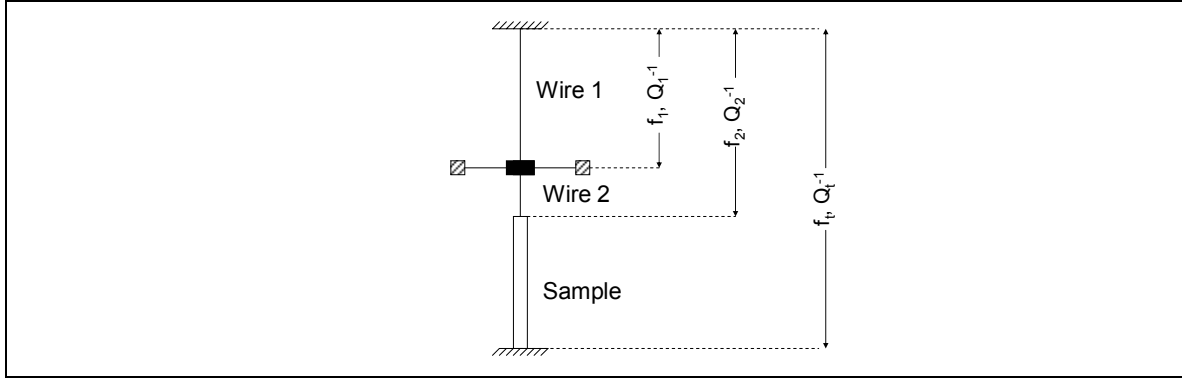


Figure 9. Diagram of a Collette torsion pendulum.

For this arrangement, a certain frequency interval can be preset by appropriate suspension wires regardless of the properties of the sample.¹⁷ For the Collette system the total measured damping (Q_t^{-1}) is never identical with that of the specimen Q_s^{-1} , but always contains significant contributions from the suspension wires. Thus, these contributions must be taken into account when calculating Q_s^{-1} from Q_t^{-1} .

Free-free Bars

In the free-free bar configuration, the sample is fixed at points of vibration nodes by fine wires, knife edges or needle points. All the natural modes of vibration of a bar (longitudinal, torsional or flexural) can be used for internal friction measurements, Q^{-1} . In fact, various specimen forms are used for such experiments: bar, rod tube, disk, etc.¹³ Damping can be obtained using the free decay method for flexural mode, or the half-power bandwidth method.

Vibrating Cantilever Beam

This technique measures the damping ability of a sample in the form of a cantilever beam anchored at one end. To do this, two transducers are used. One is used to excite the beam using a sinusoidal signal, and the second noncontacting transducer measures the beam's response. The excitation signal is swept across a range of frequencies locating the resonance frequency. When the resonance frequency is found, the loss factor (η) is computed using the half-power bandwidth method. Damping measurements are

generally done in an enclosed chamber to control temperature minimizing environmental losses.¹⁸

Laser Doppler Vibrometry

Laser Doppler vibrometry (LDV) uses a laser to measure the amplitude of vibration of an object. With this technique, it is possible to measure amplitudes on the order of half the wavelength of the laser source.¹³ This measurement is done by splitting the laser source into two beams, with one contacting the sample before being detected. To calibrate this equipment, the beams are first detected without the presence of the sample. Since they both follow different paths to the detector, they will be out of phase. Next, the equipment is run with the sample in place. The specimen is vibrated and the beams detected. The beam coming in contact with the sample will now be further out of phase with the reference due to interaction with the sample. This increased phase shift, also known as Doppler shift, can be used to calculate the change in distance traveled of the beam due to the vibrational movement of the sample. This change in distance corresponds to the amplitude of vibration of the specimen. This measurement is made repeatedly until the sample comes to rest, giving the amplitude as a function of time. This data can be interpreted using the free decay method.

Since there is no interaction between the sample and the detector, laser vibrometry has become very important in the study of very light structures, such as loudspeaker membranes, and samples of very small size. Despite this, some disadvantages exist including the dimensions and weight of the optical head, the necessity of precise optical alignment, general complexity and cost.

Dynamic Mechanical Analyzer

The dynamic mechanical analysis, DMA is a nondestructive testing technique that was utilized in this work. Here, the sample material is subjected to a forced oscillation, as shown in Figure 10.

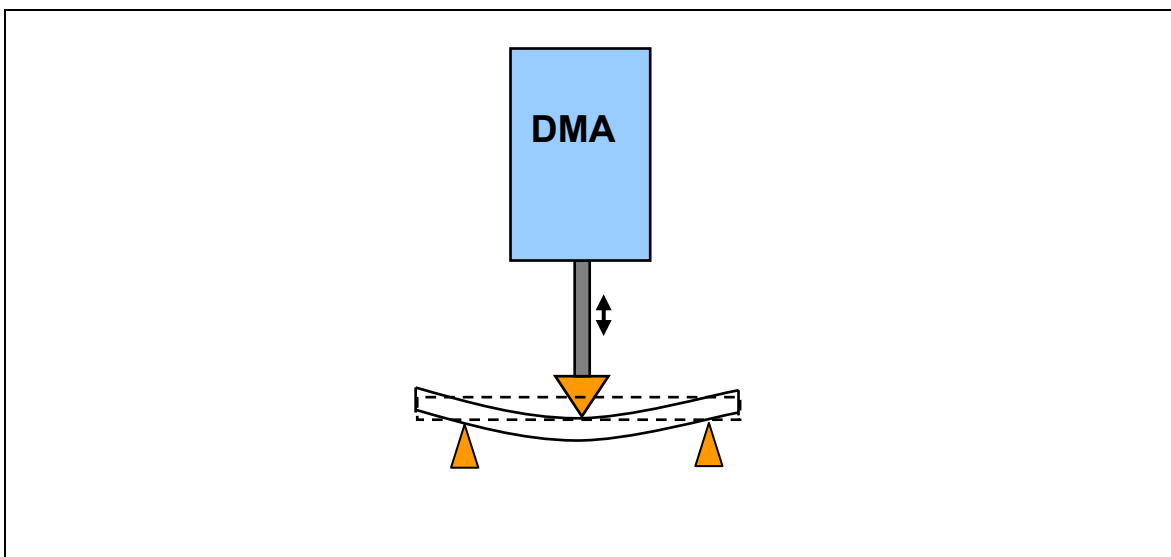


Figure 10. Schematic of a Dynamic Mechanical Analyzer, DMA

The DMA measures the raw signals of force, amplitude of deformation and phase angle. Instrument calibration constraints are applied to the raw signals. Force and amplitude are used with the phase angle to calculate the storage and loss stiffness (K' and K''). $\tan \delta$ is calculated as the ratio of K'' to K' . Storage and loss moduli are then calculated by multiplying the raw stiffness measurements by the appropriate geometry factors. A good understanding of sample stiffness is important for understanding geometry selection when conducting DMA measurements.

Depending on the equipment model, the frequency of the input signal can generally range from 0.01-100 Hz, but often at fixed frequency steps. Temperature can be adjusted in the range of -70 to 600 °C, and samples with moduli between 10^{-3} - 10^6 MPa can be tested.¹³ DMA is also very versatile in that it can accommodate many different types of sample holders depending on the bending mode tested. These include three-point bending, dual or single cantilever bending, compression, and tension. Phase shift is calculated by Fourier analysis and associated software generally allows presentation of the results as a function of temperature.

DMA is widely used to study polymeric materials, although certain units can be applied to stiffer metallic systems. In addition to damping behavior, it can determine modulus, elasticity, viscosity, creep, and glass transition temperature, along with their change as a

function of strain, strain rate, temperature, and oscillatory frequency. Damping values from the DMA are obtained using the phase-lag method.

1.5 Damping Values of Selected Engineering Materials

As a general reference, the $\tan \delta$ for several engineering materials has been given in Table 2.^{11,19}

Material	$\tan \delta$
Alumina (Al_2O_3)	$1\text{--}3 \cdot 10^{-5}$
Steel	$2 \cdot 10^{-5} \text{--} 3 \cdot 10^{-3}$
Cast Iron	$6 \cdot 10^{-3} \text{--} 3 \cdot 10^{-2}$
Concrete	$1\text{--}3 \cdot 10^{-2}$
Wood	$3 \cdot 10^{-3} \text{--} 3 \cdot 10^{-2}$
Polyethylene	0.1 – 0.3
Butyl Rubber	0.3 – 4.0

Table 2. Measured damping ability of several engineering materials at room temperature

2. Metal Matrix Composites

Metal matrix composites (MMCs) encompass a wide range of material and microstructural combinations, each of which has in common a continuous metallic matrix. MMCs can be further subdivided based on their reinforcement morphology. Reinforcements generally come in the form of continuous fibers, short fibers, or particles, each of which relies primarily on unique strengthening mechanisms.^{20,21} These are summarized in Table 3.

Type of MMC	Reinforcement Morphology	Primary Strengthening Mechanisms
Fiber Strengthened (Continuously Reinforced)	Long fibers (aspect ratio >10)	Shear lag theory (Load transfer from matrix to fiber)
Discontinuously Reinforced	Short fibers or whiskers (aspect ratio <10), and/or Large particles (diameter >1 μ m)	Combination of <u>fiber</u> and <u>dispersion</u> strengthening mechanisms
Dispersion Strengthened	Small particles (diameter <1 μ m)	Orowan inhibition of dislocation motion ²² , Boundary strengthening - Matrix/reinforcement - Grain size refinement in the matrix Coefficient of thermal expansion mismatch

Table 3. Metal matrix composite subcategories

In this work, a discontinuous MMC having a matrix of Cu- 10w% Sn bronze reinforced with ~35 μ m BaTiO₃ ferroelectric ceramic particles will be studied.

2.1 Strengthening Mechanisms in Discontinuously Reinforced Metal Matrix Composites

Discontinuously reinforced composites fall somewhere between the dispersion strengthened and fiber strengthened extremes. A discontinuously reinforced composite's place between these extremes is strongly dependent on the size and shape of its reinforcement. In general, as the aspect ratio of the reinforcement increases, the composite tends to exhibit increased amounts of fiber strengthening, but as particle size or whisker diameter decreases, the composite will tend to be primarily strengthened by

dispersion methods. With this in mind, an ideal composite may be one having a high aspect ratio, small diameter reinforcement, in that all strengthening mechanisms would be highly active. The following sections should serve to explain how reinforcement size and geometry affects the strengthening contributions by these mechanisms.

Shear Lag Theory

The shear lag theory assumes that load transfer occurs between a high aspect ratio reinforcement and the matrix by means of shear stresses at the particle-matrix interface. Through this mechanism, the particle acts to bear some of the applied load. The original model²³ of this mechanism only accounted for the shear transfer of load along the interface parallel to the applied load, but subsequent modifications have been made to account for the tensile transfer of load at the particle ends. This is important in dispersion strengthened composites, as its contribution tends to become more significant as the aspect ratio of the particle decreases.^{24,25} According to the modified shear lag theory, which assumes no slipping at the matrix/reinforcement (M/R) interface, the yield strength of a composite can be found using Eq. 5.²⁵

$$\sigma_c = \sigma_{ym} \left[1 + \frac{(L+t)S}{4L} \right] f + \sigma_{ym} (1-f) \quad [5]$$

Here σ_{ym} is the yield strength of the unreinforced matrix. L is the length of the particle perpendicular to the applied stress. t is the length of the particle parallel to the applied stress. S represents the particle aspect ratio, and f is the particle volume fraction. In the case of spherical or equiaxed particles $L \approx t$ and $S \approx 1$ reducing Eq. 5 to Eq. 6.²⁶

$$\sigma_c = \sigma_{ym} \left(1 + \frac{1}{2} f \right) \quad [6]$$

This represents a linear and very modest increase in yield strength with increasing volume fraction. Upon comparison of Eqs. 5 and 6, the dependence on aspect ratio becomes apparent. Applying this relation, Figure 11 shows the dependence of yield strength vs. volume fraction reinforcement for the composite system studied in this work, bronze reinforced with 35 μ m BaTiO₃ particles.

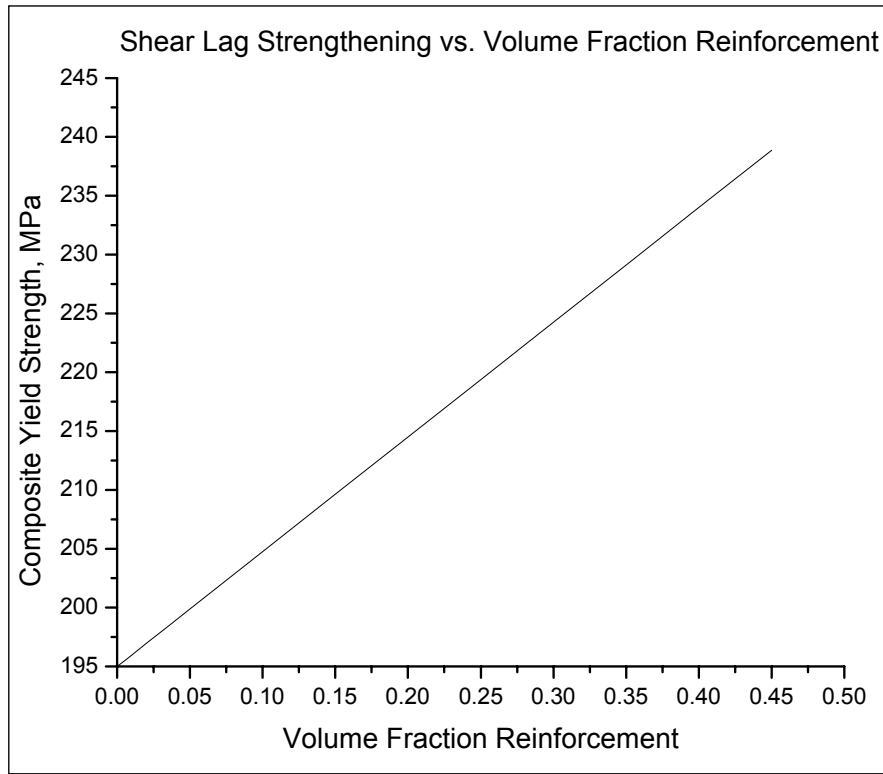


Figure 11. Calculated dependence of yield strength vs. volume fraction reinforcement according to the modified shear lag theory of the bronze-BaTiO₃ composite system.

In this work, this upward trend becomes dually important. Not only does it predict composite strengthening due to load transfer, but from the prediction of load transfer, one can predict increased damping arising from the activation of damping mechanisms in the reinforcement by the transferred load.

Orowan Strengthening

Yielding in metals generally occurs through the process of dislocation motion. In composites containing small ($<1\mu\text{m}$), incoherent particles, inhibition of dislocation motion can arise as dislocations physically interact with the small reinforcement. With small impenetrable particles, a passing dislocation will bow between particles and finally pass by leaving behind an “Orowan” loop, as illustrated in Figure 12.

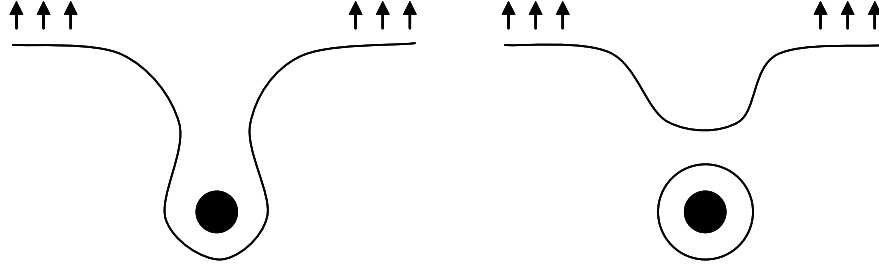


Figure 12. Formation of an Orowan loop as a dislocation bows around a particle

By increasing dislocation density through the creation of Orowan loops and by causing dislocations to increase in length, the presence of these small particles tends to increase the yield strength of the material. This was originally described by the Orowan relationship²² which predicts the shear stress (τ) required for a dislocation to by-pass a particle and is shown in Eq. 7.

$$\tau = \frac{Gb}{\lambda_{e-e}} \quad [7]$$

Here, G is the shear modulus of the material; b is its atomic spacing, and λ_{e-e} is the edge-to-edge spacing of the particles. Ashby modified the above equation to account for diminished strengthening as the particle size approaches an atomic diameter. Further modification to normal stress in polycrystalline materials yields,^{21,26}

$$\sigma_c = \sigma_m + \frac{2.4G_m b}{2\pi(1-\nu)^{1/2}} \frac{\ln \frac{2r}{r_o}}{\lambda_{e-e}} \quad [8]$$

or for rod and plate shaped reinforcement, Kelly and Street proposed a further modification.²⁷

$$\sigma_c = \sigma_m + \frac{2.4G_m \cdot b}{2\pi(1-\nu)^{1/2}} \frac{1 + \frac{L_T}{\lambda_{c-c}}}{\lambda_{c-c}} \ln \left(\frac{t}{r_o} \right) \quad [9]$$

In Eqs. 8 and 9, the factor 2.4 comes from the product of the Taylor factor (≈ 3), which relates shear to normal stresses, and a statistical/geometric factor, which discounts the overall strengthening effect that is possible. This discount is based on the fact that the wrapping of a dislocation around one particle inhibits its ability to fully wrap around and

adjacent particle. Thus the adjacent particle cannot inhibit the motion of that dislocation to its fullest ability. This discounted ability has been calculated to be roughly 0.81.²¹ Also, σ_c is the strength of the composite and σ_m is the strength of the matrix without reinforcement. G_m is the shear modulus of the matrix, which for isotropic matrices can be found using Eq. 10.

$$G_m = \frac{E}{2(1+\nu)} \quad [10]$$

Here, ν is Poisson's ratio and E the elastic modulus of the matrix.

Getting back to Eqs. 8 and 9, t is the thickness and L_T the total length of rod or plate reinforcement. b is the magnitude of the Burgers vector for deformation in the matrix, which for cubic matrices can be estimated as $b \approx 2(r_{ma})$, where r_{ma} is the atomic radius of the matrix. r_o represents the dislocation core radius which can be estimated as $r_o \approx 3b$. r is the average particle radius, and λ_{e-e} is the edge-to-edge particle spacing, which is approximated by Eq. 11.

$$\lambda_{e-e} \approx \lambda_{c-c} - 2r \quad [11]$$

λ_{c-c} is the center-to-center particle spacing according to Eq. 12.

$$\lambda_{c-c} \approx 1.23r \cdot \left(\frac{2\pi}{3f} \right)^{1/2} \quad [12]$$

Here, f is the volume fraction reinforcement.

The Ashby-Orowan Equation predicts increased strength with decreasing particles size and/or increasing volume fractions. This is particularly true for particles in the submicron range, but strengthening effects are still predicted but not expected to be dominant for particle sizes greater than 10 μ m. Figure 13 shows the predicted dependence of yield strength vs. volume fraction reinforcement according to Ashby-Orowan strengthening, for the bronze-BaTiO₃ composite system addressed in this work.

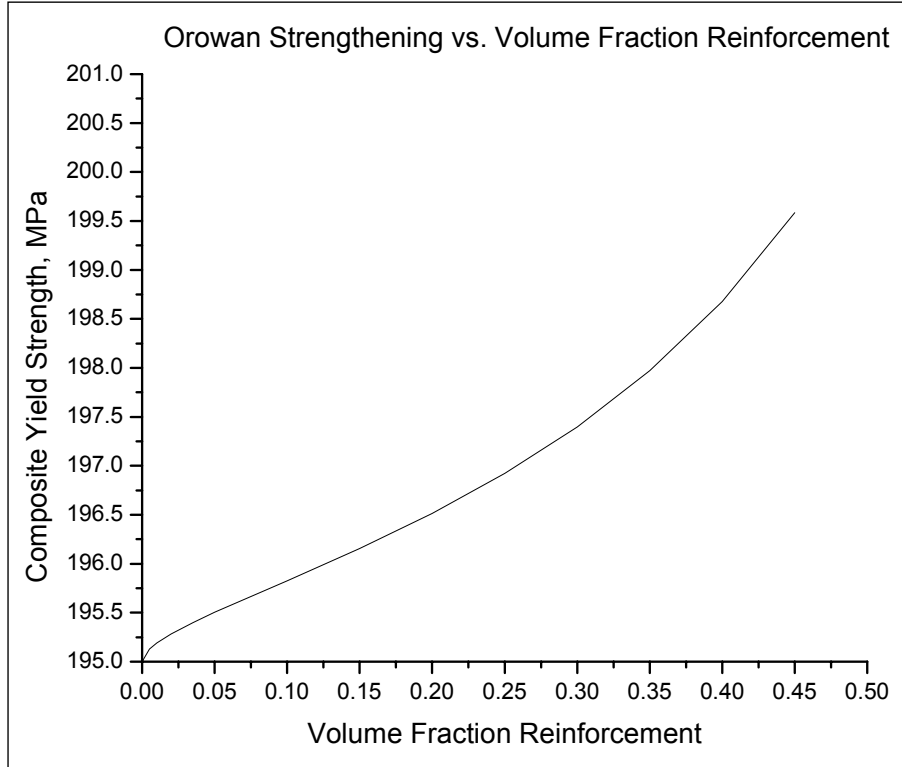


Figure 13. Calculated dependence of yield strength vs. volume fraction reinforcement according to Orowan strengthening of the bronze-BaTiO₃ composite system.

Due to the relatively large size of the particulate reinforcement (35 μ m), negligible Orowan strengthening is predicted for this system.

Boundary Strengthening

The Ashby-Orowan Equation predicts negligible strengthening in composites having coarse or widely-spaced reinforcement.²¹ This is due to the fact that composites of this type are affected mainly by another mechanism, boundary strengthening. Again, yielding in metals in general occurs primarily through the creation and motion of dislocations, and this mechanism is based on crystallographic discontinuities or boundaries impeding this motion. With the addition of reinforcement to a matrix, M/R boundaries are formed. When the material is stressed, dislocations tend to pile-up at these incoherent interfaces increasing the overall dislocation density and thus strength of the material. This is similar to Hall-Petch strengthening in metals, which can simultaneously occur in the matrix due to grain refinement.²¹

There are four different equations used to model boundary strengthening. These are based on the shear “impingement” stress (τ_{boundary}) from the matrix at the M/R boundary and also the shear properties of the matrix (τ_{matrix}) and reinforcement ($\tau_{\text{reinforcement}}$). This behavior can be difficult to predict, so often composites are stressed to failure and examined to determine which equation to use.

If the particle has fractured, then $\tau_{\text{boundary}} > \tau_{\text{reinforcement-fracture}}$, and Eq. 13 is used to calculate composite strength (σ_c).

$$\sigma_c = \sigma_m + \alpha' \sqrt{\frac{G_m G_p b}{5 \lambda_{e-e}}} \quad [13]$$

If the matrix has fractured, then $\tau_{\text{boundary}} > \tau_{\text{matrix-fracture}}$, and Eq. 14 is used to calculate σ_c .

$$\sigma_c = \sigma_m + \alpha'' \sqrt{\frac{G_m^2 b}{5 \lambda_{e-e}}} \quad [14]$$

If the particle has yielded, then $\tau_{\text{reinforcement-fracture}} > \tau_{\text{boundary}} > \tau_{\text{reinforcement-yield}}$, and Eq. 15 is used.

$$\sigma_c = \sigma_m + \alpha''' \sqrt{\frac{G_m G_p b}{10 \lambda_{e-e}}} \quad [15]$$

If the particle has neither fractured nor yielded, then $\tau_{\text{reinforcement-fracture}} \gg \tau_{\text{reinforcement-yield}} \gg \tau_{\text{boundary}}$, and Eq. 16 is used utilized.

$$\sigma_c = \sigma_m + \alpha'''' \sqrt{\frac{G_m E_p b}{10 \lambda_{e-e}}} \quad [16]$$

In Eqs. 13-16, σ_m is the matrix strength without reinforcement. G_m and G_p are the shear moduli of the matrix and particle. E_p is the elastic modulus of the particle. b represents the Burger’s vector for deformation in the matrix. λ_{e-e} is the edge-to-edge particle spacing from Eq. 11, and α is used as a fitting parameter with a value approximately equal to one.

The presence of α is an acknowledgement that the equations are predictive and that there are other factors which may influence the actual value of strength obtained through experiment. In Eqs. 13-16, the trend shown in Eq. 17 is generally true.²⁸

$$\alpha''' > \alpha'' > \alpha' > \alpha \quad [17]$$

For the bronze-BaTiO₃ system studied in this work, the reinforcement is expected to fracture upon testing based upon its low strength. Therefore $\tau_{\text{boundary}} > \tau_{\text{reinforcement-fracture}}$ and Eq. 13 might be used to calculate the composite strength. However, this cannot be verified through experiment as the reinforcement particles are already heavily cracked due to processing conditions. In cases such as this when the failure conditions cannot be determined, an underestimate of the boundary strengthening behavior can be found utilizing the experimentally determined Hall-Petch behavior of the matrix material. This is done, by combining the Hall-Petch equation,²⁹ where k_{H-P} represents the Hall-Petch constant and d the grain diameter,

$$\sigma_c = \sigma_m + k_{H-P} \sqrt{\frac{1}{d}} \quad [18]$$

with the equations for boundary strengthening. In Eqs. 13-16, the modulus and Burger's vector terms inside the square root along with the factor of 5 or 10 represent the mechanical mismatch between the matrix and the reinforcement. Large values of this term signify that the reinforcement particles are rigid with respect to the matrix, and thus would act as strong barriers to dislocation motion. This is analogous to the Hall-Petch constant which describes the rigidity of grain boundaries, as compared to the interior of grains, and their ability to impede dislocation motion. Thus a substitution can be made in Eqs. 13-16 resulting in Eq. 19, where k_{H-P} represents the Hall-Petch constant for the matrix material.

$$\sigma_c = \sigma_m + \alpha k_{H-P} \sqrt{\frac{1}{\lambda_{e-e}}} \quad [19]$$

Here, α remains as a fitting parameter with a value approximately equal to one, and λ_{e-e} is the edge to edge spacing between the particles. This distance, as with d from Eq. 18, represents the spacing between obstacles to dislocation motion in the material.

As mentioned earlier, the calculation of strengthening effects using Eq. 19 usually leads to an underestimate of true strengthening behavior. This is due to the fact that in most composite systems reinforcement particles are much better barriers to dislocation motion than are grain boundaries in a material. In the case of the bronze-BaTiO₃ system, the k_{H-P} for Cu ($0.112 \text{ MNm}^{-3/2}$)³⁰ is used to calculate boundary strengthening effects, and this has been plotted vs. reinforcement volume fraction as shown in Figure 14.

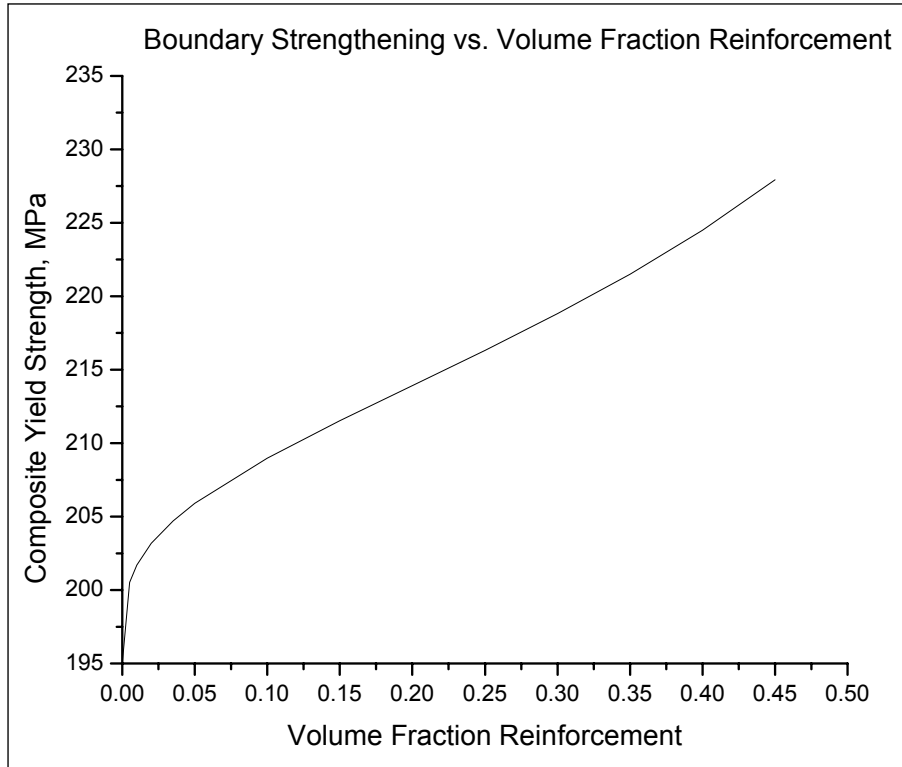


Figure 14. Calculated dependence of yield strength vs. volume fraction reinforcement according to boundary strengthening of the bronze-BaTiO₃ composite system.

Coefficient of Thermal Expansion Mismatch

Dislocation strengthening of the matrix due to thermal expansion mismatch between the matrix and reinforcement, can also play an important role in MMC strengthening.³¹ The residual stress developed due to the difference in coefficient of thermal expansion between the matrix and reinforcement (ΔCTE) can be large enough to induce plastic relaxation in the matrix. This can increase dislocation density by a few orders of

magnitude in the matrix leading to the strengthening of the composite.³² The composite strength (σ_c) can be predicted by this mechanism using Eq. 18,²⁸

$$\sigma_c = \sigma_m + \alpha G_m \left(\frac{2 f \varepsilon_{\Delta CTE} b S}{(1-f) V} \right)^{\frac{1}{2}} \quad [18]$$

or with Eq. 19²⁸ for cylindrical reinforcement.

$$\sigma_c = \sigma_m + \alpha' G_m \left(\frac{2 f \varepsilon_{\Delta CTE} b}{(1-f) t} \right)^{\frac{1}{2}} \quad [19]$$

Here, σ_m is the matrix strength without reinforcement. Again, α is used as a fitting parameter as in Eqs. 13-16 with a value approximately equal to one. As before, G_m is the shear modulus of the matrix; f represents the volume fraction of reinforcement, and t is the reinforcement thickness. b is the Burger's vector for deformation in the matrix, which can be estimated using atomic diameter. S/V is the surface to volume ratio, and $\varepsilon_{\Delta CTE}$ is predicted using Eq. 20,²⁸

$$\varepsilon_{\Delta CTE} \approx \frac{(\Delta CTE)(\Delta T)}{2} \quad [20]$$

where ΔT is the temperature change upon cool-down during processing or heat treatment.

For the bronze-BaTiO₃, ΔCTE strengthening has been calculated and plotted vs. reinforcement volume fraction. This is shown in Figure 15.

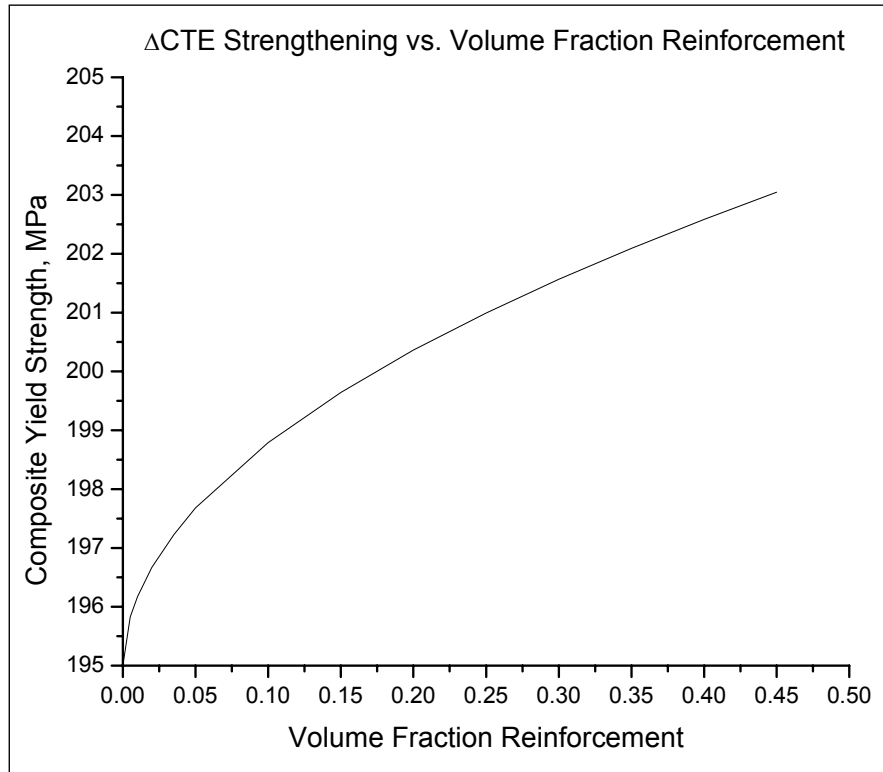


Figure 15. Dependence of yield strength vs. volume fraction reinforcement according to Δ CTE strengthening of the bronze-BaTiO₃ composite system.

As with Orowan strengthening, the Δ CTE mechanism is not predicted to have a large effect on the strength of the bronze-BaTiO₃ system.

Indirect Strengthening Mechanisms

Metal matrix composites can also be strengthened by mechanisms indirectly related to reinforcement addition. These indirect effects often stem from changes made to the matrix through reinforcement addition. Especially in the case of small particulates, the reinforcement can cause grain refinement in the matrix leading to strengthening through Hall-Petch mechanisms as previously mentioned. Primary or secondary recrystallization can also be initiated through reinforcement addition. Dissolution of the reinforcement or the formation of reaction layers at the M/R interface can also lead to strengthening in the matrix. These secondary effects will not be addressed in this work.

2.2 Additivity of Strengthening Mechanism Effects in Metal Matrix Composites

Figure 16 compares the effects of each of the previously mentioned direct strengthening mechanisms.

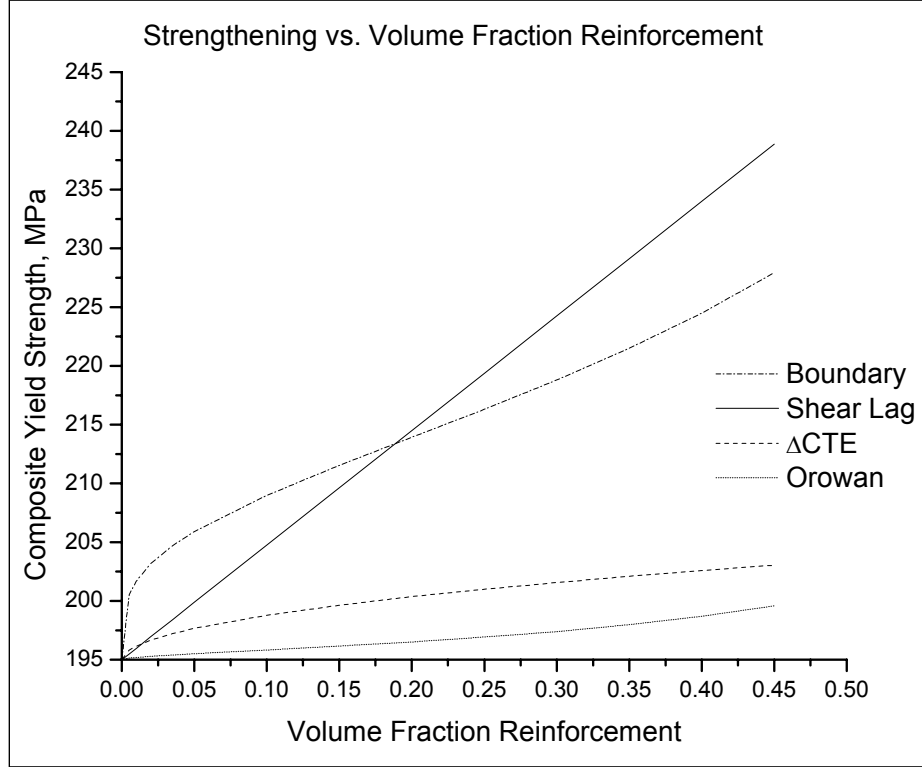


Figure 16. Dependence of yield strength vs. volume fraction reinforcement according to shear lag, Orowan, boundary, and Δ CTE strengthening of the bronze-BaTiO₃ composite system.

In general, these strengthening effects are all active in a composite at the same time leading to a combined effect on composite strength. Interdependency of these strengthening mechanisms however leads to the prediction of composite strength using an upper and lower bounds.

The upper bound assumes that each mechanism strengthens independently and combines their effects using linear additivity. This is shown in Eq. 21.

$$\sigma_c = \sigma_m + \Delta \sigma_{ShearLag} + \Delta \sigma_{Orowan} + \Delta \sigma_{Boundary} + \Delta \sigma_{\Delta CTE} \quad [21]$$

The lower bound assumes strong interdependence of the mechanisms using Pythagorean additivity, as shown in Eq. 22.

$$\sigma_c^2 = \sigma_m^2 + \Delta \sigma_{ShearLag}^2 + \Delta \sigma_{Orowan}^2 + \Delta \sigma_{Boundary}^2 + \Delta \sigma_{\Delta CTE}^2 \quad [22]$$

The predicted upper and lower bounds of the composite yield strength vs. volume fraction reinforcement can be seen in Figure 17 for the bronze-BaTiO₃ system.

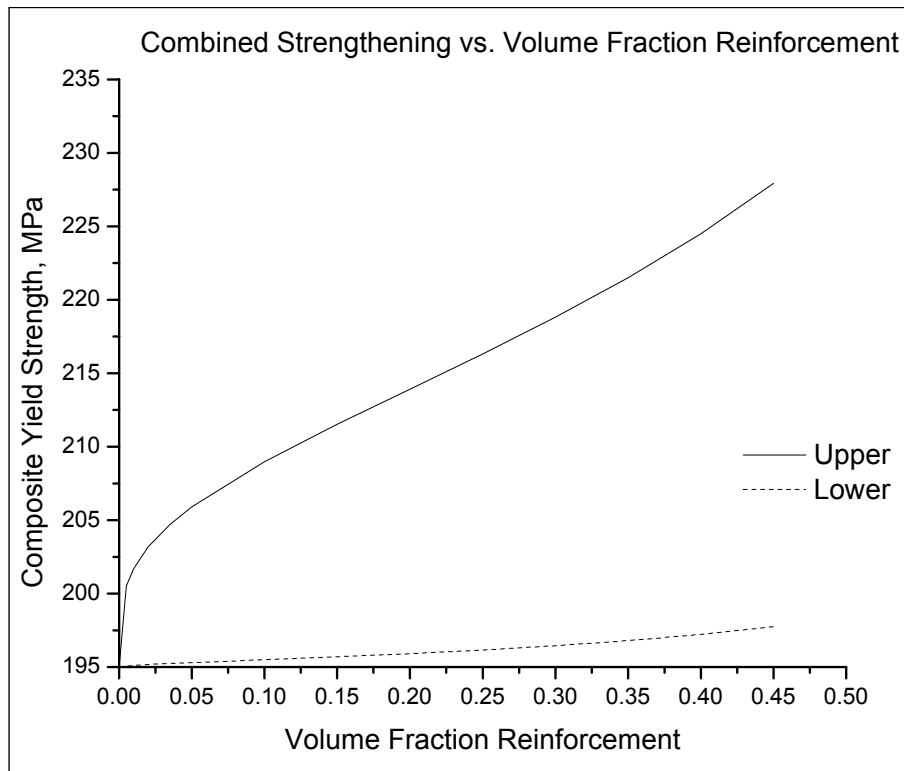


Figure 17. Dependence of yield strength vs. volume fraction reinforcement according to the combined strengthening mechanisms of the bronze-BaTiO₃ composite system.

2.3 Damping Mechanisms in Metal Matrix Composites

The damping ability of a MMC is generally greater than a simple volume fraction combination of the abilities of its constituents. This is due to a number of additional damping mechanisms involved in composite systems. This is particularly true if the matrix/reinforcement (M/R) bonding is poor. Interfacial damping mechanisms, such as frictional sliding or diffusion across the interface, are both potential energy-absorbing processes. Also, when an elastic wave strikes an imperfectly bonded interface, the imperfect transfer of elastic energy can lead to interfacial heating.

Further increases in damping ability can be attained when the presence of one constituent increases the inherent damping ability of another. In the matrix as in unreinforced metals, the local movement of dislocations can serve to dissipate energy. This occurs as they escape from pinning points, vibrate and/or relax into local low energy configurations. The main difference in MMCs is that as a consequence of CTE mismatch between the matrix and reinforcement or of the presence of Orowan loops, dislocation density is usually greater and dislocations are more efficiently pinned or tangled. Also in the matrix, as in unreinforced metals, grain boundary sliding can occur. This is further increased in MMCs however, due to the refinement of grain size induced by the reinforcement.

In MMCs, the matrix and interface are not the only sources of damping. Since some degree of stress is usually transferred to the reinforcement, all of the reinforcement's inherent damping mechanisms can be active. In the case of this work, the damping ability of BaTiO₃ is being used to increase the overall damping ability of the bronze matrix.

3. Ferroelectric Materials

Ferroelectrics are group of dielectric materials which exhibit spontaneous polarization, that is, polarization in the absence of an electric field. They are the dielectric analogue of ferromagnetic materials, which may display permanent magnetic behavior. In ferroelectric materials, there must exist permanent electric dipoles, the origin of which will be explained later for barium titanate (BaTiO_3)

3.1 Piezoelectricity

There are 32 classes or point groups of crystalline materials. Of these, 11 are centrosymmetric and contain no polarity. Therefore the center of negative charge coincides with the center of positive charge. This remains true even under stress, so this type of crystal is termed paraelectric. Of the remaining 21 non-centric crystals, 20 have one or more axes along which when stressed exhibit the piezoelectric effect.³³

Piezoelectricity is the ability to develop an electric charge proportional to a mechanical stress. This is the direct piezoelectric effect. Here the electric charge (Q) developed is proportional to the force (σ), and is therefore opposite in sign between compression and tension. This can be seen in Eq. 23, where P is the charge per unit area (Q/A).^{34,35}

$$P_i = d_{ijk} \sigma_{jk} \quad [23]$$

There also exists a converse effect. An applied field (E) produces a proportional strain (ϵ), expressed in Eq. 24.^{34,35} Here the sign of ϵ in expansion or contraction depending on the polarity of the applied field.

$$\epsilon_{jk} = d_{ijk} E_i \quad [24]$$

In each case, d is the material dependent piezoelectric constant which is numerically identical for both the direct and converse effect having units of coulombs/Newton in Eq. 23 and meters/Volt in Eq. 24.³⁴

Electric field (E) and polarization (P) are described by vectors whose directional properties may be symbolized by pointed arrows, while mechanical stress (σ) and strain (ϵ) are described by tensors which do not have this directional characteristic. A more complete explanation of vector and tensor properties is given by Nye.³⁵

3.2 Curie Temperature

As mentioned previously, piezoelectricity is dependent on crystal structure, so in piezoelectric materials, phase changes are very important. During a phase change a non-piezoelectric (paraelectric) phase may become piezoelectric or vice versa, and the temperature at which such phase change occurs is known as the Curie point or Curie temperature (T_c).

Barium titanate (BaTiO_3) is given as an example in Figure 18.

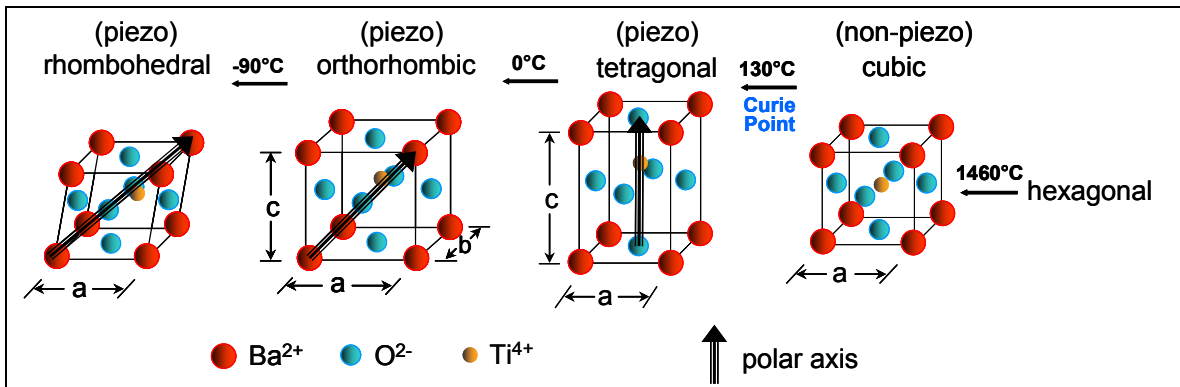


Figure 18. Crystal phases of barium titanate

From the figure it can be seen that the Curie point of BaTiO_3 is at $\sim 130^\circ\text{C}$, where there is a phase change between the piezoelectric tetragonal phase and the paraelectric cubic phase.

3.3 Pyroelectricity

Of the 20 piezoelectric crystal classes, 10 contain at least one spontaneous polar axis in the unit cell, i.e. an axis which shows properties at one end different from those at the other. This polarization is spontaneous in that it exists without external influence, such as an electric or stress field. Crystals of this type are deemed pyroelectric, due to the fact

that the magnitude of this spontaneous polarization (P_s) varies with temperature. In order to minimize energy, polarized unit cells arrange themselves in likely oriented groups called domains. The size and arrangement of these domains is the result of two competing energies, the domain wall energy and the depolarization energy of the surroundings (E_{dp}).

To explain this further, imagine a pyroelectric single crystal consisting of many polarized unit cells aligned in the same direction as seen in Figure 19.

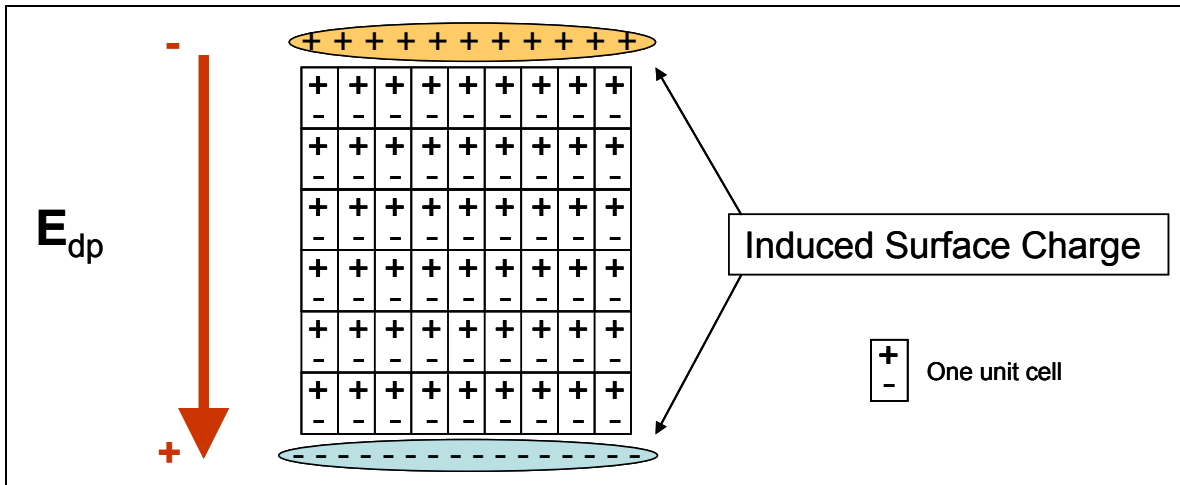


Figure 19. Charge arrangement in a single crystal pyroelectric

In this state, the crystal would have one single domain. In this domain, the net polarization of the like-oriented unit cells creates a net polarization across the crystal. Since the crystal is polarized, surface charges are induced on its surface. The surface charges create a depolarizing electric field (E_{dp}) whose energy is proportional to the volume of the crystal and the square of the polarization.³³ Here E_{dp} is essentially the result of the resistance of the surroundings to become polarized; thus, the aligned single domain state which opposes the depolarizing field is a very high energy state for the crystal.

To avoid this high energy state, the unit cells arrange themselves into several domains. The domains themselves remain polarized, but their antiparallel arrangement causes the overall net polarization of the crystal to approach zero, as in Figure 20. At this point,

although the individual unit cells are of a piezoelectric class, the crystal as a whole will not exhibit the piezoelectric effect.

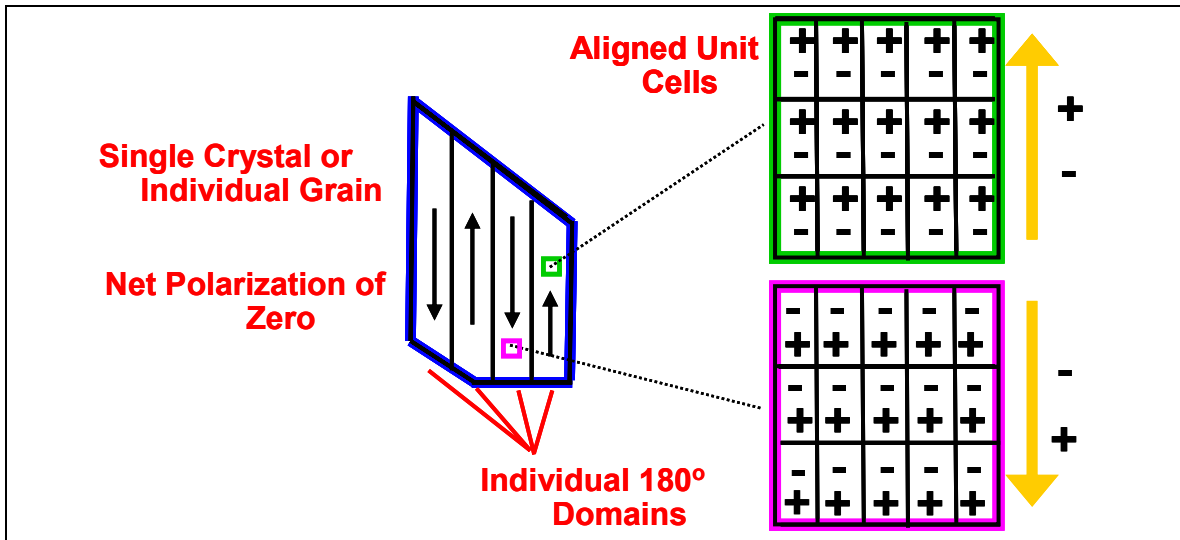


Figure 20. Antiparallel domains

This arrangement occurs upon normal cooling through the Curie temperature (T_c). As the pyroelectric phase nucleates, the 180° domains arrange to minimize the overall electrostatic energy state^{36,37} i.e., to minimize the overall polarization. A minimum energy state, however, cannot generally be achieved through 180° domain formation alone. Local thermal stresses affect 180° domain formation creating 90° domains in the form of twins within the 180° domains. These 90° domains serve to stabilize the tetragonal phase by relieving compressive stress along the polarized axis of the material,^{36,37} Figure 21.

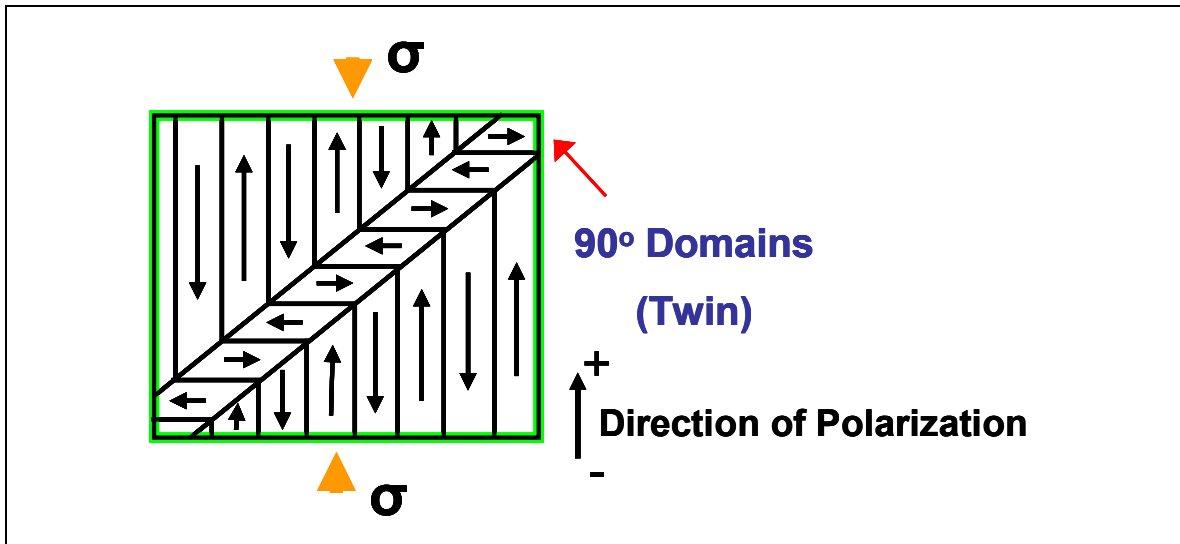


Figure 21. A twin (90° domains) across the 180° domains

As an increasing number of domains are formed and rearranged, energy is stored in the boundaries or “walls” between them. At the same time though, the energy of the crystal is lowered as its net polarization is reduced. An actual resulting domain structure, is seen in Figure 22, showing the metastable compromise reached as domain mobility drops off with temperature from its peak at T_c .

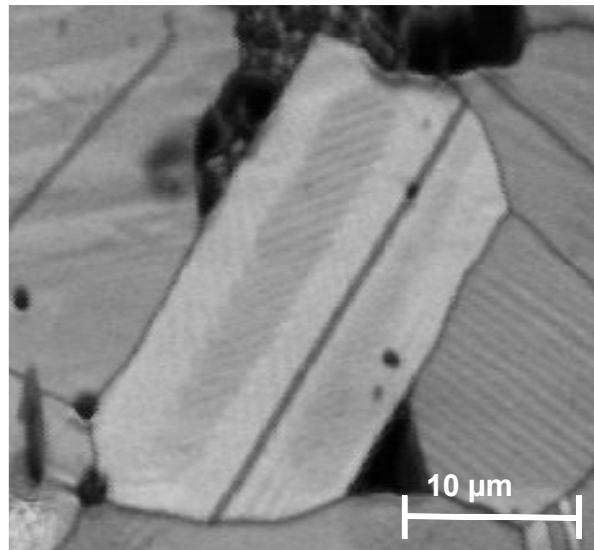


Figure 22. Antiparallel domains showing unit cell and domain wall placement

This same process occurs in the individual grains of polycrystalline pyroelectrics, with each grain consisting of its own multi-domain structure.

3.4 Poling

Poling is the process of using an external force to bias the alignment of the polar axes in a multi-domain material. In the case of pyroelectrics, this force is usually in the form of an electric field. If a DC electric field is applied to a pyroelectric crystal having several randomly oriented domains, each of the domains contained in the crystal will show a tendency to align in the direction of the applied field (E_{app}). This realignment of domains takes place by way of nucleation and domain wall motion, which comes at an energy cost overcome by E_{app} .

Suppose that the crystal is initially composed of an equal number of positive and negatively oriented domains, meaning the overall polarization (P) is zero. If E_{app} is small and applied in the positive direction, there is only a linear relationship between P and E_{app} , as the field stretches positive and compresses negative domains, but cannot completely rearrange them. In the plot of P vs. E_{app} , shown in Figure 23, this is shown in the portion OA. Here the crystal acts like a normal dielectric.

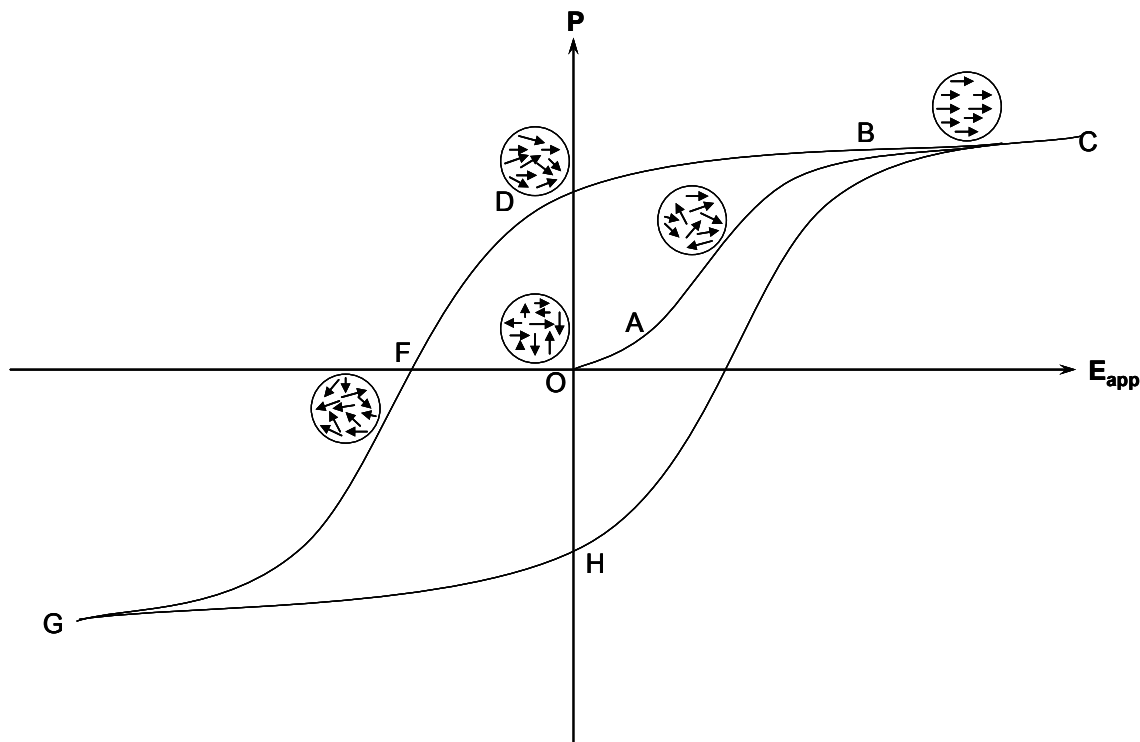


Figure 23. Poling hysteresis loop

As the electric field strength is increased, a number of negative domains will rearrange to the positive direction and the polarization increases rapidly, seen in AB. This continues until all domains are aligned in the positive direction and the crystal is said to be saturated, seen in BC, and the crystal now consists of a single domain. It should be noted that the magnitude of the field required to reach full saturation is time and temperature dependent, having a minimum at T_c , but even more dependent on the material itself, with some pyroelectrics being virtually impossible to pole completely or at all.³⁴

If the field strength is now decreased, the polarization will not follow the same path back to zero, rather it will continue along CD. When the field is reduced to zero, some of the domains will remain aligned in the positive direction, and this is known as remnant polarization (P_r). At this point the crystal is said to be poled, and P_r is used to define this degree of this polarization.³³ When poling polycrystalline materials, the P_r is generally greatly reduced vs. the single crystal of the same type. In barium titanate, the P_r of a single crystal is $\sim 26 \mu\text{C}/\text{cm}^2$, while that of the well-poled ceramic is $\sim 8 \mu\text{C}/\text{cm}^2$.³⁴ This difference is attributed to inhibition of domain alignment caused by grain boundaries.

In practice, the poling field is applied as the material is cooled through its Curie point. This technique causes maximum P_r using the minimum field strength, since the dipoles are aligned as they appear spontaneously and not rearranged from a preexisting domain configuration. Upon further cooling, these aligned dipoles are “frozen” into place with only a fraction relaxing to form other domains as the applied field is removed. This occurs, since with decreasing temperature, the driving force of the induced depolarization field becomes increasingly small compared to that of domain wall formation.

To annihilate P_r and bring the crystal polarization back to zero, it is necessary to apply an electric field in the opposite (negative) direction. The value of the field required to reduce P_r to zero (OF) is called the coercive field (E_c). The magnitude of E_c can give a qualitative idea of the domain mobility in a material. E_c generally decreases with increasing temperature, having a minimum at T_c , but is also strongly dependent on crystal perfection and even more dependent on the time of application of the field.³⁴ A further increase in the field strength then causes complete alignment of the dipoles in the

negative direction along FG, and the cycle is completed by reversing the field again along GHC. The relation between P and E_{app} is thus represented by the hysteresis loop CDGHC in Figure 18.

One common example of a poling device is a capacitor in which the pyroelectric acts as the dielectric material between the electrodes. When poling large ceramic samples, two thin layers of conductive material are plated onto the sample at opposite ends. These layers are used as electrical contacts for the positive and negative electrodes of the poling device. Once an electric field of sufficient magnitude is created across the pyroelectric, its random domains align, creating a piezoelectric material. Consequently, it is along the axis of polarization that the poled material will exhibit maximum piezoelectric properties.

3.5 Ferroelectricity

Within the 10 pyroelectric crystal classes, there exists a subset of materials known as ferroelectrics. Ferroelectrics are materials whose spontaneous polar axes can be reversed 180° with the application of an electric field. This property, known as switching, allows for greater ease and quality of poling. Through this phenomenon, existing antiparallel domains can simply reverse their orientation to align with the applied electric field. This facilitates domain reorientation with a lesser dependence on the high energy mechanisms previously mentioned. The result is that, in general, bulk ferroelectric materials can be more readily made piezoelectric and with a larger degree of remnant polarization than other pyroelectric materials.

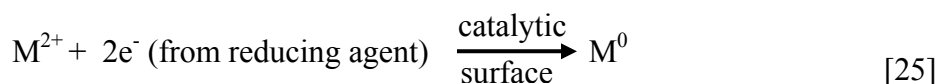
3.6 Ferroelastic Damping

As previously mentioned, stress can have an effect on domain structure and orientation. External or internal stresses can cause the formation of 90° domains, which form through the twinning of existing 180° domains.^{37,38} As this occurs, a portion of the applied stress energy is dissipated, as it is utilized for domain reorientation. In the case of a cyclic applied stress, as with vibrational energy, the induced twinning is also cyclic. With each cycle, energy is dissipated, effectively damping the vibrational stress. As will be discussed later, this mechanism is thought to play a large role in the damping ability of

FR-MMCs. It should be noted however, that this effect is sensitive to the existing domain structure and material grain size. This is a direct result of the limiting effect on domain wall motion of grain boundaries in materials having grains smaller than $1\mu\text{m}$.¹

4. Electroless Plating

Electroless (autocatalytic) plating involves the use of a chemical reducing agent to reduce dissolved metallic ions at the solution/substrate interface forming a uniform deposition upon the surface. This process is deemed “electroless” due to the lack of a need for external electrodes or a power supply. There is however a transfer of electrons from the reducing agent to the metal ion. This takes place at the substrate/solution interface according to Eq. 25.



However, as indicated in the simplified reaction above, the reducing action occurs only on a catalytic surface.³⁹ Thus, once the initial layer is deposited, the metallic layer itself becomes the catalytic surface allowing for the process to continue. For most nonconductors, plating can be done but only after some surface preparation including sensitizing and activation.

4.1 Sensitizing/Activation

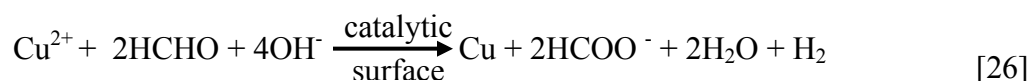
Sensitizing and activation involve the application of a catalytic metal to a non-catalytic surface. As implied by the name, this involves two steps. The first step, sensitizing, consists of adsorbing a readily oxidized material onto the surface to be plated. Solutions containing tin(II) or titanium(III) salts and small amount of acid are commonly used. The addition of acid inhibits the formation of insoluble oxychlorate. This is normally done at 20°-30°C for 1-3 min. Agitation can improve results, especially when plating complicated shapes. After this step, pieces must be thoroughly rinsed, as drag-in of the sensitizer will destroy the activation bath.⁴⁰

It is during the activation step that the surface truly becomes catalytic. The most effective solutions contain precious metal salts, such as gold, silver, and the platinum group metals, along with small additions of acid.⁴⁰ Here the acid stabilizes the bath by both limiting the precipitation of Pd particles and decreasing the deposition rate. When

the sensitized piece comes in contact with the activation solution, the adsorbed sensitizer is readily oxidized, thereby reducing the activating metal and depositing it in the metallic state forming nucleation centers on the surface. Thorough rinsing should also follow this step, as drag-in of precious metal salts will cause spontaneous seeding and breakdown of the plating bath.

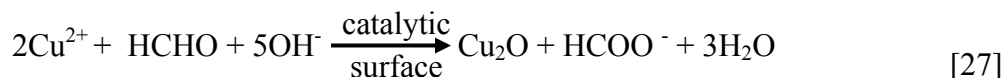
4.2 Electroless Plating of Copper

Formaldehyde (HCHO) is a commonly used reducing agent for the electroless plating of copper. The Cu^{2+} ions are generally added in the form of a Cu salt, such as CuSO_4 . The OH^- is usually supplied by the addition of NaOH, which elevates the pH to 12-13 where the plating rate reaches a maximum. The overall reaction is given in Eq. 26.



Formic acid (HCOO^-) is the oxidation product of the reducing agent, formaldehyde.⁴¹ Evolved H_2 gas and excess H_2O are formed as byproducts of the reaction.

In addition to deposition of copper on the catalytic surface, there is a competing reaction that is noncatalytic. It results in a tendency for cuprous oxide particles to form spontaneously within the plating bath according to Eq. 27.



The Cu_2O particles then become catalytically active and lead to decomposition of the plating bath, resulting in the formation Cu_2O cored Cu powder.⁴² Vigorous agitation of or the controlled bubbling of air or O_2 through the solution can prevent this by reoxidizing the cuprous oxide.⁴² Certain catalytic poisons, if present in sufficiently small concentrations to still enable plating at a practical rate, can also stabilize the plating bath. These compounds function by preferentially adsorbing upon freshly formed, minute particles, making the surface unavailable for plating. Some of these poisons can also serve a dual purpose by also acting as a buffer of pH.

The solubility of Cu ions decreases with increasing pH.⁴¹ To avoid the precipitation of copper(II)hydroxide ($\text{Cu}(\text{OH})_2$) at the high pH needed for efficient plating, complexing (chelating) agents are also commonly added to the plating bath.³⁹ These ligands form coordinate bonds with the Cu^{2+} ions allowing them to stay in solution. Complexing agents are usually organic acids or their salts, such as EDTA, EDTP, and tartaric acid.^{39,41}

The recipe used in this work for the electroless plating of Cu on BaTiO_3 , can be found in the experimental procedure section.

Chapter Three- Experimental Procedure

Several different techniques were utilized in the fabrication and evaluation of the ferroelectric reinforced metal matrix composites (FR-MMCs) studied in this work. This chapter will attempt to describe and discuss in depth each of these techniques in a manner which would allow the reader to recreate them in a laboratory setting.

1. Materials Selection

Copper was initially selected as the matrix material. Elemental Cu can be sintered at $\sim 900\text{-}1050^\circ\text{C}$.^{29,43} This is much lower than for other structural metals such as Ni, Ti, Fe and Mo. Cu is also much less reactive than structural metals having a lower melting point such as Al and Mg. To further reduce the sintering temperature an alloy of Cu- 10 w% Sn (bearing bronze) was finally selected for the matrix metal. This alloy can be liquid phase sintered at 820°C and is resistant to oxidation leading to greater ease in lab handling.

Selected properties of annealed Cu- 10w% Sn bronze are shown in Table 4.⁴⁴

Yield Strength, σ_y	Tensile Strength, σ_T	Elastic Modulus, E	Density, ρ	Poisson's Ratio ν	Melting Temp. T_m	Coef. of Thermal Expansion α_l	Electrical Resistivity at 20°C
195 MPa	455 MPa	110 GPa	8.78 g/cm^3	0.34	1000°C	1.84×10^{-5} $1/^\circ\text{C}$	157 $\text{n}\Omega$

Table 4. Selected properties of Cu- 10w% Sn bronze

The ferroelectric reinforcement, BaTiO₃ was chosen primarily on the basis of thermodynamic stability. Many of the current Pb based ferroelectric ceramics (PZT, PLZT, PMN, etc.) are unstable in most structural metals, such as Fe, Ni, Al, and Cu-Sn bronze, at temperatures above 300°C, as manifested by excessive reactions between the metal matrix and the reinforcement. BaTiO₃ also has a distinct Curie temperature (T_c), associated with the tetragonal-cubic phase change near 130°C.³³ This is opposed to the gradual transition typical of Pb-based solid solutions, and allows for quantification of ferroelastic damping through the comparison of data just before and after T_c . Selected properties of ceramic BaTiO₃ are shown in Table 5.^{34,45,46}

Modulus of Rupture, MOR	Elastic Modulus, E	Theoretical Density, ρ_{th}	Melting Temp. T_m	Piezoelectric Constant d_{33}	Electro-mechanical Coupling Factor, k	Coef. of Thermal Expansion α_l	Curie Temp. T_c
82 MPa	67 GPa	6.02 g/cm ³	1618 °C	191 pC/N	0.5	0.9x10 ⁻⁵ 1/°C	130 °C

Table 5. Selected properties of ceramic BaTiO₃

2. Matrix Preparation

To produce the bearing bronze powder mixture, -325 mesh Cu powder of 99.9% purity (Atlantic Equipment Engineers, Bergenfield, NJ) was first reduced in H₂ for 30min at 250°C. The Cu powder was then blended with -325 mesh Sn of 99.9% purity (Atlantic Equipment Engineers, Bergenfield, NJ) powder in a jar mill for 2 hours. After blending, the powder mixture was maintained in a glove box under argon atmosphere.

3. Reinforcement Preparation

BaTiO₃ powder with a particle size (diameter) ranging from 25 - 45µm (-325 +500 mesh) was prepared by the crushing and sieving of as-delivered bulk 3 - 12 mm pieces of 99.99% purity (Sigma-Aldrich, St. Louis, MO). The bulk pieces were initially crushed to a ≤1mm size 1 tablespoon at a time using a mortar and pestle. The BaTiO₃ was then poured in 1 tablespoon increments over a stack of successively finer sieves including - 120, -200, -325, and -500 mesh sizes. The sieves were shaken and rotated and fines were collected at the bottom. To prevent overfilling and clogging of the mesh, the stack was

periodically emptied and cleaned, and the powders caught by each mesh were extracted. Once all of the initial BaTiO_3 had been passed through the top sieve in the stack, that sieve was removed, and material that had not passed through the second sieve was re-crushed. The re-crushed powder was then passed through the stack as before and the process was repeated until only the -500 mesh sieve remained. At this point, all of the powder that had not passed through as fines was collected. It was then mixed 1 tablespoon at a time with ethyl-alcohol and again passed wet over the -500 mesh sieve. The alcohol served to break up agglomerations of fines that would otherwise not pass, allowing for the further elimination of fines. This wet sieving was repeated three times and the powder was oven-dried at 110°C . The Horiba LA-700 particle size analyzer was used to confirm the 30 - $44\mu\text{m}$ (-325 +500mesh) powder particle size. Here, approximately 1 gram of barium titanate powder was dispersed in 150ml of ethanol and agitated for 5 minutes in an ultrasonic bath. Laser scattering was then used to analyze the particle size distribution of barium titanate particles yielding a median diameter of $35.475\mu\text{m}$.

4. Electroless Plating

In order to improve the quality of the matrix-reinforcement (M/R) interface, the reinforcement particles in some of the composites samples were electrolessly plated. For this, Cu was chosen, due to its compatibility with the bronze matrix. The presence of Sn in the bronze alloy serves to strengthen the M/R interface through interdiffusion and solid solution formation with the electrolessly plated Cu surrounding the reinforcement. Not only does a Cu layer strengthen the M/R bond, but it also decreases the amount of porosity which had formerly agglomerated at the interface due to the lack of wettability of the reinforcement powder by the matrix material.⁶

The BaTiO_3 reinforcement powder was electrolessly plated by a process outlined in Table 5. Here, all of the solutions were prepared in 600ml Pyrex beakers and the bath temperature was maintained using a hotplate equipped with a temperature probe and controller. Between each step, the material was rinsed using deionized (DI) water. In doing this, most of the solution was first siphoned away and replaced with DI water,

completely submersing the material being plated. The mixture is then stirred for 5 seconds and the liquid is again siphoned away. DI water is again added, and this process is repeated three times.

Purpose	Constituents	notes	time, min	°C
Cleaning	ultrasonically cleaned in an ethyl-alcohol bath	- rinse when done	5	room
Alkaline Cleaning	- 100ml DI water - 4.0g NaOH 97%	- stir until NaOH is dissolved - bring to temperature - pour over powder and stir - DI rinse when done	15	65-70
Acid Cleaning	- 75ml DI water - 25ml HCl 36.5-38%	- stir and bring to temperature - pour over powder and stir - DI rinse when done	15	30-35
Sensitizing	- 120ml DI water - 3.0g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ 98.2% - 5ml HCl	- stir and bring to temperature - pour over powder and stir - do not allow undissolved SnCl_2 to be transferred - DI rinse when done	10	25-30
Activating	- 125ml DI water - 0.03g PdCl_2 99.9+% - 0.063ml HCl (2 drops)	- stir and bring to temperature - pour over powder and stir - do not allow undissolved PdCl_2 to be transferred - DI rinse when done - rinse once in ethyl-alcohol - allow to dry in air	25	40-45
Plating 1 - adjusts pH	- 30ml DI water - 4.0g NaOH	- stir until NaOH is dissolved	until dissolved	room
Plating 2 - provides Cu ions	- 80ml DI water - 1.25g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 98+% - 7.5g EDTA 99.0-101.0%	- stir vigorously - slowly add plating solution 1 until solution 2 becomes deep blue, pH ~9.0 - bring to temp - slowly add additional plating solution 1 until solution 2 becomes light blue, pH ~12.5	to temp	40
Plating 3 - reduces Cu ions	- 2.5ml HCOH 37w% in H_2O (10-15% methanol) - 0.002ml Pyridine 99+%	- put Pyridine on the lip of the beaker containing HCOH - slowly pour HCOH into solution 2, running the last of it over the Pyridine - add material to be plated - bring to temperature	~4 $\mu\text{m/hr}$	50

Table 6. Electroless copper plating recipe

This recipe remained stable in contact with, and was sufficient to plate, $4,000\text{cm}^2$ of surface area at a rate of $\sim 4\mu\text{m/hr}$ (decreased plating surface area will result in faster plating rates). The surface area of the BaTiO_3 powder was first estimated to be $2,734\text{cm}^2/\text{g}$ based on the median diameter of $35\mu\text{m}$ and the assumption that the particles were spherical. A Quantachrome Instruments gas sorption system was then used to run a Brunauer, Emmett, and Teller (BET) surface analysis. This involves the flowing of an adsorbing gas over a sample cooled with liquid nitrogen, and using the amount of gas adsorbed to determine surface area. This test yielded a value of $2,960\text{cm}^2/\text{g}$, which was in close agreement with the earlier estimate of $2,734\text{cm}^2/\text{g}$. Thus in the future, the surface area of crushed BaTiO_3 powder prepared in the manner outlined in this work can be reasonably estimated based on the median particle diameter and a spherical shape assumption.

5. Composite Fabrication

FR-MMCs were created using the bearing bronze matrix (Cu-10 w% Sn) reinforced with particulate BaTiO_3 . Sample preparation involved three primary variables: volume percent BaTiO_3 (15, 30 and 45v%), reinforcement surface preparation (plated vs. unplated), and number of times the composite was pressed and sintered (1 vs. 2). Overall, 12 unique composite combinations were produced according to Table 7.

15v% unplated, 1 pressing	15v% plated, 1 pressing	15v% unplated, 2 pressings	15v% plated, 2 pressings
30v% unplated, 1 pressing	30v% plated, 1 pressing	30v% unplated, 2 pressings	30v% plated, 2 pressings
45v% unplated, 1 pressing	45v% plated, 1 pressing	45v% unplated, 2 pressings	45v% plated, 2 pressings

Table 7. Twelve unique types of composites produced

In order to understand damping and mechanical behavior with respect to processing conditions, 4 samples of each possible combination were fabricated, and control samples of bulk BaTiO_3 and bronze were also created.

In producing each formulation, the appropriate amounts of each powder (Cu, Sn, BaTiO_3) were combined and blended in a jar mill for 2 hours. The Cu-Sn- BaTiO_3 powder mixtures were then uniaxially pressed at 280 MPa into disk shaped powder compacts and

liquid phase sintered in argon at 820°C for six minutes. The heating rate was 10°C/min, and the cooling rate was 10°C/min between 820-300°C. Below 300°C, samples were furnace cooled, which has been found to result in greater tetragonality in the BaTiO₃ reinforcement and to minimize possible residual stresses in the matrix.

To produce repressed samples, the composite discs were then cut in two, with one half being retained as a source of single pressed samples. In creating the repressed samples, the second half was simply pressed a second time at 280 MPa and sintered again in argon. To avoid warping and/or blistering, resintering was done at 790°C, staying well below the solidus temperature of 845°C.⁴⁴ Test samples were extracted from each of the resulting half-disks. Pure bronze specimens were made through the same pressing and sintering process as the composite samples. BaTiO₃ control samples were prepared directly from the as received 3 - 12 mm pieces. Test samples had nominal dimensions of 1.0 x 1.5 x 10 mm.

6. Density and Porosity Calculations

Density measurements were utilized to calculate the % porosity of each composite for varying v% reinforcement and processing conditions. This was done incorporating the bulk (ρ_{bulk}) and theoretical ($\rho_{theoretical}$) densities according to Eq. 28.⁴⁷

$$\left[1 - \frac{\rho_{bulk}}{\rho_{theoretical}} \right] 100 = \% \text{ porosity} \quad [28]$$

Bulk density is the weight of an object divided by the bulk volume (V_{bulk}), which is the volume of solid plus all open and closed pores. ρ_{bulk} was calculated using the liquid displacement Archimedes principle as shown in Eq. 29.⁴⁷

$$\rho_{bulk} = \frac{w_{dry} \rho_{liquid}}{w_{saturated} - w_{in-liquid}} \quad [29]$$

The bulk density of the samples was calculated from precise measurements of the dry (w_{dry}), saturated ($w_{saturated}$), and submersed ($w_{in-liquid}$) weight using an Archimedes scale. Theoretical density ($\rho_{theoretical}$) was calculated using the rule of mixtures shown as Eq. 30.⁴⁷

$$\rho_{\text{theoretical}} = \rho_{\text{matrix}} V_{\text{matrix}} + \rho_{\text{reinforcement}} V_{\text{reinforcement}} \quad [30]$$

Here, V_{matrix} and $V_{\text{reinforcement}}$ represent the volume fraction of the matrix and reinforcement, and ρ_{matrix} and $\rho_{\text{reinforcement}}$ the densities. These densities were taken from the literature and can be found in Tables 3 and 4 of this work. The density and percent porosity values attained for each composite are shown in Table 8.

Composite	Bulk Density g/cm ³	Theoretical Density g/cm ³	Skeletal Density g/cm ³	Porosity %
15v% unplated, 1 pressing	6.30	8.37	8.81	24.68
30v% unplated, 1 pressing	6.60	7.95	8.68	17.05
45v% unplated, 1 pressing	5.13	7.54	7.81	31.90
15v% plated, 1 pressing	4.50	8.37	7.80	46.20
30v% plated, 1 pressing	5.51	7.95	8.11	30.67
45v% plated, 1 pressing	4.74	7.54	7.52	37.05
15v% unplated, 2 pressings	6.99	8.37	8.78	16.48
30v% unplated, 2 pressings	5.29	7.95	8.17	33.45
45v% unplated, 2 pressings	4.83	7.54	7.16	35.93
15v% plated, 2 pressings	6.27	8.37	9.71	25.10
30v% plated, 2 pressings	6.79	7.95	7.56	14.64
45v% plated, 2 pressings	5.50	7.54	7.17	27.10

Table 8. Density and % porosity values for each composite produced

All mass measurements were done with an Archimedes scale using ethanol, however due to the small mass of the samples, the error involved in the mass measurements was great enough to cause this data to be unusable.

7. Stress/Strain Analysis

Stress/strain (s/s) analysis was performed using a TA Instruments Q 800 model dynamic mechanical analyzer (DMA), using the roller-edged three-point bend clamp kit. s/s calculations, based on the signals of force and displacement, are made using three-point bending equations included in the software package provided with the DMA. The end result is a curve representing the maximum s/s, which occurs at the top (compression) and bottom (tension) edges at the midspan of the sample. This is discussed in detail in section 7.1 .

The strain rate was 0.1% strain/min and each sample was loaded to 2.0% strain or failure, depending on which came first. These curves were used to evaluate changes in composite quality based on changes in processing conditions and also to monitor the effect of volume % reinforcement on mechanical properties. The s/s curves were also utilized in determining the appropriate strain to be used during dynamic mechanical analysis. To obtain accurate an measure of damping ability, it is necessary to insure that tests are done well within the elastic region of the composites.

7.1 Stress/Strain Calculations in Three-Point Bending

In three-point bending, since the actual stress and strain varies through the sample cross section, the DMA produces a stress/strain (s/s) curve based on the σ_{max} and ϵ_{max} in the sample. This is logical, as one would expect a sample to fail at the point of greatest s/s.

In three-point bending, assuming a homogeneous specimen free of significant stress concentration sites, the maximum stress (σ_{max}) and maximum strain (ϵ_{max}) occur respectively on the top and the bottom surface of the sample at the midspan.⁴⁸ This is where the DMA drive applies the load (P) causing deflection (δ), as illustrated in Figure 24.

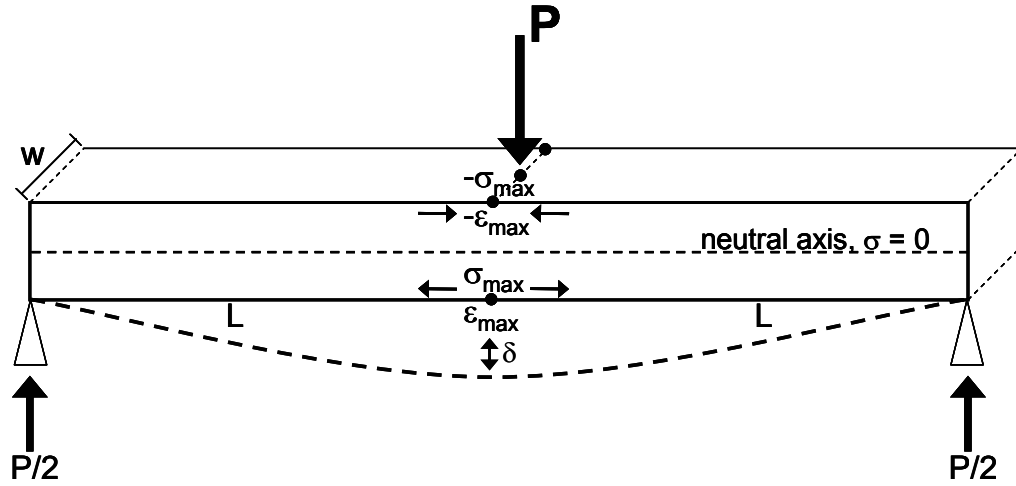


Figure 24. Location of maximum stress and strain of a member in 3-point bending

The TA Instruments Q 800 model DMA measures the raw signals of applied force and displacement. These, combined with the manually entered sample dimensions and Poisson's ratio, are used by the DMA software to obtain the maximum stress and strain experienced by the sample using Eqs. 31, 32 and 33.

$$\sigma_{\max} = \frac{PLt}{4I} = \frac{3PL}{wt^2} \quad [31]$$

$$S = K \frac{L^3}{6I} \left[1 + \frac{6}{10} (1 + \nu) \left(\frac{t}{L} \right)^2 \right] \quad [32]$$

$$\varepsilon_{\max} = \frac{6\delta t}{2L^2 \left[1 + \frac{6}{10} (1 + \nu) \left(\frac{t}{L} \right)^2 \right]} \quad [33]$$

In Eqs. 31, 32 and 33, P is the load. L is one half of the sample length. t is the sample thickness. I represents the moment of inertia. w is the sample width. δ is the deflection. ν is the Poisson's ratio of the sample material, and S is the slope of the stress/strain curve.

For the linear (elastic) region of the curve, S is a constant value which corresponds with the elastic modulus (E). This allows the use of Hooke's law to relate $\sigma_{\max}$ and $\varepsilon_{\max}$ for the

entire linear region of the s/s curve. Once plastic deformation begins and the curve strays from linearity, S can no longer be treated as E , and thus S can no longer be used to relate σ_{max} and ε_{max} between data points. It does however remain the slope of the curve for each individual point on the curve and can therefore be used to relate σ_{max} and ε_{max} at each data point. This distinction between S as the elastic modulus (E) versus S being treated simply as the slope of the curve at any point should be noted in the derivations of Eqs. 31, 32 and 33, which are given in Appendix A.

8. Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) was used to characterize the relative damping properties of both the bulk BaTiO₃ and the FR-MMCs. All tests were conducted using a TA Instruments model Q 800, using the roller-edged three-point bend clamp kit. For each sample the static strain was set to 0.05%, well within the elastic region. The ratio of static/dynamic strain was configured at 1.25, and the dynamic strain was driven at 1 Hz. Each run began with a temperature equilibration at 25°C, at this point data collection was turned on. Once data was being collected, the sample was held at 25°C for 0.25min followed by a temperature ramp at 3°C/min to 200°C. Upon reaching 200°C, the sample temperature was held for 1min. Data collection was then turned off and the sample was cooled to 25°C at 3°C/min under no load. For each sample this process was repeated twice. Data was collected during the first run but not used in the analysis as this run was simply used to erase any processing history that the sample may have had. Further discussion of DMA in general is addressed in the Background section of this thesis.

9. Polished Specimen Preparation

After consolidation, specimens from each composite were mounted in 2-part epoxy resin and cured overnight at room temperature. Samples of the plated BaTiO₃ powder were also mounted in this manner. Each mounted sample was ground using 240, 400, 600, and 1200 grit paper and polished using 1.0, 0.3, and 0.05 μm Al₂O₃ suspensions. This allowed for the examination of the cross-section of both the composite discs and the plated particles using electron microscopy.

10. Scanning Electron Microscopy

Backscattered scanning electron microscopy (SEM) was used to examine the plated BaTiO₃ powder as well as the structure of the composites. Here, the features of primary importance included porosity in the matrix, reinforcement, and at the matrix/reinforcement interfaces. The backscatter detector is sensitive to contrast between phases of different average atomic number.

Chapter Four- Results and Discussion

1. Plating of the Reinforcement

Electroless plating of the BaTiO_3 reinforcement resulted in a uniform copper coating of 3-4 μm about each particle, as shown in Figure 25.

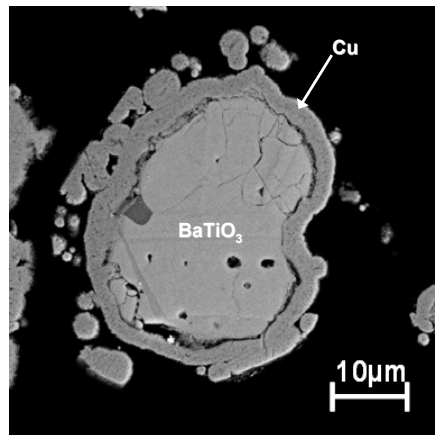


Figure 25. SEM image of a copper plated BaTiO_3 particle

Although there appears to be a separation between the plated layer and the particle, this is an artifact of the sample preparation. During polishing, the BaTiO_3 is worn away at a faster rate than the surrounding copper resulting in their surfaces resting on different planes. As a result the BaTiO_3 is shadowed causing it to appear black in the areas near the plated layer.

In previous work,³⁻⁶ FR-MMCs have been produced using the powder metallurgy (PM) route. However relatively poor physical and mechanical properties were obtained due to the existence of large amounts of residual porosity which tended to agglomerate at the matrix/reinforcement (M/R) interface. This is not unusual, and is thought to be the result of the non-wetting characteristics between the metal matrix and the ceramic reinforcement.⁴⁹ Plating of the particles seems to reduce this problem. This is shown in Figure 26, which contains backscattered SEM images of both plated and unplated BaTiO_3 particles embedded in a bronze matrix.

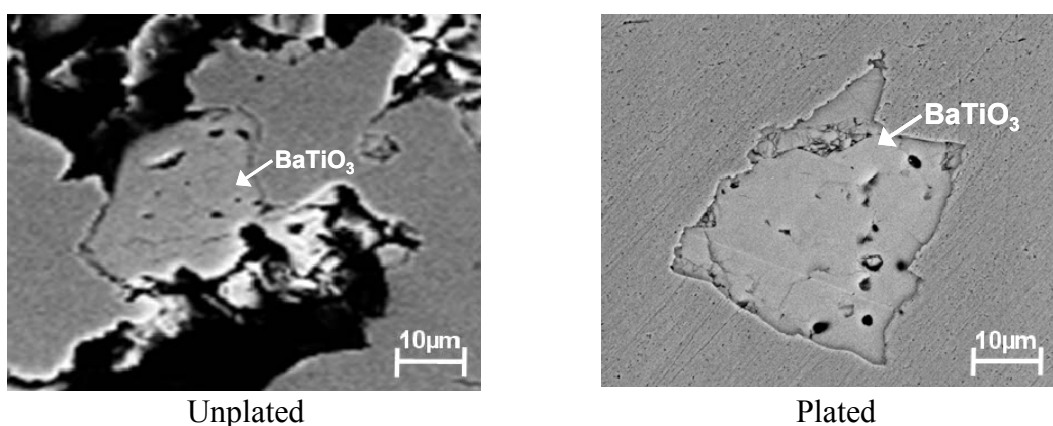


Figure 26. Unplated and plated BaTiO_3 particles embedded in a bronze matrix

The image on the left is an example of an unplated BaTiO_3 particle embedded in a bronze matrix. Here pores have collected at the interface causing a significant portion of the particle surface to not be in contact with the matrix. The image on the right is that of a plated BaTiO_3 particle embedded in a bronze matrix. A sound interface appears to exist across nearly the entire particle surface. As the tin becomes liquid during sintering it is able to wet the Cu surface of the reinforcement, decreasing the tendency for pore agglomeration at the interface and allowing it to be spread more evenly throughout the composite. Plated particles not only provide increased M/R interface, but the interface created is also of higher quality, as better adhesion is created through the formation of a Cu-Sn solid solution with the plated layer associated with tin interdiffusion from the bronze matrix into the Cu layer of the particle.⁴⁹

2. Composite Structure

2.1 Structure vs. Processing Conditions

Figure 27 shows a set of 45v% BaTiO₃ composites with varying processing methods. A full set of composite structure images can be found in Appendix B.

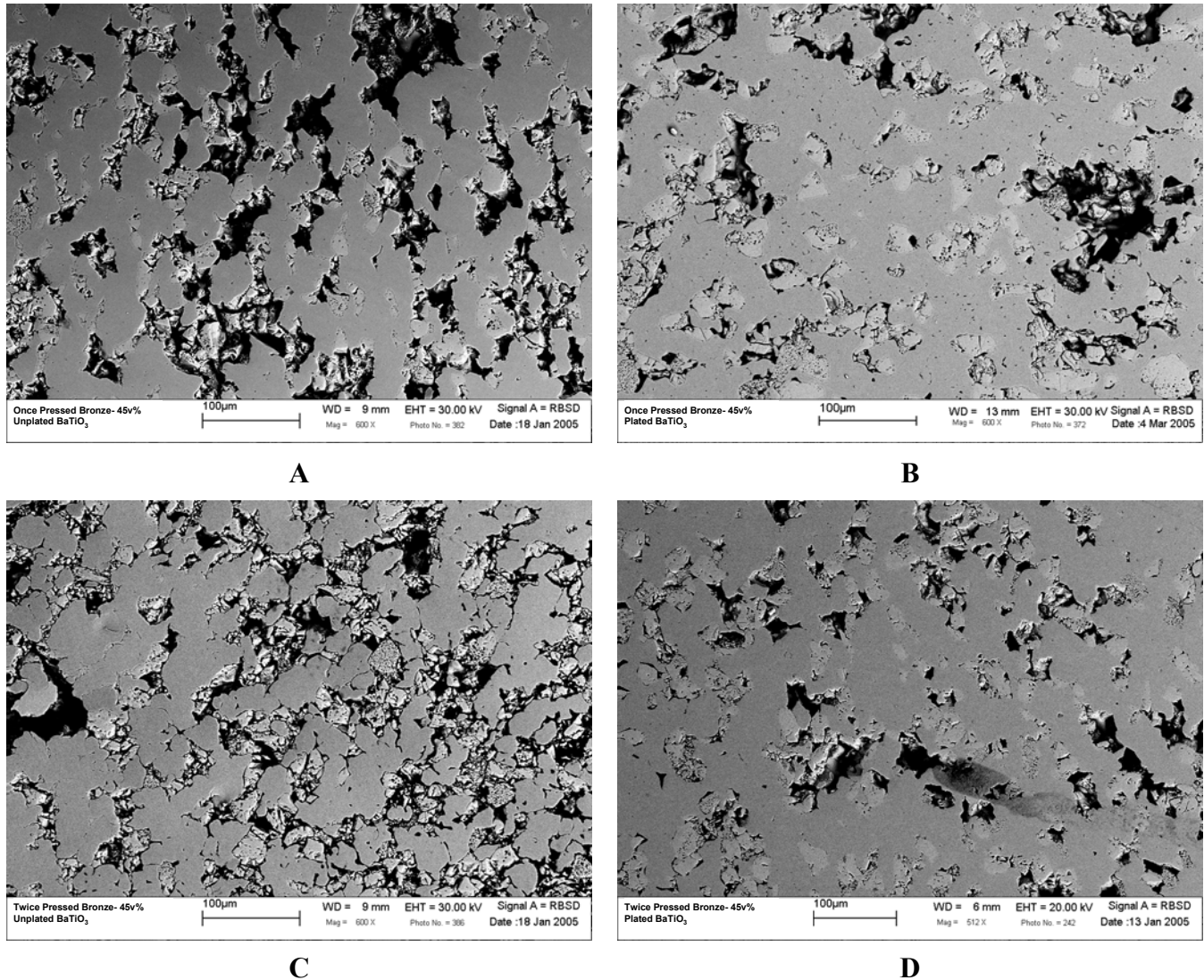


Figure 27. A.) Bronze- 45v% unplated BaTiO₃, 1 pressing B.) Bronze- 45v% plated BaTiO₃, 1 pressing C.) Bronze- 45v% unplated BaTiO₃, 2 pressings D.) Bronze- 45v% plated BaTiO₃, 2 pressings

It can be noted that the overall quality of the structure seems to significantly improve with the use of plated reinforcement and secondary pressing and sintering, Figure 27-D.

This increased composite quality is most easily noted by a decrease in overall porosity and the lesser extent at which pores have agglomerated at the matrix/reinforcement interface.

2.2 Structure vs. Reinforcement Volume Percent

To examine the effect of volume percent reinforcement on composite structure, images of composites having like processing conditions were also compared. Images of twice pressed composites of varying v% plated BaTiO_3 reinforcement are shown in Figure 38.

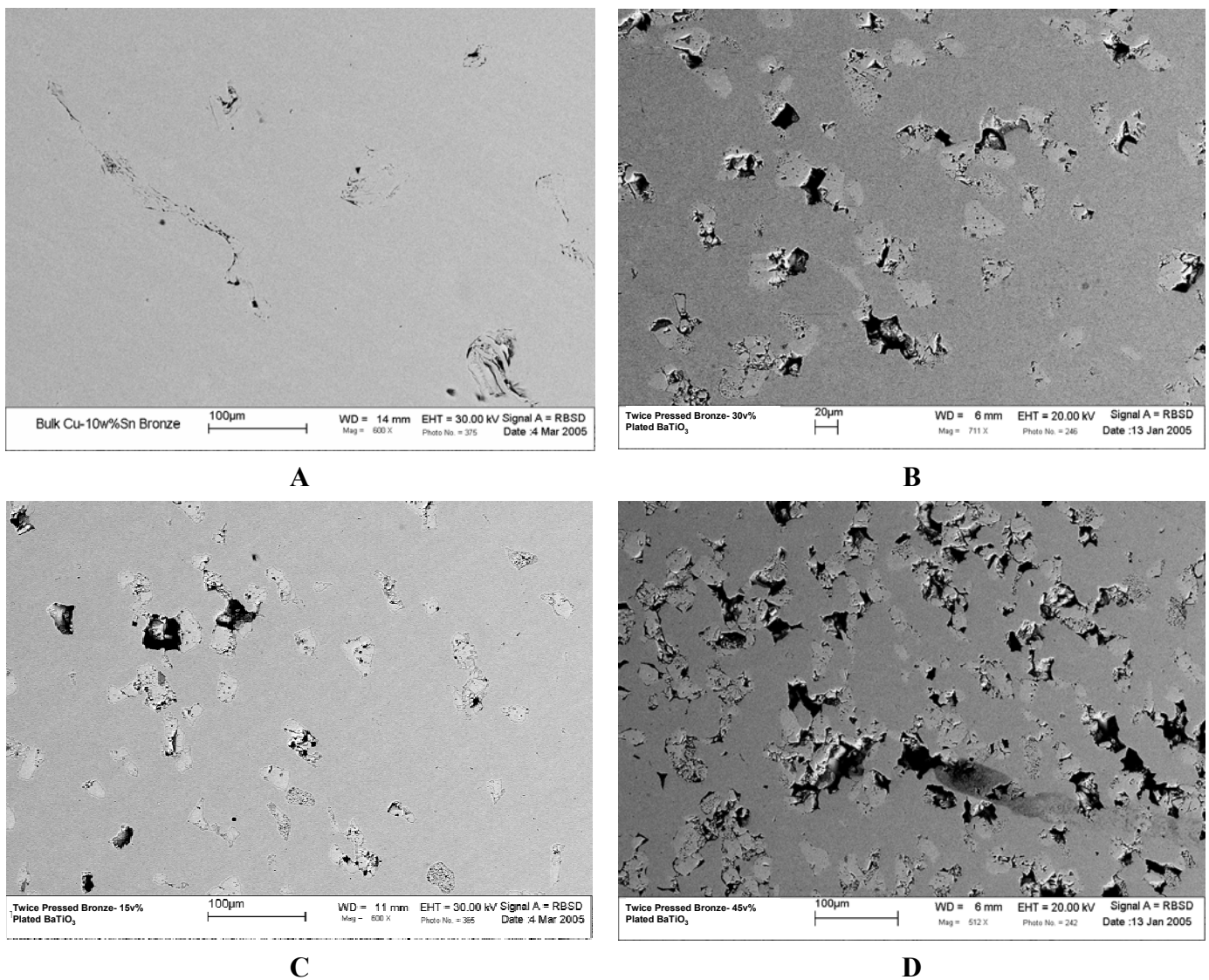


Figure 28. A.) Bronze- 0v% plated BaTiO_3 , 2 pressings B.) Bronze- 30v% plated BaTiO_3 , 2 pressings C.) Bronze- 15v% plated BaTiO_3 , 2 pressings D.) Bronze- 45v% plated BaTiO_3 , 2 pressings

Upon inspection it can be seen that porosity increases with increasing volume percent reinforcement. As mentioned previously, a full set of all composite structure images can be found in Appendix B.

This upward trend in porosity with v% ceramic is not unusual. Before sintering, the composite is simply a pressed mixture of metal and ceramic powder. When hard and soft powders are mixed together the compaction behavior is dominated by the connectivity of the hard material.⁴³ In this work Cu, Sn and BaTiO₃ powders having yield strengths of 69²⁹, 11⁵⁰, 82⁴⁵ MPa respectively were combined, therefore, this would cause the pressed green density of the discs to decrease with increasing ceramic BaTiO₃ content. Upon sintering, this decreased green density should in turn lead to decreased density (increased porosity) in the composite disks. Although structural improvements have been made through secondary pressing and sintering and by utilizing plated BaTiO₃, the resulting composite continues to be a model system and is still far from ideal.

3. Strength behavior in the Composites

Porosity degrades the mechanical properties of PM materials. As an example, strength generally decreases with increasing porosity since pores reduce the load bearing cross-sectional area, and concentrate stress. Secondary pressing and sintering serves to mechanically and thermally close pores, while reinforcement plating results in stronger M/R interface by decreasing pore formation around the embedded particles and allowing them to diffusion bond with the matrix. Here, strength is strongly related to the M/R interface. In composites with strong interfaces, stress can be transferred from the matrix to the reinforcement allowing for combined load bearing, while at the same time coefficient dispersion mechanisms can add to the strengthening of the matrix. As interfacial integrity decreases, M/R interaction decreases, and the role of the reinforcement approaches that of traditional porosity.

3.1 Strength vs. Reinforcement Volume Percent

Based on the negative effects of volume percent reinforcement on composite structure, one would predict that increases in ceramic volume percent lead to decreases in the mechanical properties of the composite. Based on the results of the engineering stress/strain (s/s) analysis in three-point bending found in Figure 29, this assumption appears to be correct. Similar graphs for each set of processing conditions can be found in Appendix C.

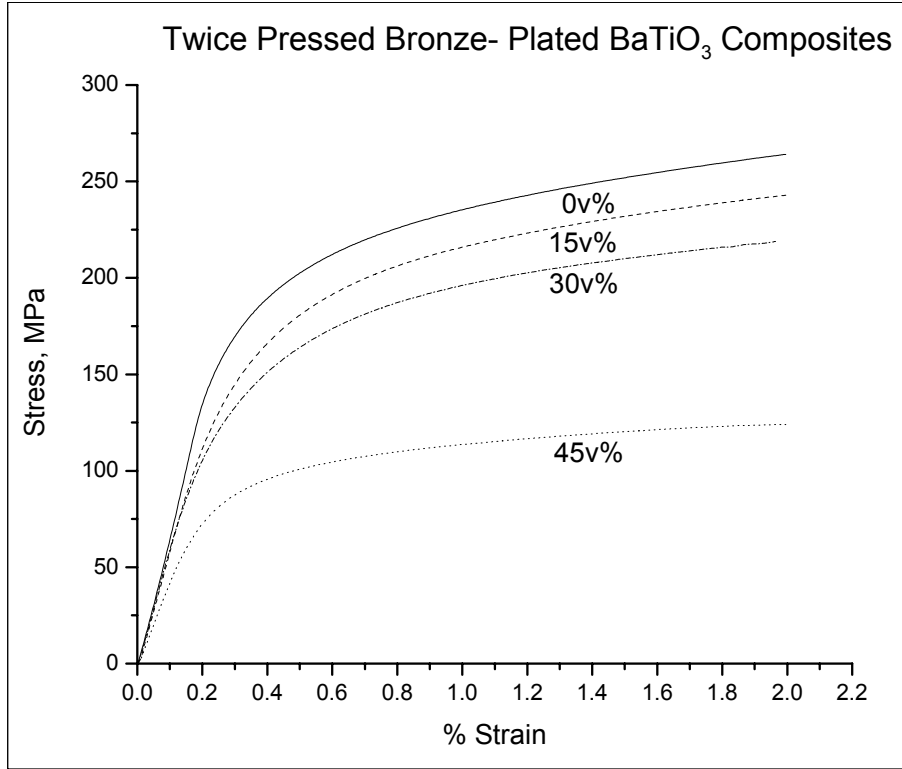


Figure 29. Stress/Strain curves of twice pressed bronze- plated BaTiO₃ composites of various v%

Again, this trend is directly related to the amount of porosity in the matrix, and it becomes obvious that even further improvements in consolidation are necessary before the benefits from composite strengthening can overcome strength decreases due to porosity. Decreased porosity should also serve to strengthen M/R interfaces. Without a strong interface, the reinforcement can simply act as added porosity. This further decreases the effective load bearing surface area of the composite, while adding sites of stress concentration in the matrix, with all of this leading to further decrease in composite mechanical properties. Experimentally, it has been shown that strength decreases exponentially with increasing volume percent porosity as,⁵¹

$$\sigma = \sigma_o e^{-n \cdot V_p} \quad [34]$$

where σ is the resulting strength of the material. σ_o is the material's theoretical strength. n is a material constant, and V_p is the volume percent of porosity.

To test this here, yield strengths, taken from Figure 31, have been plotted vs. volume fraction reinforcement in Figure 30. Similar curves for each set of processing condition can be found in Appendix D.

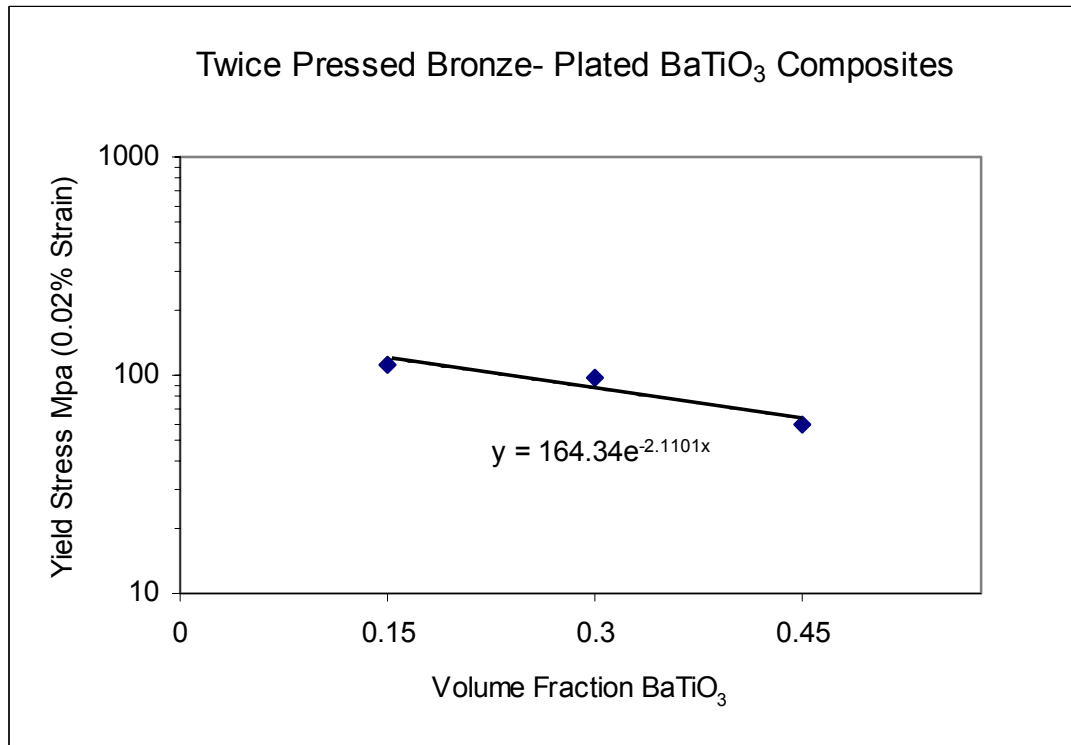


Figure 30. Composite yield strength vs. volume fraction plated BaTiO₃

Here, the same trend is shown for increasing v% reinforcement, which could be the case if a weak M/R interface is assumed and the reinforcement is treated as porosity in the matrix.

3.2 Strength vs. Processing Conditions

Based on visual inspection of the composite images having varying process conditions, it appears that secondary pressing and the use of plated reinforcement significantly improves the composite structure. In agreement with the images seen earlier, Figure 31 shows how strength seems to improve with secondary pressing and sintering as well as with the use of plated reinforcement at a constant volume percent. Curves for 15 and 30v% can be found in Appendix E.

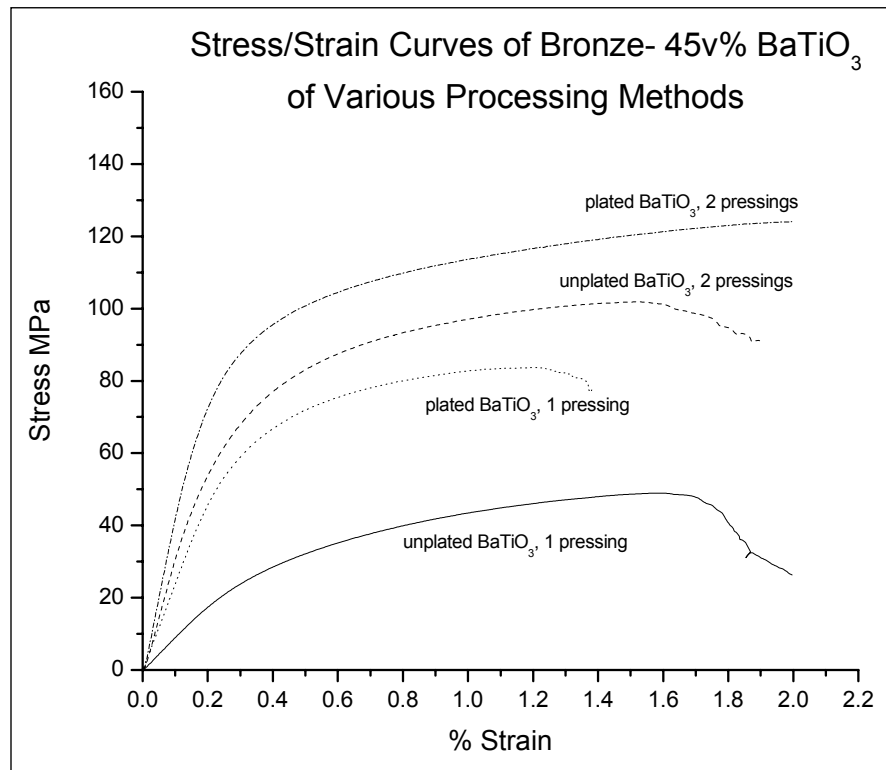


Figure 31. Stress/Strain curves of bronze- 45v% BaTiO₃ composites of various processing methods

These improvements are directly related to decreased porosity⁴³ and an improved matrix/reinforcement interface.²⁰

4. Damping Ability of the Composites

4.1 The Damping Versus Temperature Curve in FR-MMCs

Figure 32 shows a typical $\tan \delta$ (damping) vs. temperature curve for a FR-MMC.

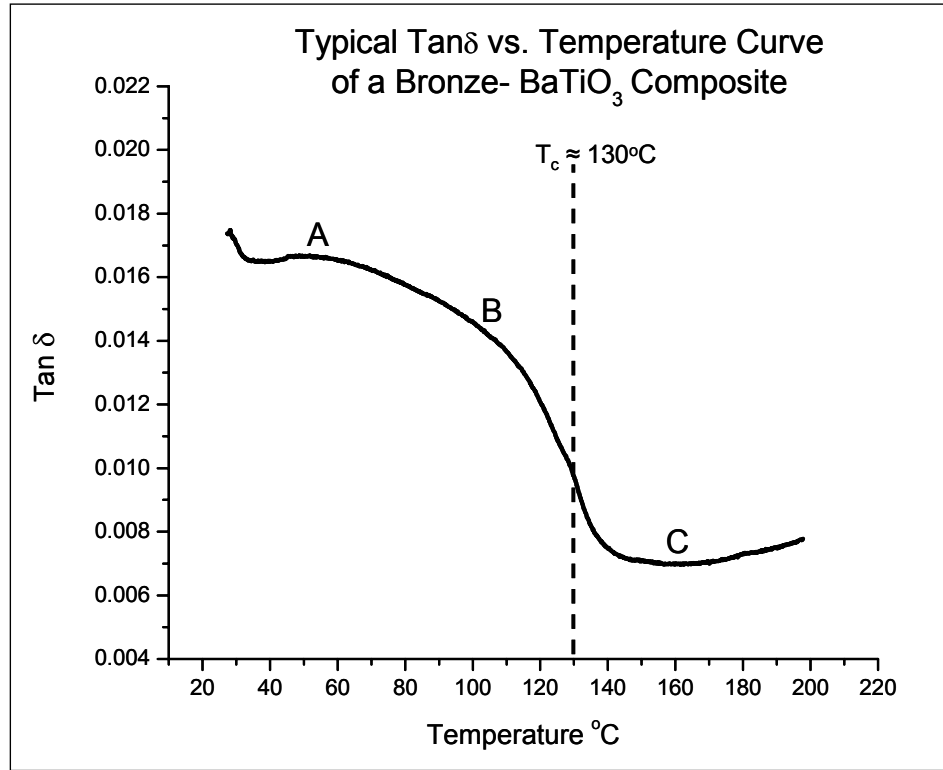


Figure 32. $\tan \delta$ vs. temperature curve of a bronze- BaTiO₃ FR-MMC

These curves can be broken into three parts labeled A, B, and C. Part A represents the total damping behavior of the composite, in which traditional and ferroelastic mechanisms are active. Part B represents the sharp drop in $\tan \delta$ associated with the ferroelectric to paraelectric phase change at the Curie temperature (T_c). The fact that this drop exists at T_c represents a proof of concept showing that increased damping associated with the ferroelectric nature of the reinforcement is exhibited by the composite. Part C represents the region in which only the traditional damping mechanisms are active. The difference in damping behavior between A and C can be used to estimate the magnitude of ferroelastic damping in the composite. It should be noted however that the boundaries

between regions A, B, and C are not considered sharp, and an interpretation of their overlap is represented in the texture overlap in the figure.

4.2 Damping Ability vs. Volume Percent

Figure 33 shows the effect of volume percent reinforcement on the $\tan \delta$ of twice pressed bronze-plated BaTiO₃ FR-MMCs over the temperature range of 25-200°C. Similar graphs for each set of processing conditions can be found in Appendix F.

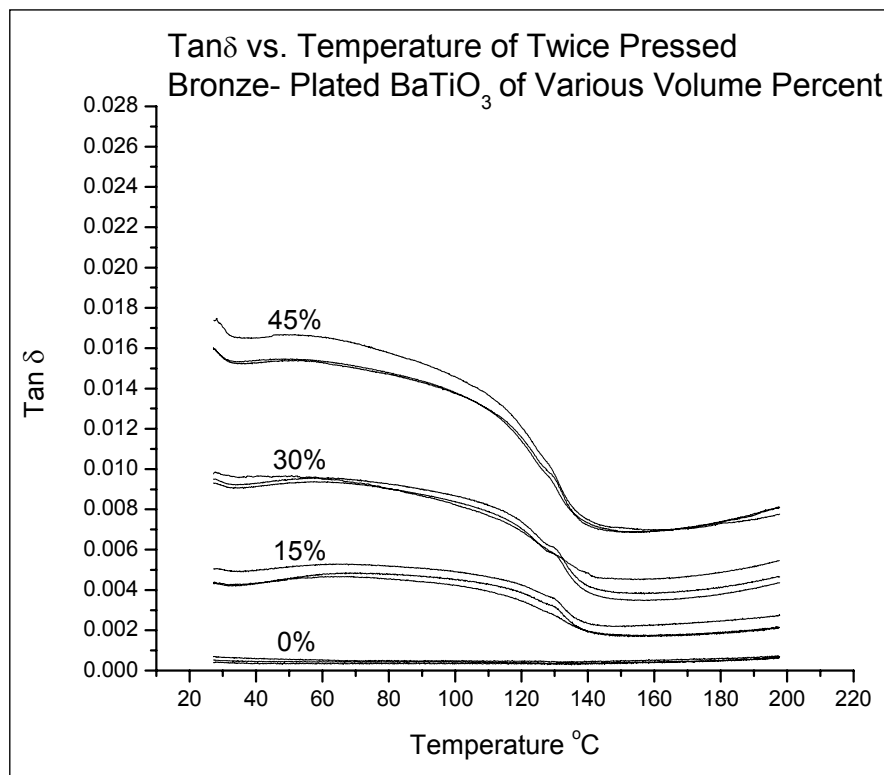


Figure 33. Tan δ vs. temperature of twice pressed bronze-plated BaTiO₃ of various v%

It is apparent here that increasing the volume percent of the reinforcement leads to an increased damping ability in the composite. This follows intuition as the reinforcement is the primary source of energy dissipation in the composite. Increased volume percent reinforcement leads to a greater amount of internal interface in the material. Frictional sliding occurs at these interfaces causing anelastic behavior in the material as stress energy is dissipated.

Not only do metal-ceramic interfaces in the system increase its damping ability, but energy is also dissipated through mechanisms related to the ferroelectric domains in the ceramic reinforcement. As the ceramic is mechanically strained, domain wall motion in the form of twinning is induced.⁵² This occurs as the ceramic strives to maintain its current degree of polarization by arranging unit cells in such a way that they are not stressed along the axis of polarization. Above T_c though, both of these mechanisms disappear, allowing for their quantification through comparison of damping values just before and after T_c .

4.3 Damping Ability vs. Processing Conditions

Figure 34 shows the effect of processing conditions on the $\tan \delta$ of bronze- 45v% BaTiO₃ from 25-200°C. Curves for 15 and 30v% can be found in Appendix G.

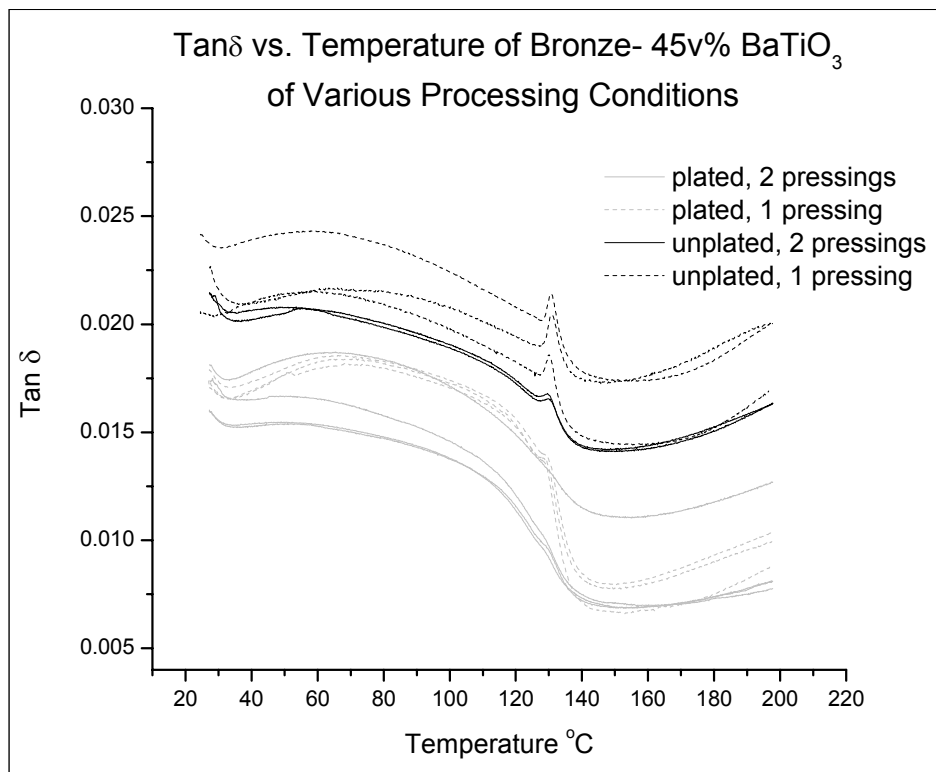


Figure 34. $\tan \delta$ vs. temperature of bronze- 45v% BaTiO₃ of various processing methods

Although they improve the overall composite structure, there appears to be a downward trend in $\tan \delta$ as more processing steps are applied. As shown earlier, when improved

processing techniques are applied to the composite, porosity is decreased and the matrix/reinforcement interface is greatly improved. With many of these defects eliminated, they can no longer act as sites for frictional sliding, thus decreasing the overall damping ability of the composite. Damping based on porosity and poor interface however have little value since they come at great cost. The artifacts that cause increased damping are flaws in the composite structure, which greatly decrease the mechanical properties of the system. This contradicts the “multifunctional” focus of this work, as both strength and damping should be increased by the addition of ferroelastic reinforcement. Thus attention should be paid only to ferroelastic damping the BaTiO₃.

The amount of damping that can be attributed to the embedded particles can be quantified by the difference between damping behavior below T_c from that above. As previously mentioned, below T_c ferroelastic damping mechanisms are active, whereas due to a phase change, above T_c these mechanisms are not. As outlined in Figure 35, the damping values at 150°C were subtracted from those at 70°C resulting in an estimate of the overall decrease in $\tan \delta$ due to the ferroelectric, tetragonal to paraelectric, cubic phase change.

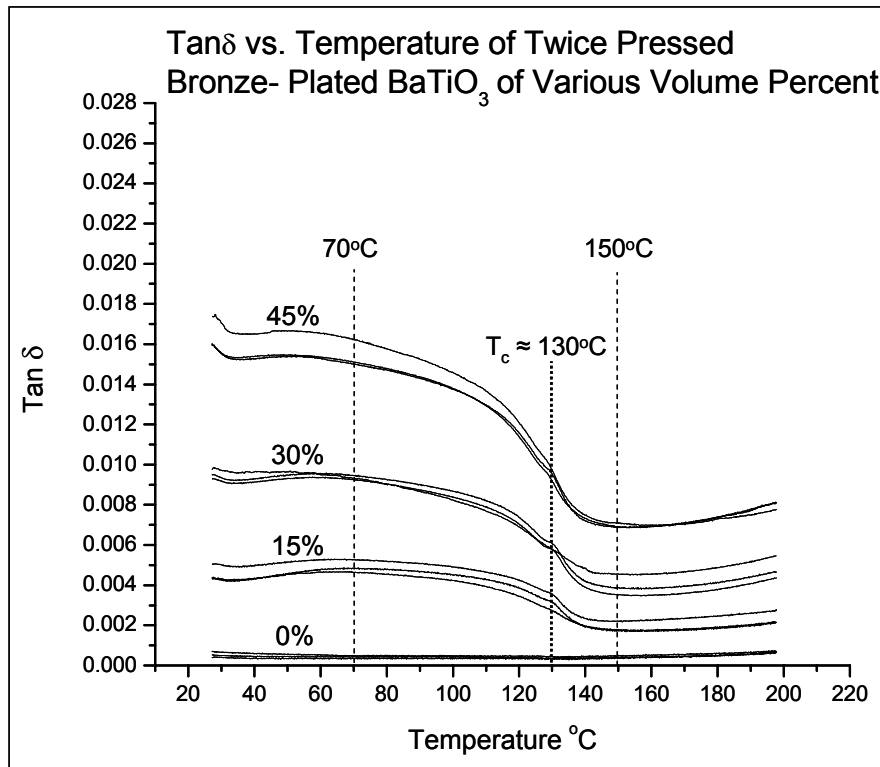


Figure 35. Points of measure to quantify the drop in $\tan \delta$ at T_c .

Figure 36 shows how this drop in $\tan \delta$ appears to increase with increasing reinforcement volume percent, using the curve for the twice pressed bronze-plated BaTiO_3 composite as an example. Curves for all processing conditions can be seen in Appendix H.

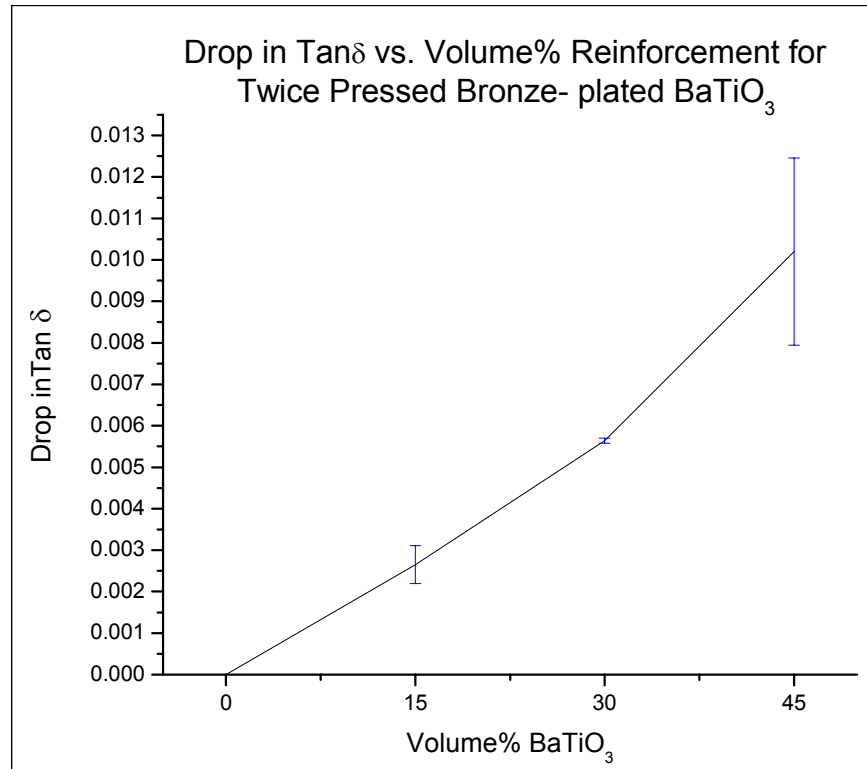


Figure 36. Drop in $\tan \delta$ across T_c with increased v% BaTiO_3

From this, the drop in $\tan \delta$ appears to follow a linear relationship with increased v%. This would follow intuition, but when the change associated with bulk BaTiO_3 is included in the graph, as in Figure 37, the trend appears to stray from linearity.

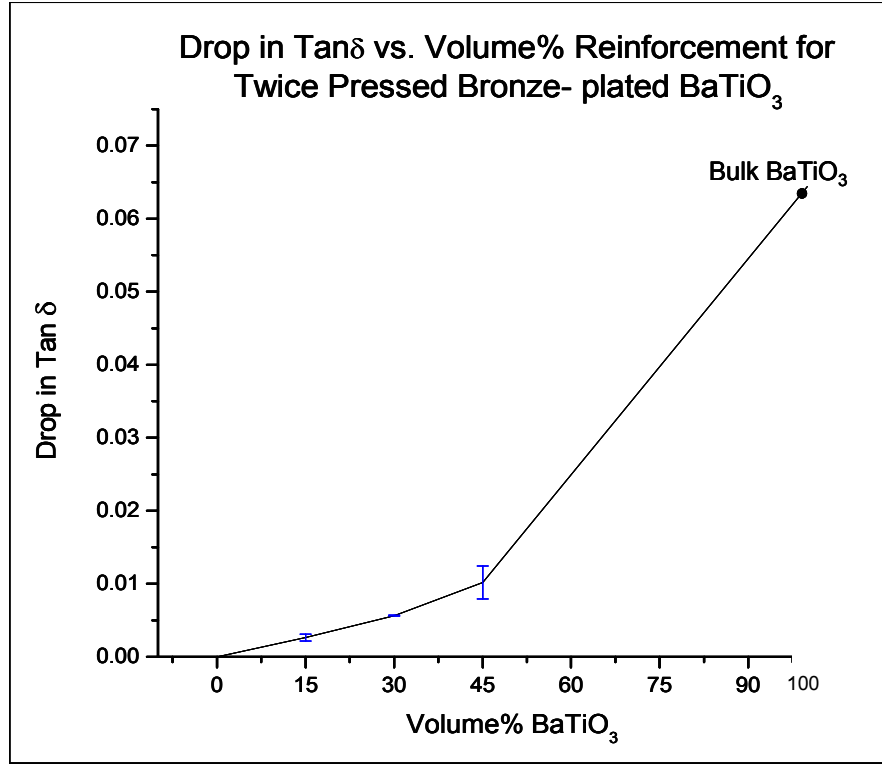


Figure 37. Drop in $\tan \delta$ across T_c with increased v% BaTiO₃, including bulk BaTiO₃

In fact, this trend would most likely be a linear relationship, if the composite was fully dense with ideal M/R interfaces. Flaws in the composite, decrease stress transfer to the reinforcement, so the full damping capacity of the BaTiO₃ is never reached. This accounts for the lower than predicted damping capacity in the composites, which also leads to a decrease in the drop in $\tan \delta$ across T_c .

Figure 38 gives an example of how composite damping behavior can be predicted based on the damping curves for bulk BaTiO₃ and bulk bronze. This theoretical curve was obtained by taking the measured $\tan \delta$ values for both bulk bronze and bulk BaTiO₃ and combining them using the rule of mixtures based on a composite of bronze- 45v% BaTiO₃ having a flaw-free matrix and strong M/R interfaces. This was accomplished using an upper Voight bounds:

$$\tan \delta_{Composite} = \tan \delta_{Bronze} V_{Bronze} + \tan \delta_{BaTiO_3} V_{BaTiO_3} \quad [35]$$

which assumes no interdependence of the damping mechanisms, and a lower Ruess bounds:

$$\frac{1}{\tan \delta_{Composite}} = \frac{V_{Bronze}}{\tan \delta_{Bronze}} + \frac{V_{BaTiO_3}}{\tan \delta_{BaTiO_3}} \quad [36]$$

assuming strong interdependence of the damping mechanisms.

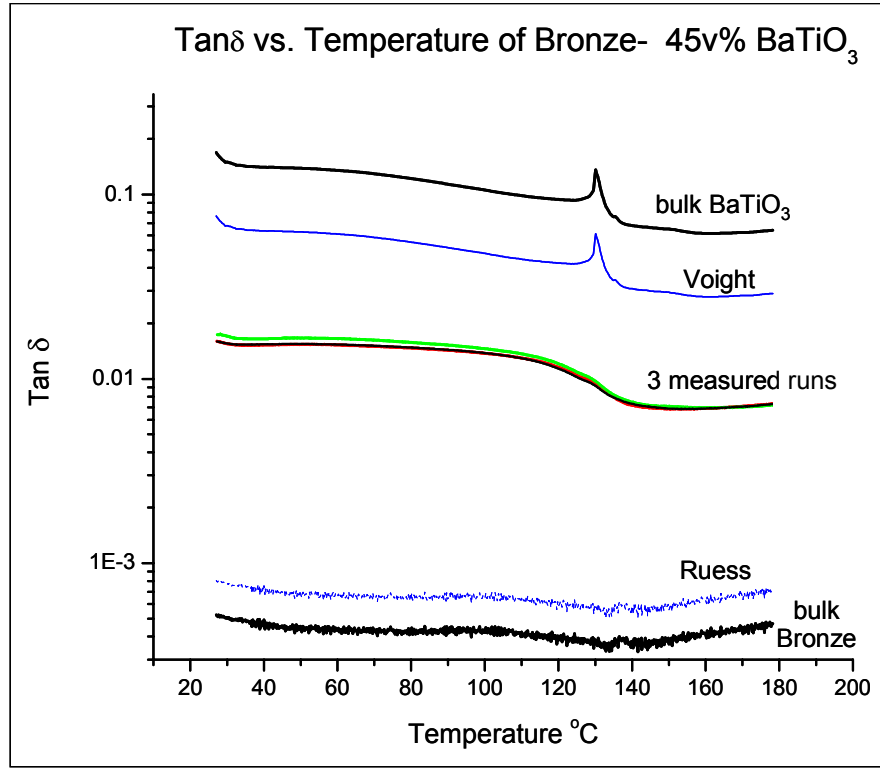


Figure 38. Measured vs. predicted $\tan \delta$ curves for bronze-45v% BaTiO₃

The three measured runs seem to fall within the Voight and Ruess bounds, however there may still be some room for improvement, due to porosity in the matrix.

This straying from ideal damping behavior cannot be entirely laid on the matrix however, because the reinforcement could also be greatly improved. The embedded BaTiO₃ particles were produced through mechanical grinding of monolithic sintered pieces. As a result, this grinding, left many residual cracks throughout the individual particles, which can be seen in Figure 39.

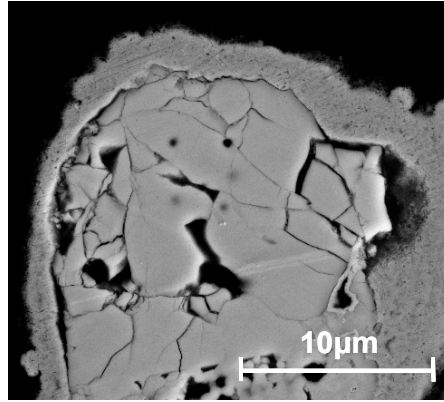


Figure 39. Cracks in individual reinforcement particles left by grinding for size refinement

Due to these cracks, the reinforcement phase can no longer be thought of as individual particles but as tight agglomerations of smaller ones. This decrease in effective particle size has most likely led to a drastic decrease in the overall ferroelastic damping capability of the reinforcement. First, a portion of the stress that would normally activate twinning in the BaTiO_3 can be dissipated through frictional sliding in the cracks. Secondly, the ferroelastic damping ability in the reinforcement is very sensitive to domain structure and grain size. The decrease in effective particle size due to cracking, also leads to decreased grain size as grains are fractured. As particle size drops below $1\mu\text{m}$, this becomes increasingly important due to the limiting effects of grain boundaries on the mobility of domain walls and the twinning responsible for ferroelastic damping.¹

Porosity also seemed to be significant in the BaTiO_3 reinforcement particles, an example of this can be seen in Figure 40.

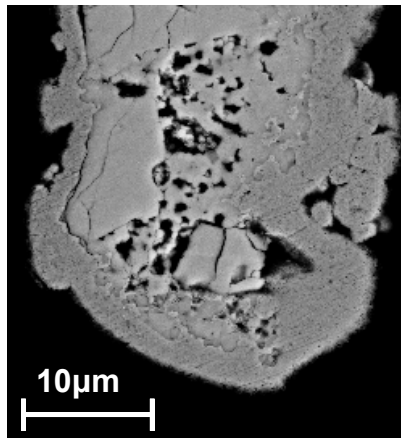


Figure 40. Porosity in the reinforcement material

Porosity can cause a significant decrease the mechanical properties in the reinforcement,⁴³ while at the same time promote further cracking stemming from stress concentration in the pores. These pores, like grain boundaries, can also limit domain wall motion and thus the ferroelastic damping ability of the embedded particles.

Chapter Five- Conclusion

Overall, significant evidence has shown that the ferroelectric reinforced metal matrix composite system utilizing structural metals as a matrix is indeed a material system exhibiting increased damping as compared to its matrix alone. This system however, using current processing techniques, is far from ideal. The effects of increased volume percent reinforcement on $\tan \delta$, although shown to increase the overall ferroelectric damping, are masked by the increase in $\tan \delta$ stemming from additional porosity present as the $v\%$ BaTiO₃ is increased. Although improved processing tends to improve interface quality and decrease porosity leading to increased ferroelectric damping. This effect is overshadowed by the loss of traditional damping ability associated with these defects.

To more effectively study these effects, materials of greater quality should be utilized and other fabrication methods should be explored. Composites of greater quality consisting of less flaws, would allow not only for a greater ferroelastic effect, but also a more precise quantification of that quantity, as the signal to noise ratio vs. that of other damping mechanisms would be increased.

Improvements in the reinforcement would increase the damping ability of the bulk reinforcement. This in turn should upwardly shift the theoretical composite damping curve at all volume percents. Reinforcement improvements are not only limited to improving the quality of BaTiO₃. Other materials of superior ferroelastic damping ability

could be utilized further shifting the bulk curve upward. Increased mechanical properties of the reinforcement should also increase the mechanical properties of the composite. This will be increasingly important as the M/R interface is improved allowing for greater stress transfer between them, at which point an increase in the aspect ratio of the embedded material may be warranted. Improvements in the matrix will be primarily effective through a decrease in overall porosity, which can be blamed for the decrease in mechanical properties as reinforcement is added, shadowing any gains made through compositing. This decrease in stress concentration sites coupled with an increase in effective cross-sectional area, can lead to improved mechanical properties as well as damping ability.

Chapter Six- Future Work

Upon further study of the damping behavior of FR-MMCs there are several changes that could be made to improve the magnitude of ferroelastic damping, as well aid in the distinction between damping associated with tradition mechanisms from those stemming from ferroelastic behavior.

As previously mentioned, since matrix/reinforcement interface improvements lead to increased stress transfer, this interface is extremely important when attempting to maximize ferroelastic damping in the embedded ceramic. To improve the interface, future consolidation methods should result in a decreased level of porosity as compared to the current method of liquid phase sintering. An obvious choice might be hot isostatic pressing (HIP). However elevated temperatures and isostatic pressures tend to favor the non-ferroelastic cubic phase of the reinforcement.³³ Cooling through the Curie temperature (T_c) at increased pressure prevents the efficient phase transition from the paraelectric, cubic phase to the ferroelastic/electric, tetragonal phase, by effectively decreasing T_c and stabilizing the cubic phase in BaTiO₃ as well as in most perovskite-type oxides.³³ Uniaxial pressure, however causes the polar c axis in a tetragonal structure to form perpendicular to the axis of the applied pressure,^{33,37} which can cause anisotropy in damping behavior.

In the ideal case, the consolidation process should be done at low pressure and temperatures well below those required by sintering. Decreased temperature during processing would also allow for the use of better performing ferroelastic ceramics that are currently unstable in most metal matrices at current processing temperatures.

With respect to the ceramic reinforcement itself, increased ferroelastic behavior could be seen by increasing grain size or through the use of single crystals. Damping could be further increased by using a ceramic fabrication method resulting in decreased porosity and that did not require grinding to reach the final particle size. High levels of porosity and residual internal cracks in the reinforcement not only lead to decreased damping ability, but also decreased mechanical properties. Finally the aspect ratio of the ferroelastic particles could be increased. The use of elliptical shaped particles or ideally short fibers would increase stress transfer allowing for greater activation of the reinforcement leading to more energy being dissipated (damped) by the composite.

Once a FR-MMC has been fabricated, damping due to ferroelastic mechanisms must be distinguished from that due to traditional mechanisms. In this work, this was done by comparing the damping behavior above and below the T_c of the ceramic reinforcement. This is effective, since the ferroelastic properties are active below T_c , and cease completely above it. To further increase this difference or drop in damping upon heating through T_c , a low damping, high stiffness matrix should be utilized. Ideally, this stiff metal should have a high melting temperature relative to the T_c of the reinforcement to minimize changes in the matrix's damping ability upon heating through T_c . At the same time the improvement of the matrix/reinforcement interface will also increase the magnitude of this change. Since high quality interfaces exhibit less slip or internal friction, the non-ferroelastic damping ability of the FR-MMC will be further reduced.

In addition, it is proposed by the authors that by using poled ferroelectric reinforcement, Joule heating can be induced in the matrix due the traditional piezoelectric effect. Stress in the matrix would be transferred to the embedded piezoelectric particles creating a voltage across the material. Through this effect, stress would then be transferred into

electrical energy and dissipated through resistive heating in the matrix. This would be another and possible more effective mechanism for the dissipation of vibrational energy in FR-MMCs.

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**Appendix A: Derivations of the Maximum Stress,
Maximum Strain and Instantaneous Slope
Equations in Three-Point Bending**

A-1 Maximum Stress Equation in Three-Point Bending

Three point bending is a form of pure bending.⁴⁸ Pure bending theory can be used to calculate the stress (σ) at any point in a member based on the force applied and the member geometry. The original load (P) applied at the midspan from Figure 24 in Chapter 3, can be represented by one half of P translated to either end of the member combined with the two moments M , as illustrated in Figure 41.

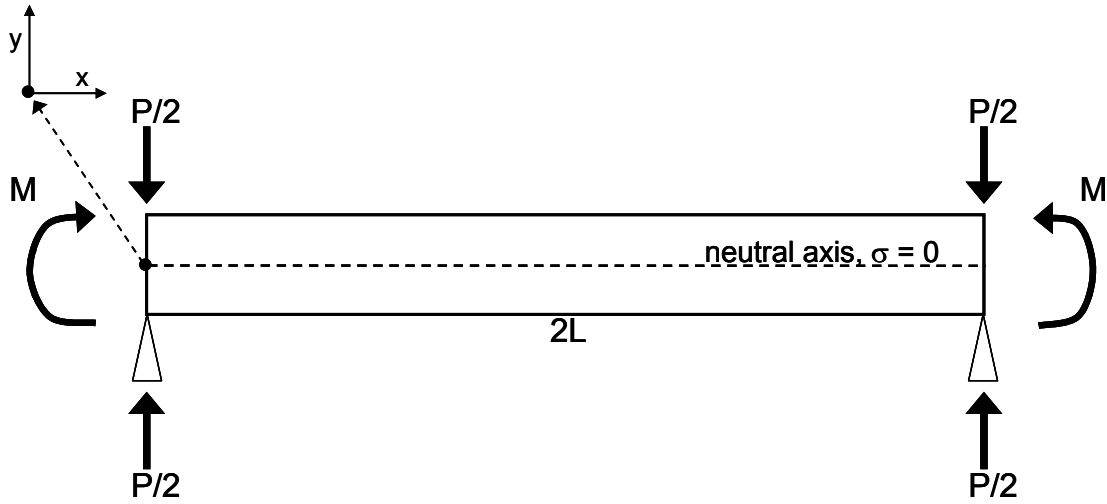


Figure 41. Three-point bending represented by two moments combined with translated stresses

Based on this rearrangement, an expression for stress (σ_x) at coordinates xy inside the member is given by Eq. 37.⁴⁸ This relation is known as the elastic flexure formula for beams.

$$\sigma_x = -\frac{My}{I} \quad [37]$$

Here M is the moment from Figure 41, y is the distance from the neutral axis and I is the moment of inertia. M and I can be broken down further as shown in Eqs. 38 and 39.⁴⁸

$$M = \frac{PL}{2} \quad [38]$$

$$I = \frac{1}{12} wt^3 \quad [39]$$

Eq. 35 stems from the definition of a moment, and Eq. 39 from the definition of the moment of inertia of a member having a rectangular cross-section. By combining Eqs. 37-39, a new expression for σ_x can then be found as shown in Eq. 40.

$$\sigma_x = -\frac{6PLy}{wt^3} \quad [40]$$

Finally since it is known that $\sigma_{\max}$ occurs at the surface of the member, one half of the member thickness ($t/2$) can be substituted for y in Eq. 40, resulting in the expression for $\sigma_{\max}$, shown in Eq. 41.

$$\sigma_{\max} = \frac{3PL}{wt^2} \quad [41]$$

Eq. 41 is identical to Eq. 31, which as previously mentioned in Chapter 3 is the equation used by the DMA software to calculate the maximum stress.

A-2 Equation for the Slope of the Stress/Strain Curve in Three-Point Bending

This relationship stems from Lagrangian mechanics which makes use of energy concepts using scalar functions instead of the vectorial representations found in Newtonian treatments. In mechanics, energy is defined as the capacity to do work, and work is the product of a force and the distance in the direction the force moves. In solid deformable bodies, stresses multiplied by their respective areas are forces, and deformations are distances. The product of these force and distance quantities represents the internal work done in a body by externally applied forces. This internal work is stored in a body as the internal elastic strain energy.

The internal elastic strain energy (U) can be represented in terms of stress and strain. This is done in an analogous manner for both normal and shear. For an infinitesimal element of a member, the definition of stress and the definition of strain are used to solve for the force and distance terms used to find the internal strain energy for uniaxial stress (dU_{normal}) and the internal strain energy in pure shear (dU_{shear}), respectively. An example involving uniaxial stress in the x direction (σ_x) is shown in Eq. 42, and for pure shear in the xy plane (τ_{xy}) in Eq. 43.⁵³

$$dU_{xnormal} = \underbrace{1/2 \sigma_x dydz \varepsilon_x dx}_{\substack{\text{average force distance} \\ \text{work (energy)}}} = 1/2 \sigma_x \varepsilon_x dxdydz = 1/2 \sigma_x \varepsilon_x dV \quad [42]$$

$$dU_{xy\text{shear}} = \underbrace{1/2 \tau_{xy} dxdz \gamma_{xy} dy}_{\substack{\text{average force distance} \\ \text{work (energy)}}} = 1/2 \tau_{xy} \gamma_{xy} dxdydz = 1/2 \tau_{xy} \gamma_{xy} dV \quad [43]$$

Through the addition of dU_{normal} and dU_{shear} for each direction and with rearrangement, an expression for the total internal strain energy for an infinitesimal element (dU) can be found.⁵³

$$\frac{dU}{dV} = 1/2 \sigma_x \varepsilon_x + 1/2 \sigma_y \varepsilon_y + 1/2 \sigma_z \varepsilon_z + 1/2 \tau_{xy} \gamma_{xy} + 1/2 \tau_{yz} \gamma_{yz} + 1/2 \tau_{zx} \gamma_{zx} \quad [44]$$

Integrating over the volume of the member gives Eq. 45.⁵³

$$U = \frac{1}{2} \iiint_V (\sigma_x \varepsilon_x + \sigma_y \varepsilon_y + \sigma_z \varepsilon_z + \tau_{xy} \gamma_{xy} + \tau_{yz} \gamma_{yz} + \tau_{zx} \gamma_{zx}) dxdydz \quad [45]$$

This expression is used for general elasticity. In the technical mechanics of solids a more specific class of problems is considered and Eq. 45 simplifies to Eq. 46.

$$U = \frac{1}{2} \iiint_V (\sigma_x \varepsilon_x + \tau_{xy} \gamma_{xy}) dxdydz \quad [46]$$

This relation is sufficient for determining the strain energy in axially loaded bars as well as in bent and sheared beams.⁵³ This is because nearly all of the axial strain is occurring in the x direction and the shear strain in the xy plain.

For linearly elastic material, under uniaxial stress, $\varepsilon_x = \sigma_x/E$, and for pure shear, $\gamma_{xy} = \tau_{xy}/G$, according to Hooke's Law. Thus, with substitution and rearrangement, Eq. 46 transforms into Eq. 47, with E and G being the elastic and shear moduli, respectively.

$$U = \underbrace{\iiint_V \frac{\sigma_x^2}{2E} dx dy dz}_{\text{for axial loading and bending in beams}} + \underbrace{\iiint_V \frac{\tau_{xy}}{2G} dx dy dz}_{\text{for shear in beams}} \quad [47]$$

In the case of strain energy in bending, the first term in Eq. 47 can be further simplified through a substitution for σ_x according to Eq. 37. Then since both M and I are functions of x only and that by definition $\iint_A y^2 dy dz = I$, the first triple integral in Eq. 47 transforms to the last term in Eq. 48.

$$\begin{aligned} \iiint_V \frac{\sigma_x^2}{2E} dx dy dz &= \iiint_V \frac{1}{2E} \left(-\frac{My}{I} \right)^2 dx dy dz \\ &= \iint_L \frac{M^2}{2EI^2} \left[\iint_A y^2 dy dz \right] dx = \int_L \frac{M^2}{2EI} dx \end{aligned} \quad [48]$$

This result is Eq. 49 describing the total strain energy stored in the system (U) for beams in bending.

$$U = \int_L \frac{M^2}{2EI} dx + \iiint_V \frac{\tau_{xy}}{2G} dx dy dz \quad [49]$$

With this, an expression for deflection in the beam (δ) can be found by first setting U equal to the external work (W_e) using the principle of conservation of energy. The first law of thermodynamics expresses this principle, in Eq. 50,⁵³ stating that energy can neither be created nor destroyed.

$$\text{work done} = \text{change in energy} \quad [50]$$

For an adiabatic process, no heat is added or subtracted from the system. When no heat is generated (meaning forces are applied to the body so slowly that the kinetic energy can be neglected), the special form of this law for conservative systems reduces to Eq. 51.

$$W_e = U \quad [51]$$

Here W_e is the total work done by the externally applied forces during the loading process and U is the total strain energy stored in the system. It should be noted that the external work (W_e) added to the internal work (W_i) must equal zero.

$$W_e + W_i = 0 \quad [52]$$

Therefore, from Eqs. 52 and 53, the total strain energy is equal to the internal work,

$$U = -W_i \quad [53]$$

where W_i has a negative sign since the deformations are opposed by the internal forces. This can then be applied to the case of a single elastic cantilever with a rectangular cross section in which a force (P) is applied at the free end as in Figure 42.

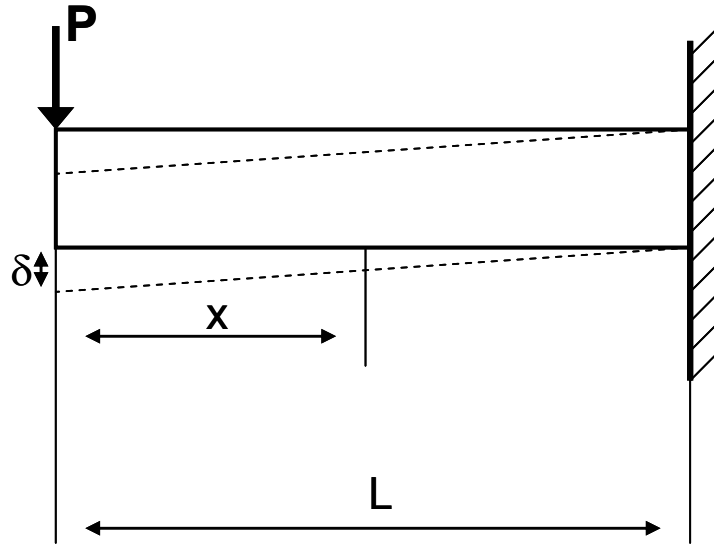


Figure 42. Single cantilever beam

As P is applied to the beam, Eq. 54 holds.

$$W_e = \frac{P\delta}{2} \quad [54]$$

In this case, the total strain energy (U) consists of two parts. One part is due to the bending stresses ($U_{bending}$) and the other is caused by the shearing stresses (U_{shear}). Expressions for these parts can be found directly from Eq. 49 by the first and second terms on the right-hand side, respectively. The expression for $U_{bending}$ can be further simplified through substitution for M by noting $M = -Px$, and integrating along the length.

$$U_{bending} = \int_0^L \frac{M^2 dx}{2EI} = \int_0^L \frac{(-Px)^2 dx}{2EI} = \frac{P^2 L^3}{6EI} \quad [55]$$

The expression for U_{shear} is found using the second term of Eq. 49. In the case of a single cantilever with a rectangular cross section, the shear at every section is equal to P , while the shear stress (τ) is a maximum at the neutral axis and is distributed parabolically across the plane of the cross section⁵³ as

$$\tau = \left[\frac{P}{2I} \right] \left[\left(\frac{t}{2} \right)^2 - y^2 \right] \quad [56]$$

with t being the thickness of the beam and y the distance from the neutral axis. At increasing distances from the neutral axis, the shearing stresses gradually diminish, ceasing to exist at the upper and lower boundaries of the beam ($y = t/2$).

The infinitesimal volume ($dx dy dz$) in Eq. 49, can be represented as $L \cdot w \, dy$. Making this substitution, along with that for τ in Eq. 56 and some additional rearrangement, one obtains the relation for U_{shear} , found in Eq. 57.

$$\begin{aligned} U_{shear} &= \int_V \frac{\tau^2}{2G} dV = \frac{1}{2G} \int_{-t/2}^{t/2} \left[\frac{P}{2I} \left(\left(\frac{t}{2} \right)^2 - y^2 \right) \right]^2 L w dy \\ &= \frac{P^2 L w}{8GI^2} \frac{h^5}{30} = \frac{P^2 L w t^5}{240G} \left(\frac{12}{wt^3} \right)^2 = \frac{3P^2 L}{5AG} \end{aligned} \quad [57]$$

From Eq. 54, and substituting using Eqs. 53 and 55, a relation involving U and δ is found.

$$\begin{aligned} W_e &= U = U_{bending} + U_{shear} \\ \frac{P\delta}{2} &= \frac{P^2 L^3}{6EI} + \frac{3P^2 L}{5AG} \end{aligned} \quad [58]$$

Finally, by rearranging, the Langrangian equation for deflection in the single cantilever mode is found as shown in Eq. 59.⁵³

$$\delta = \frac{PL^3}{3SI} + \frac{6PL}{5AG} \quad [59]$$

The 3-point bending case can be treated as two single cantilevers.⁵³ In this case, the deflection for two single cantilevers ($2 \cdot \delta$) should total twice that of one (δ), so Eq. 57 becomes Eq. 60.

$$2\delta = \frac{PL^3}{3SI} + \frac{6PL}{5AG} \quad [60]$$

From here a substitution is made for G according to Eq. 59,¹⁴ and also for A ,

$$G = \frac{S}{2(1+\nu)} \quad [61]$$

resulting in Eq. 62.

$$2\delta = \frac{PL^3}{3SI} + \frac{12PL(1+\nu)}{5wtS} \quad [62]$$

Solving for S gives Eq. 63.

$$S = \frac{PL^3}{6\delta I} + \frac{12PL(1+\nu)}{10wt\delta} \quad [63]$$

Multiplying the second term on right side by L^2/L^2 and making a substitution involving the stiffness (K) according to Eq. 64,

$$K = \frac{P}{\delta} \quad [64]$$

gives Eq. 65.

$$S = \frac{KL^3}{6I} + \frac{12KL^3(1+\nu)}{10wtL^2} \quad [65]$$

Substituting for I according to Eq. 36, and multiplying the second term on right side by t^2/t^2 leads to Eqs. 66.

$$S = \frac{KL^3}{6I} + \frac{KL^3t^2(1+\nu)}{10IL^2} \quad [66]$$

Rearranging gives Eq. 67.

$$S = \frac{KL^3}{6I} + \frac{KL^3}{I} \frac{1}{10} (1 + \nu) \left(\frac{t}{L} \right)^2 \quad [67]$$

Multiplying the second term on right side by 6/6 and simplifying leads to Eq. 68.

$$S = \frac{KL^3}{6I} \left[1 + \frac{6}{10} (1 + \nu) \left(\frac{t}{L} \right)^2 \right] \quad [68]$$

Eq. 68 is identical to Eq. 32, which as previously mentioned is the equation used by the DMA software to calculate the slope at each data point in the s/s curve.

The direct Lagrangian solution of problems by equating the external work to the internal strain energy turns out to be useful in cases where only one force is applied to a member, as in three-point bending. To understand elastic systems subjected to any number of loads, a more general theorem for determining deflections and rotations of any element is needed. This theorem is associated with the name of Castigliano (1847-1884), and when applied to the simple case of an elastic beam having only one applied load, the solution simply becomes that of the Lagrangian equation for deflection in the single cantilever mode,⁵³ shown in Eq. 59.

In order to determine not only elastic deformations but also deformations due to temperature changes, plastic deformations, and those due to misfit of the fabricated elements, a still more general procedure based on the concept of virtual work is required.⁵³ When the virtual work concept is applied to find the deflection at a point for the simple case of a linearly elastic beam, the solution becomes that of Castigliano's theorem.⁵³ Following, in the case of a single applied load (3-pt. bending), Castigliano's theorem in turn simplifies to the Lagrangian equation for deflection in the single cantilever mode. When this equation is rearranged and the deflection is doubled to account for the use of two single cantilevers to represent three-point bending, it becomes the equation used by the DMA software to calculate the slope of the s/s curve at each data point.

A-3 Maximum Strain Equation in Three-Point Bending

With the equations. for σ_{max} and S known, the equation for ε_{max} is derived from a modified Hooke's Law.

$$\varepsilon = \frac{\sigma}{S} \quad [69]$$

Since S is the slope at each point, his relation remains valid even for the nonlinear region of the s/s curve. This is only true however, when S is applied to each data point individually. Thus, S can be used to relate σ and ε , resulting in Eq. 70,

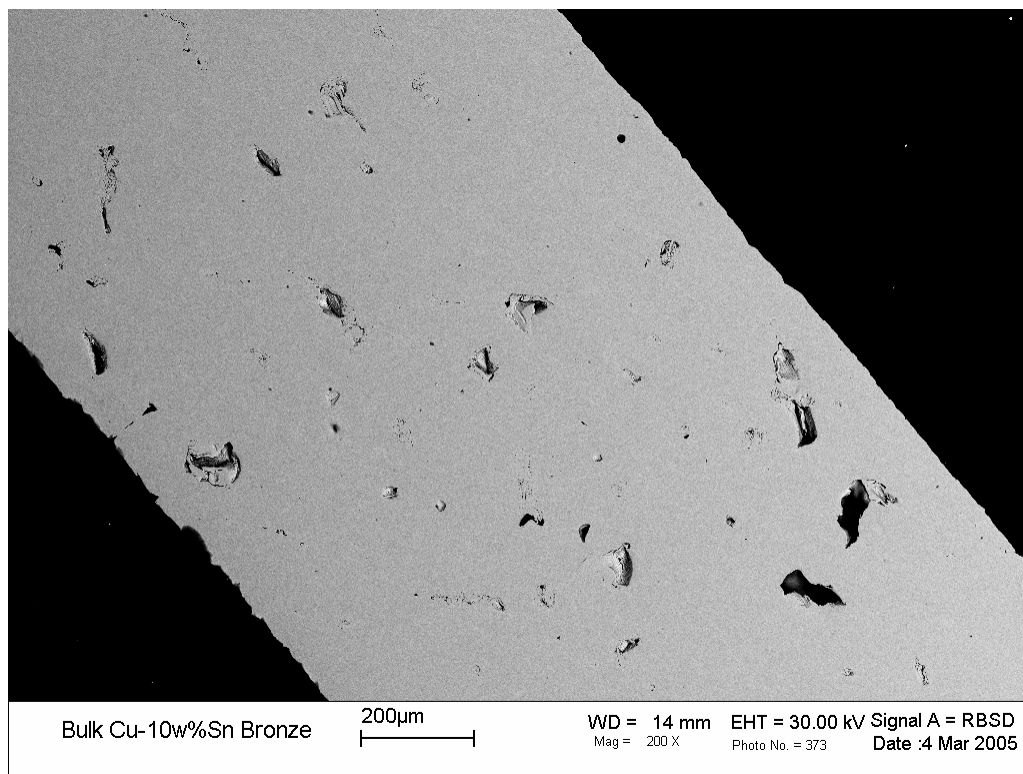
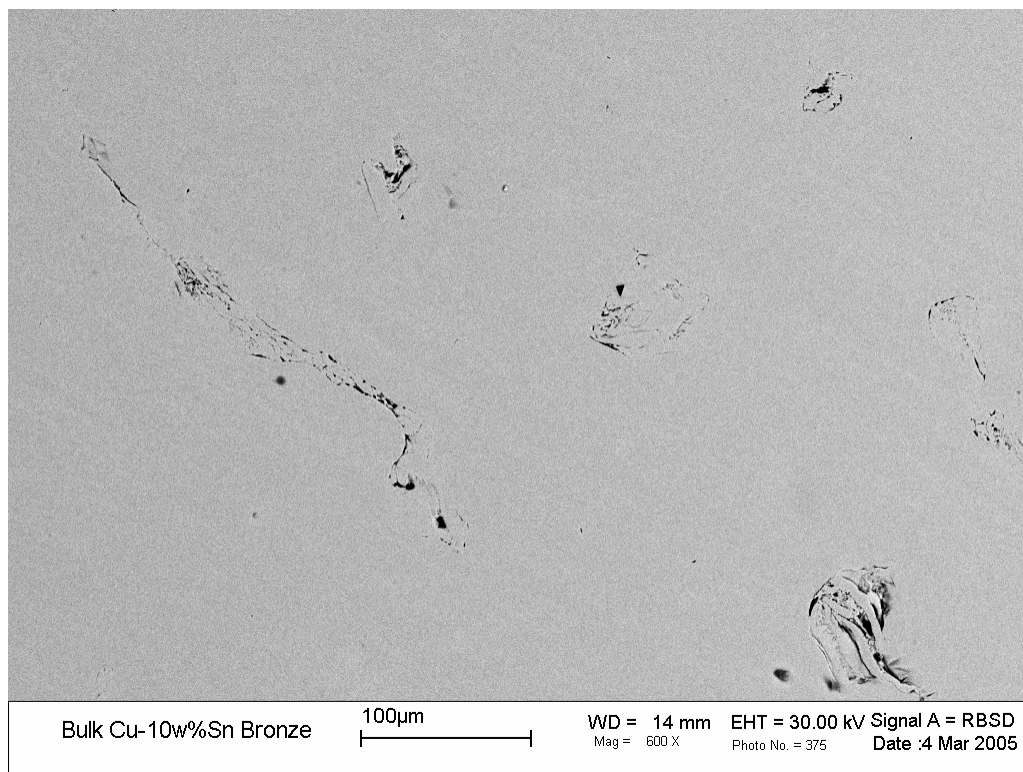
$$\varepsilon = \frac{\frac{PLt}{4I} = \frac{3PL}{wt^2}}{K \frac{L^3}{6I} \left[1 + \frac{6}{10} (1 + \nu) \left(\frac{t}{L} \right)^2 \right]} \quad [70]$$

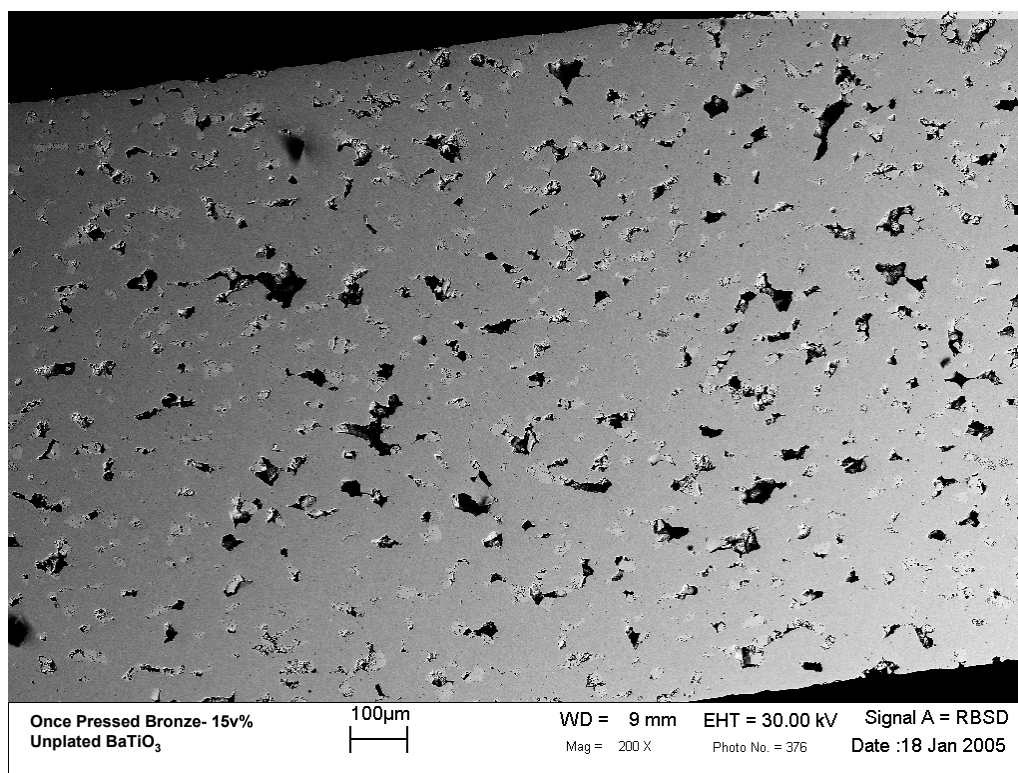
which simplifies to Eq. 71.

$$\varepsilon_{max} = \frac{6 \delta t}{2 L^2 \left[1 + \frac{6}{10} (1 + \nu) \left(\frac{t}{L} \right)^2 \right]} \quad [71]$$

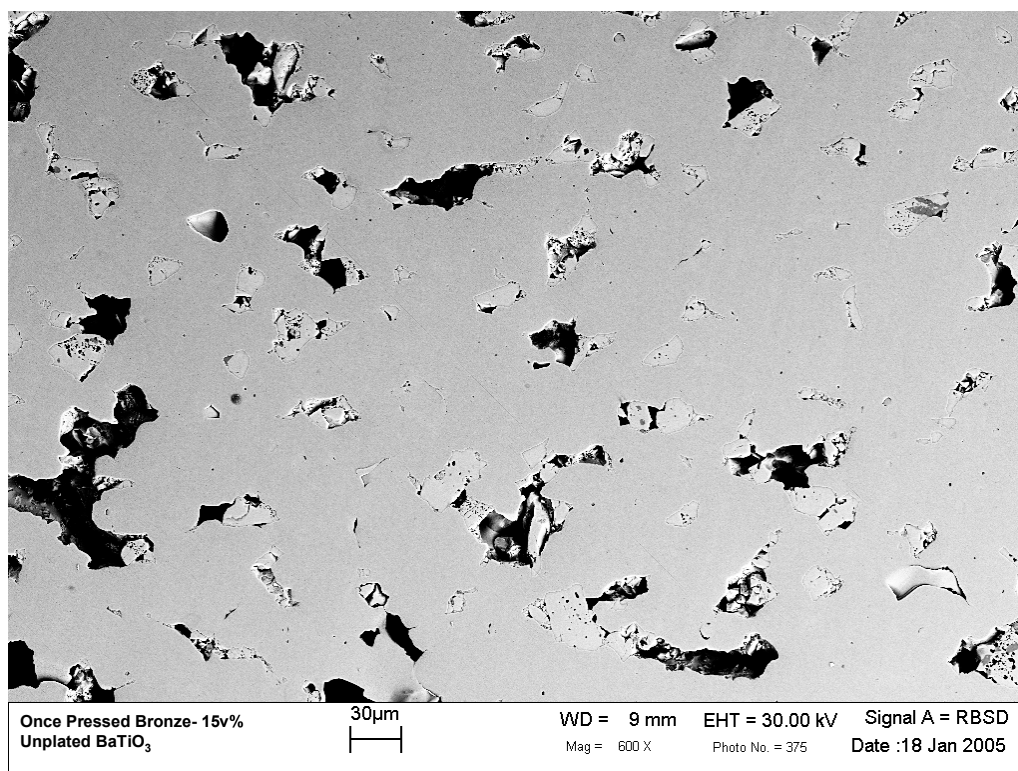
Eq. 71 is identical to Eq. 33, which as previously mentioned is the equation used by the DMA software to calculate the maximum strain.

Appendix B: Composite Structures

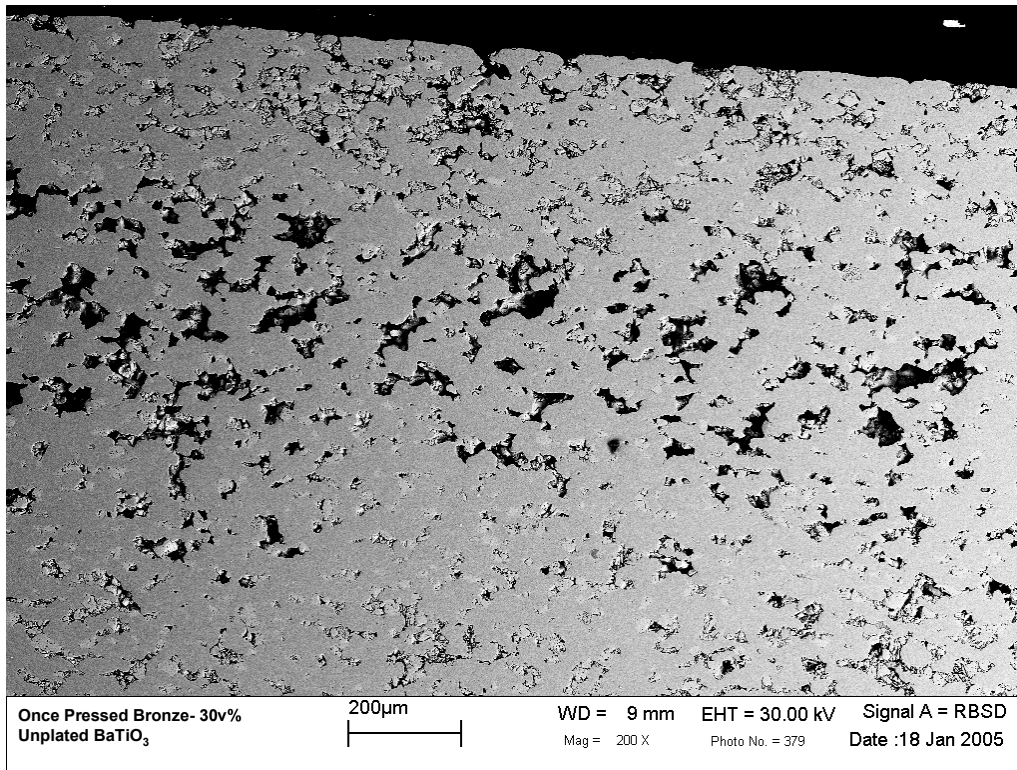
**B 1. Bronze- 0v% BaTiO₃****B 2. Bronze- 0v% BaTiO₃**



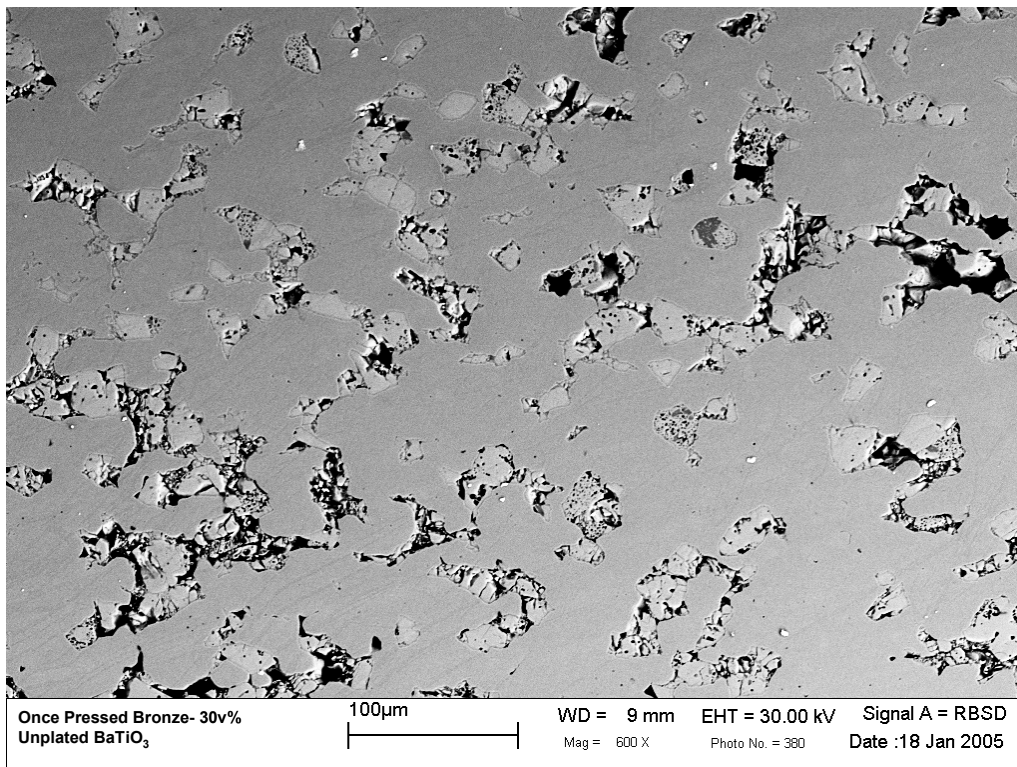
B 3. Bronze- 15v% unplated BaTiO₃ pressed once



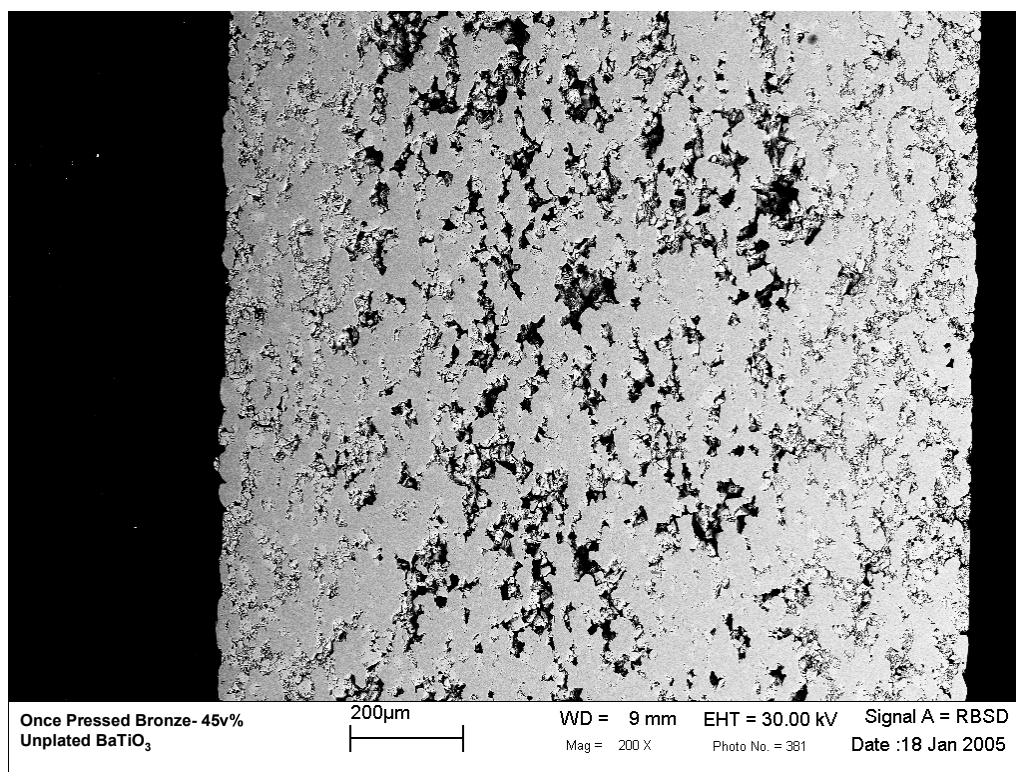
B 4. Bronze- 15v% unplated BaTiO₃ pressed once



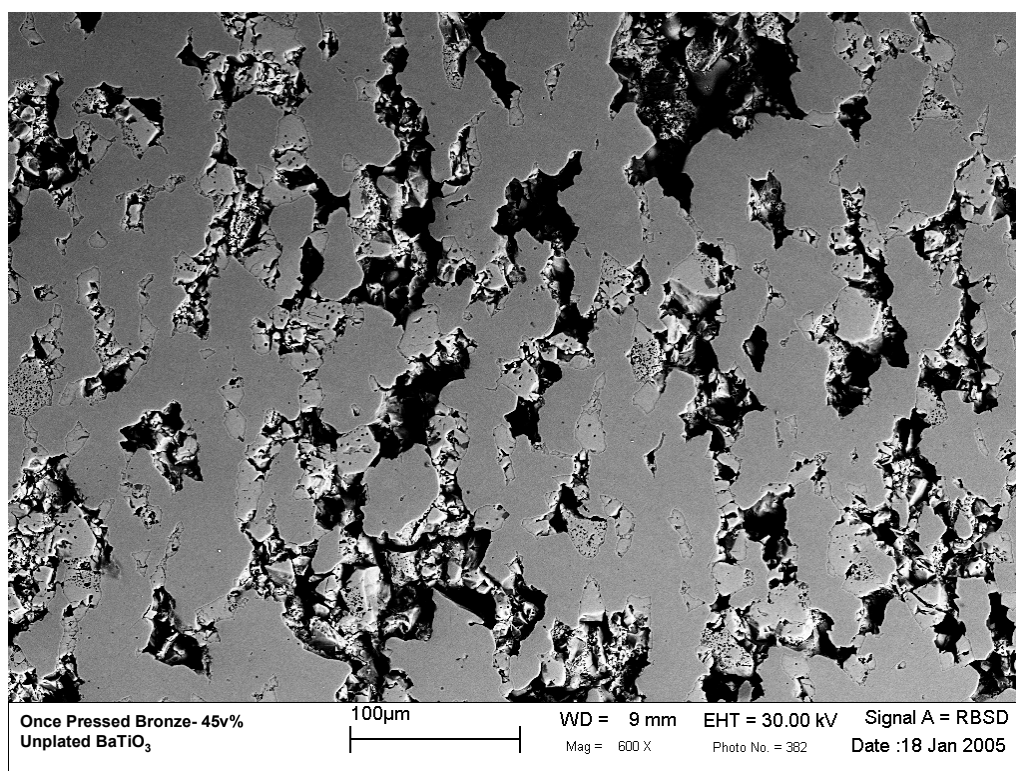
B 3. Bronze- 30v% unplated BaTiO₃ pressed once



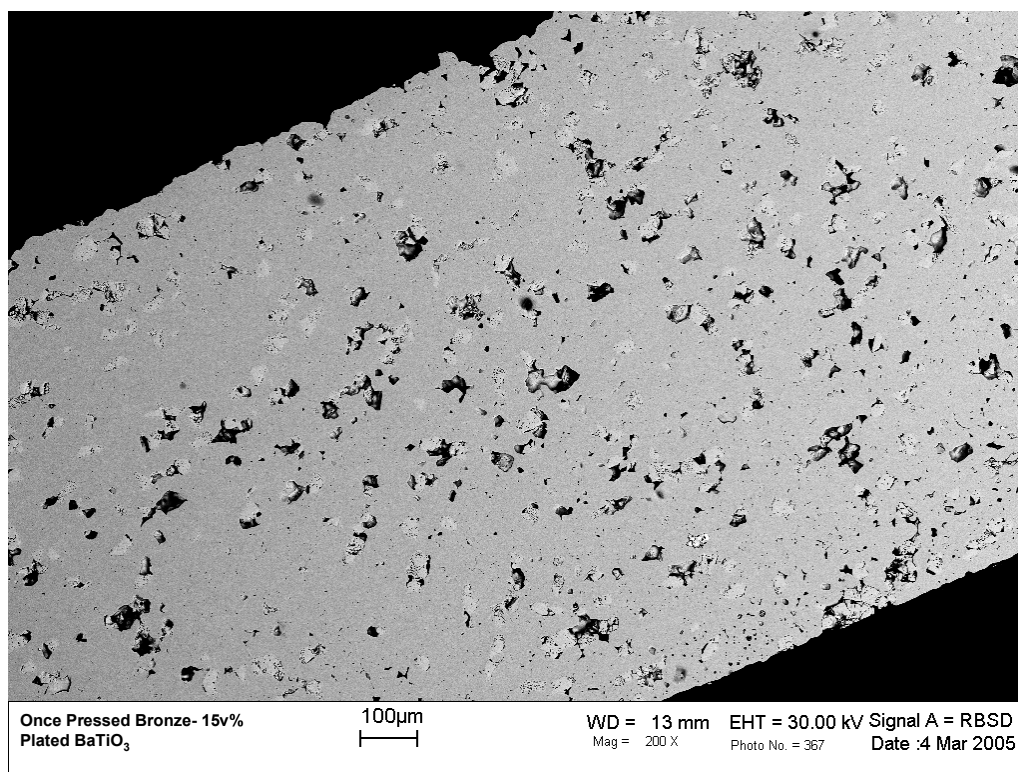
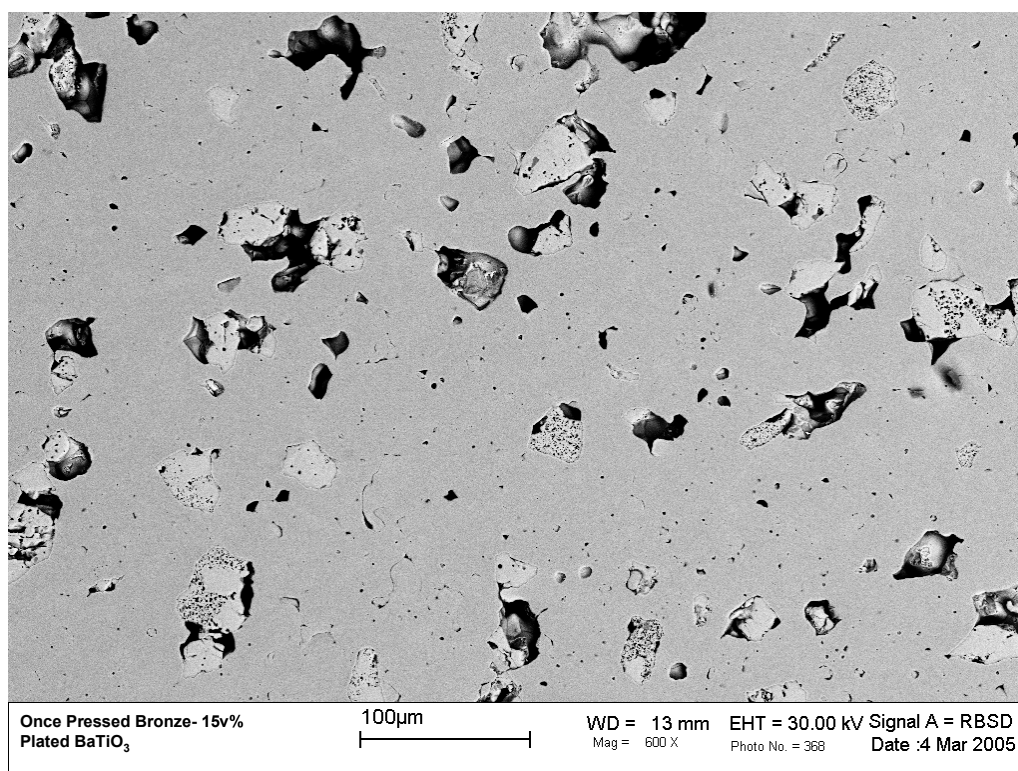
B 4. Bronze- 30v% unplated BaTiO₃ pressed once

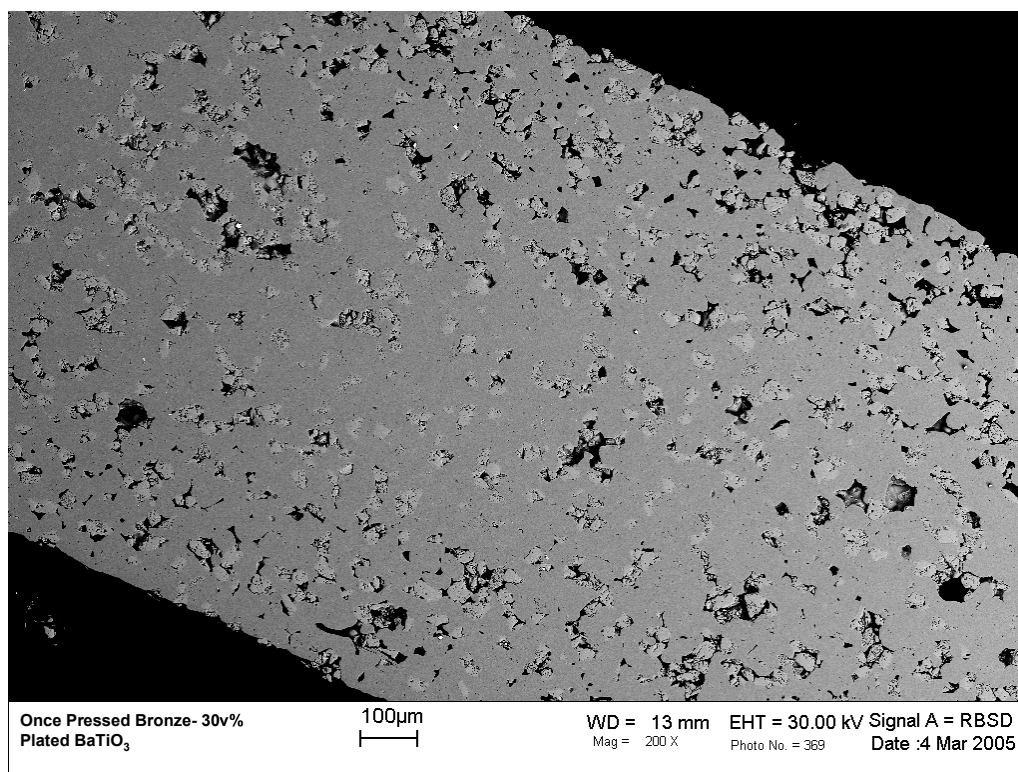


B 5. Bronze- 45v% unplated BaTiO₃ pressed once

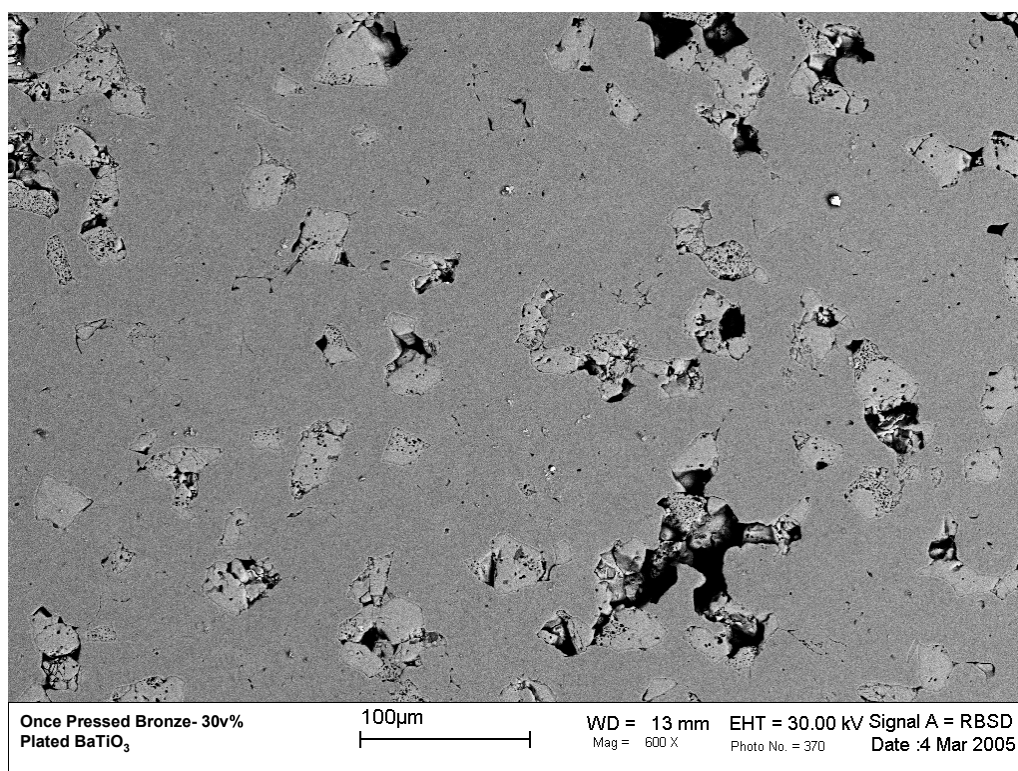


B 6. Bronze- 45v% unplated BaTiO₃ pressed once

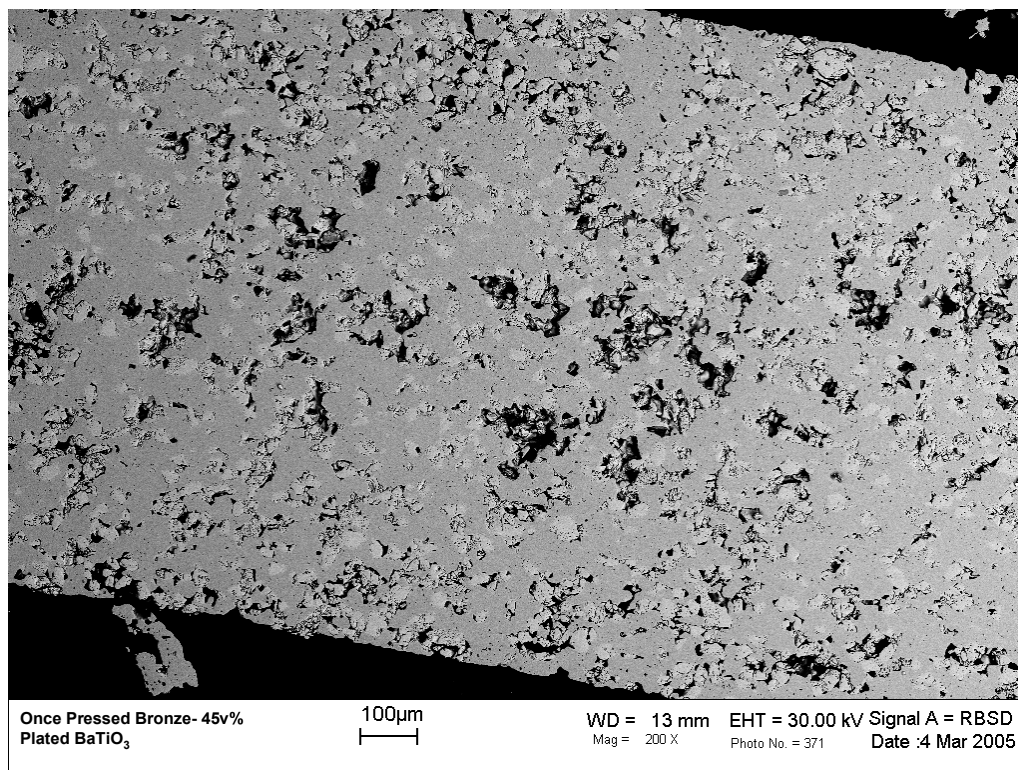
**B 7. Bronze- 15v% plated BaTiO₃ pressed once****B 8. Bronze- 15v% plated BaTiO₃ pressed once**



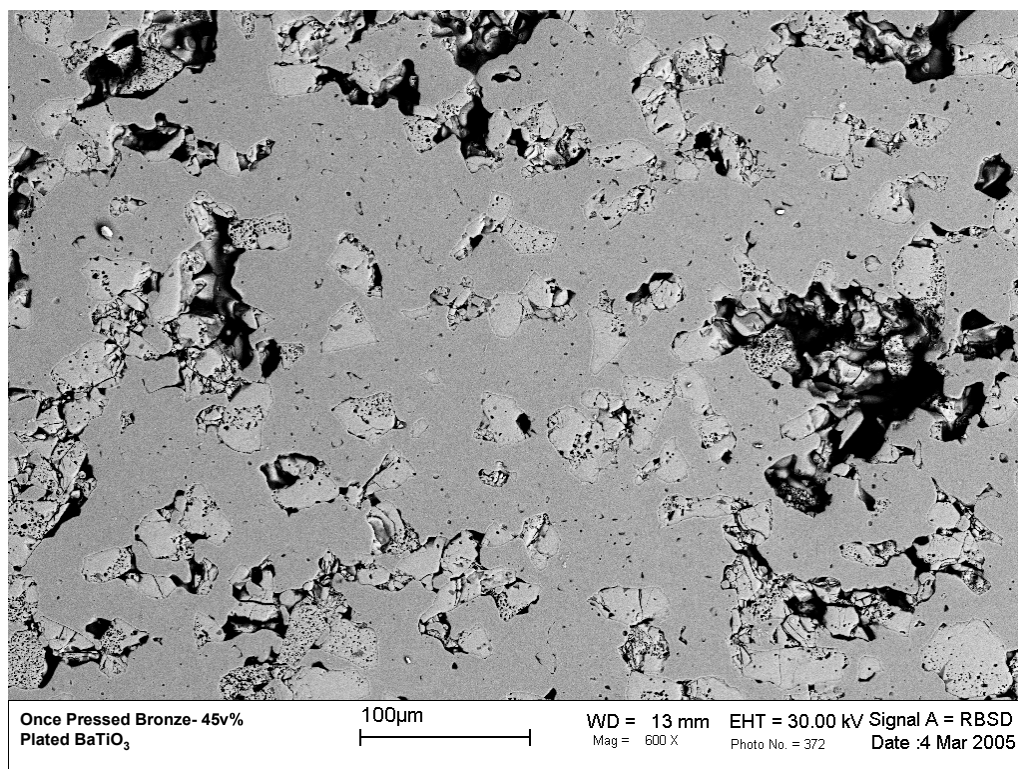
B 9. Bronze- 30v% plated BaTiO₃ pressed once



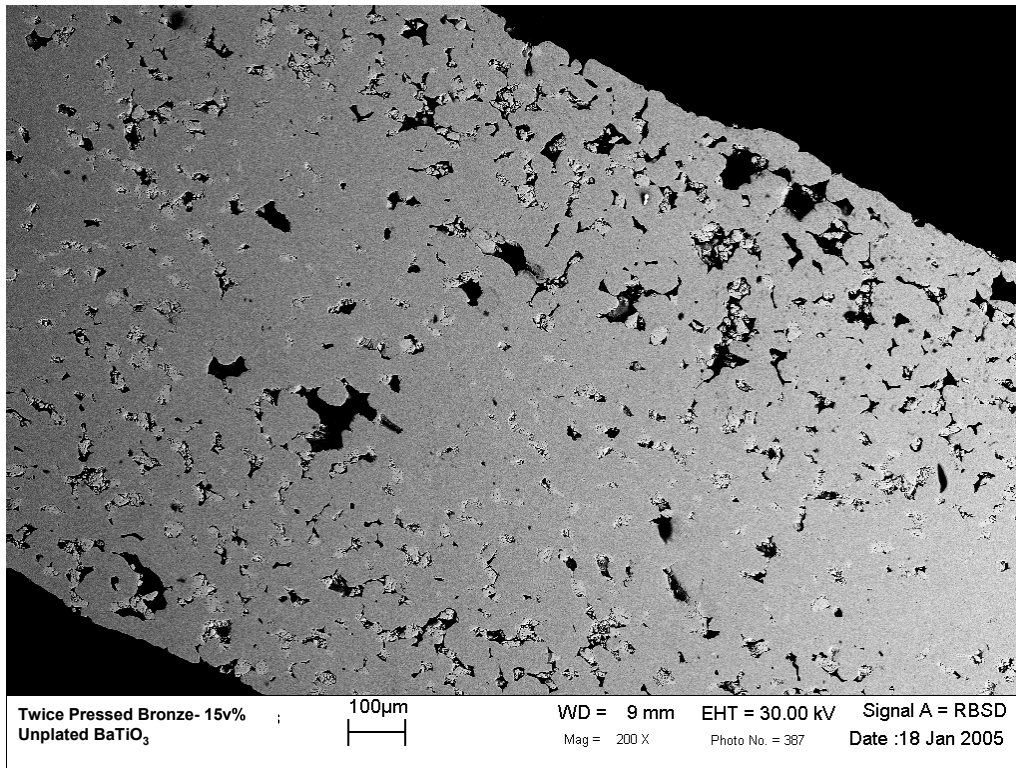
B 10. Bronze- 30v% plated BaTiO₃ pressed once



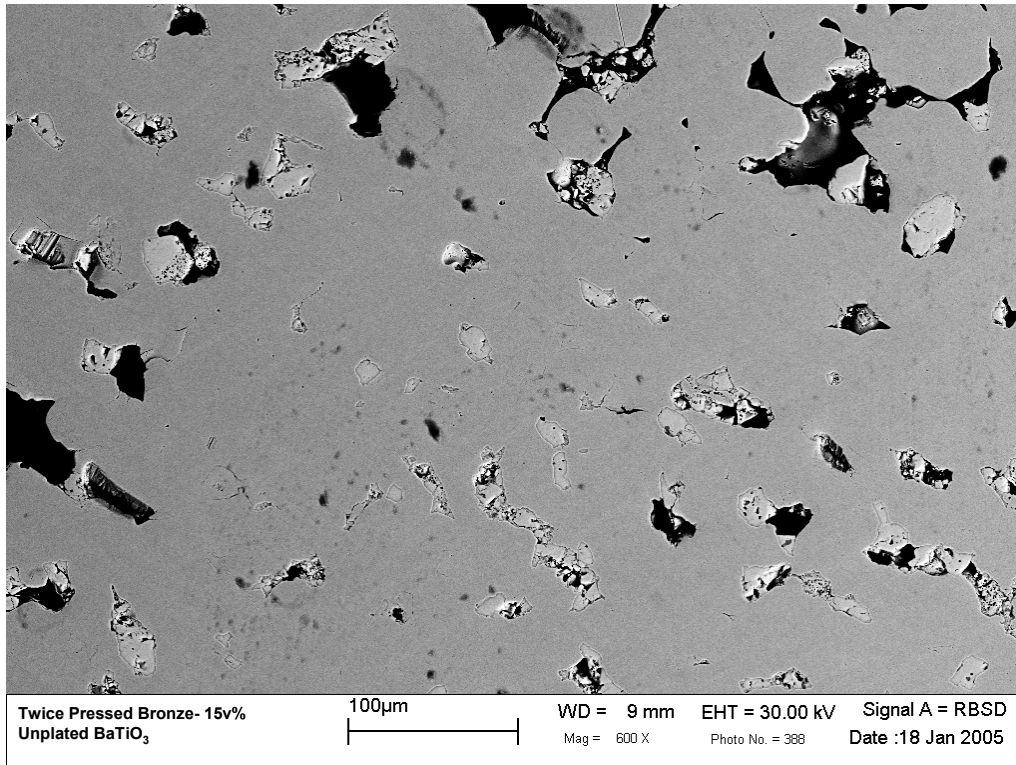
B 11. Bronze- 45v% plated BaTiO₃ pressed once



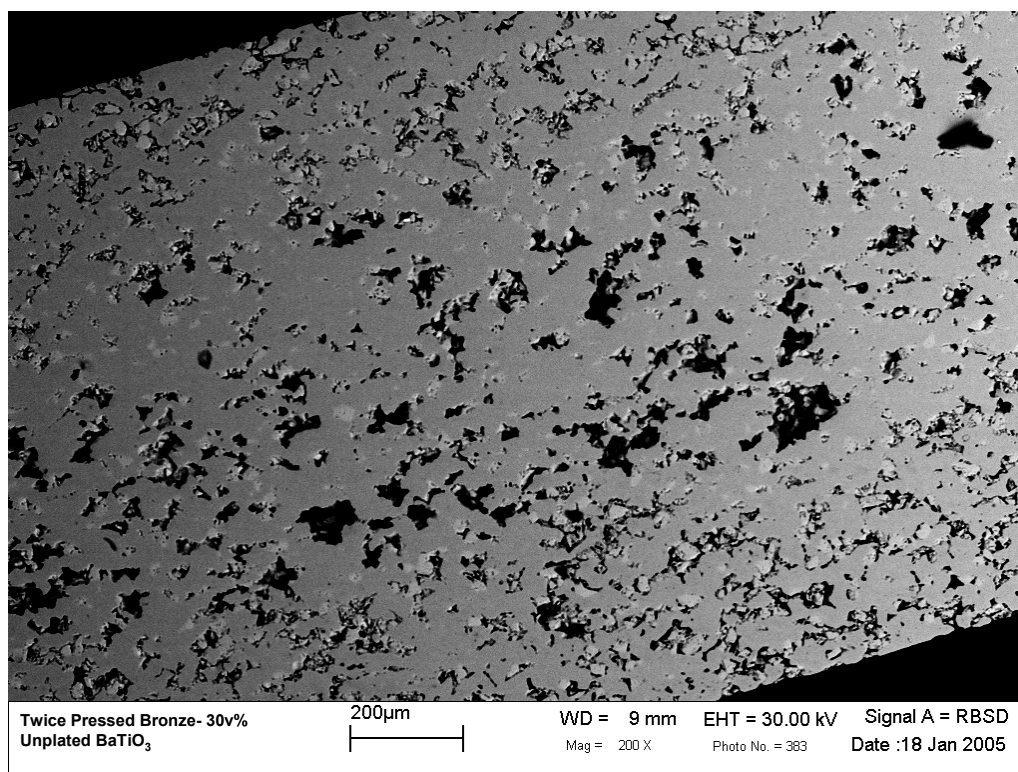
B 12. Bronze- 45v% plated BaTiO₃ pressed once



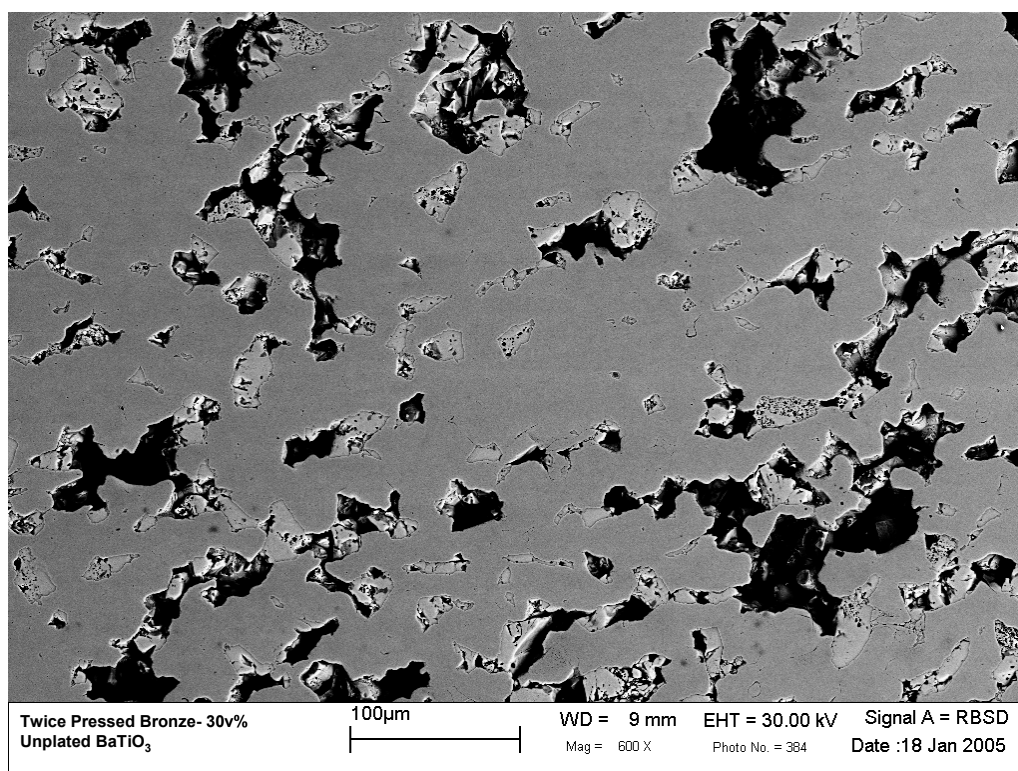
B 13. Bronze- 15v% unplated BaTiO₃ pressed twice



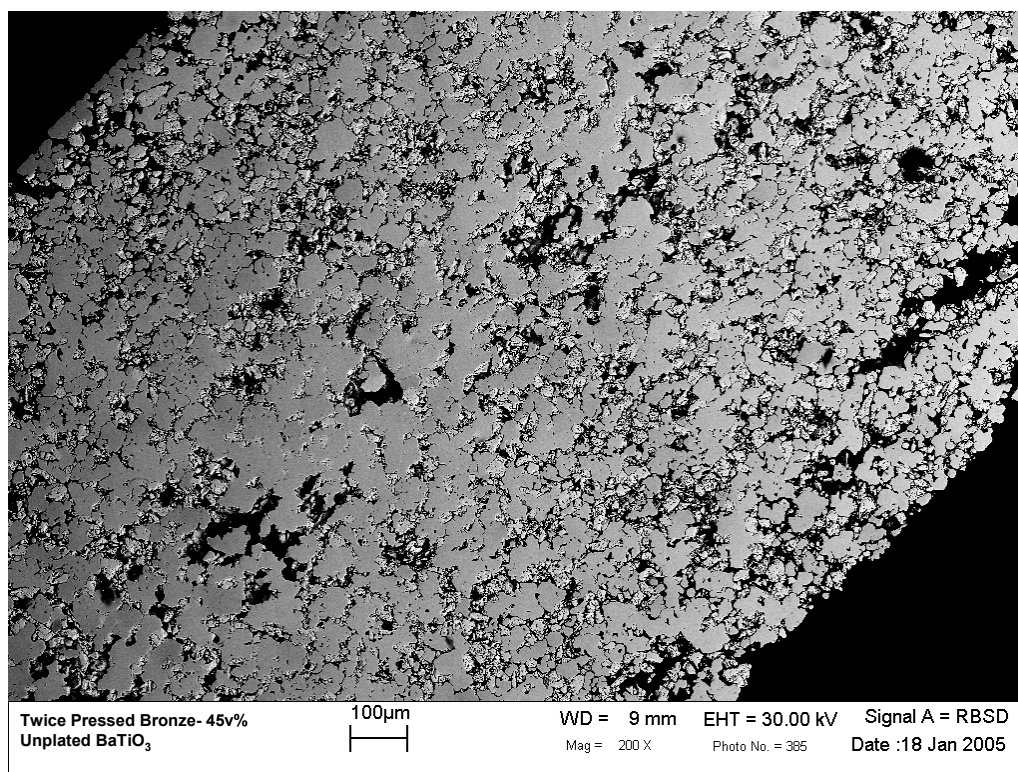
B 14. Bronze- 15v% unplated BaTiO₃ pressed twice



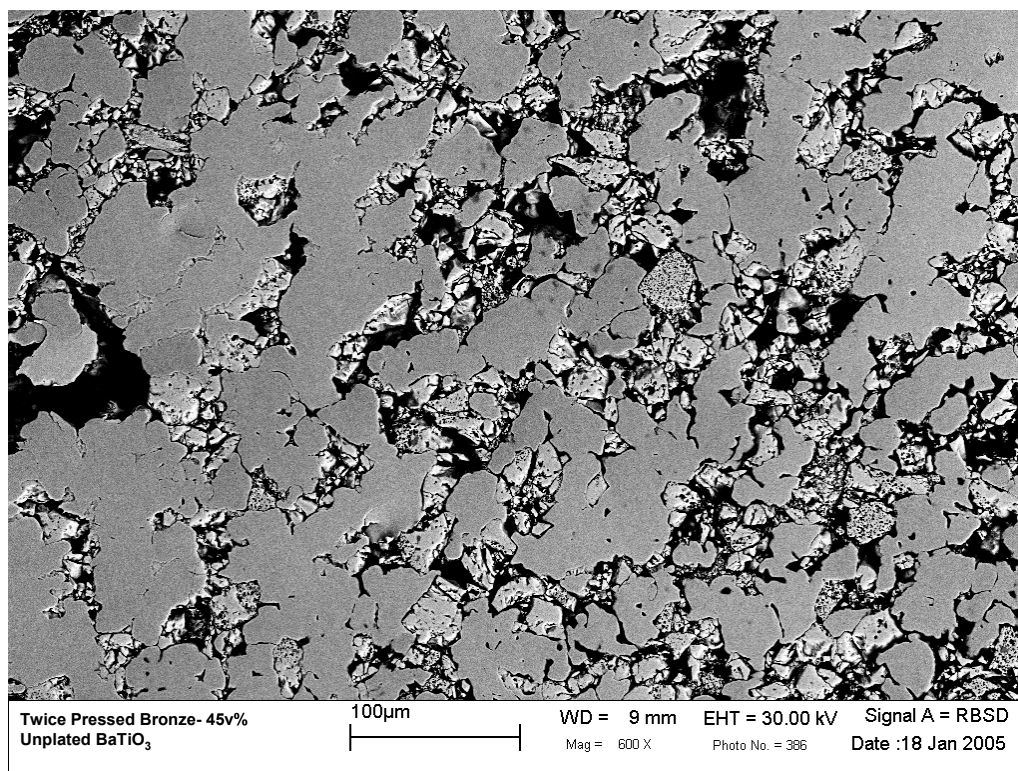
B 15. Bronze- 30v% unplated BaTiO₃ pressed twice



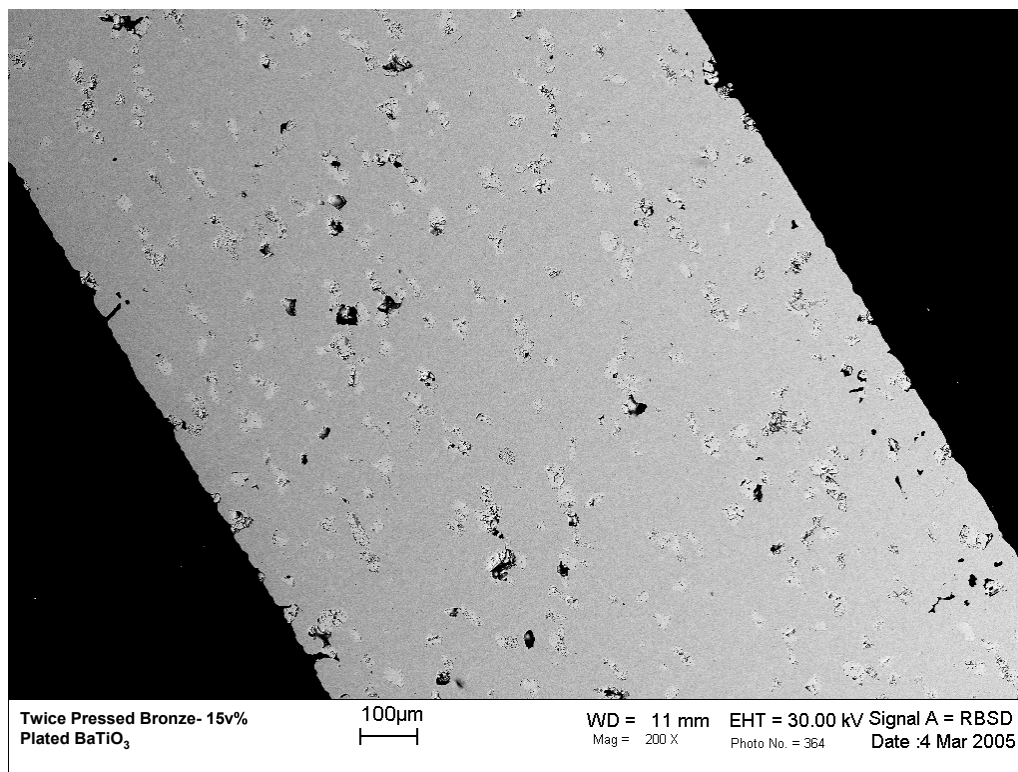
B 16. Bronze- 30v% unplated BaTiO₃ pressed twice



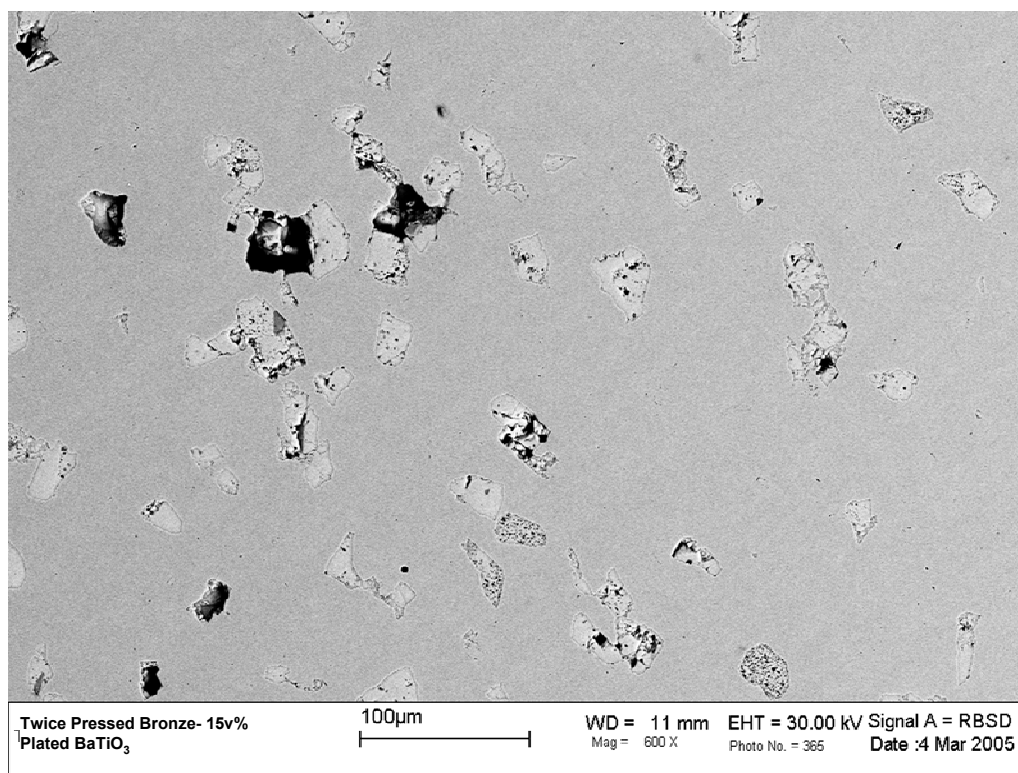
B 17. Bronze- 45v% unplated BaTiO₃ pressed twice



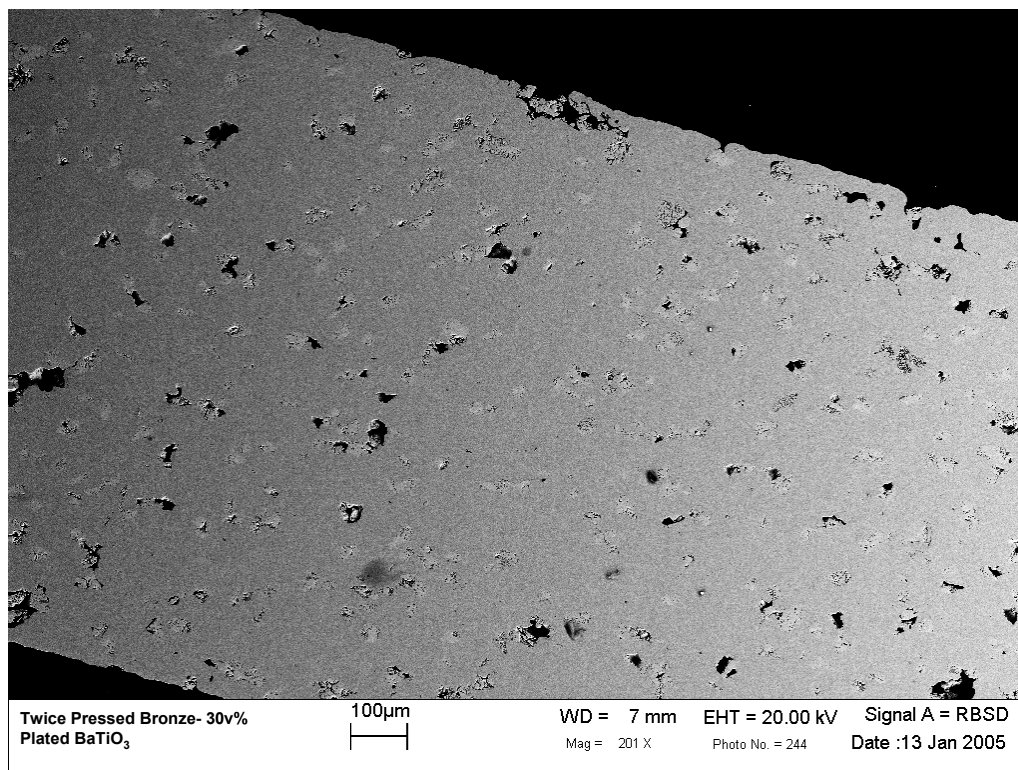
B 18. Bronze- 45v% unplated BaTiO₃ pressed twice



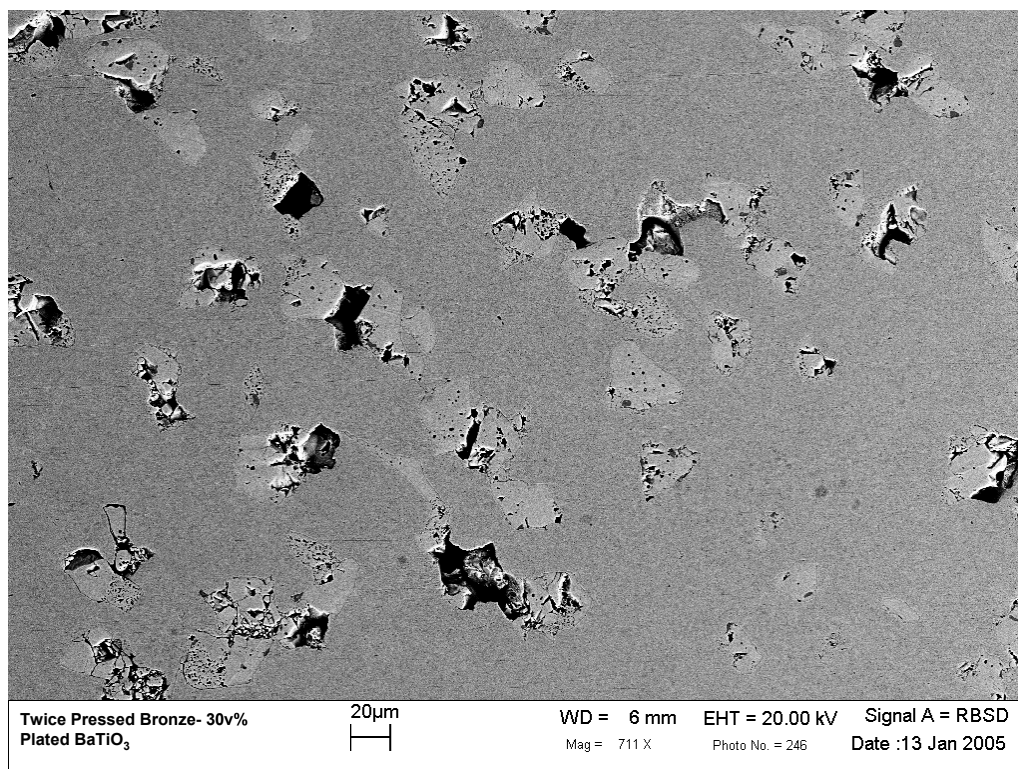
B 19. Bronze- 15v% plated BaTiO₃ pressed twice



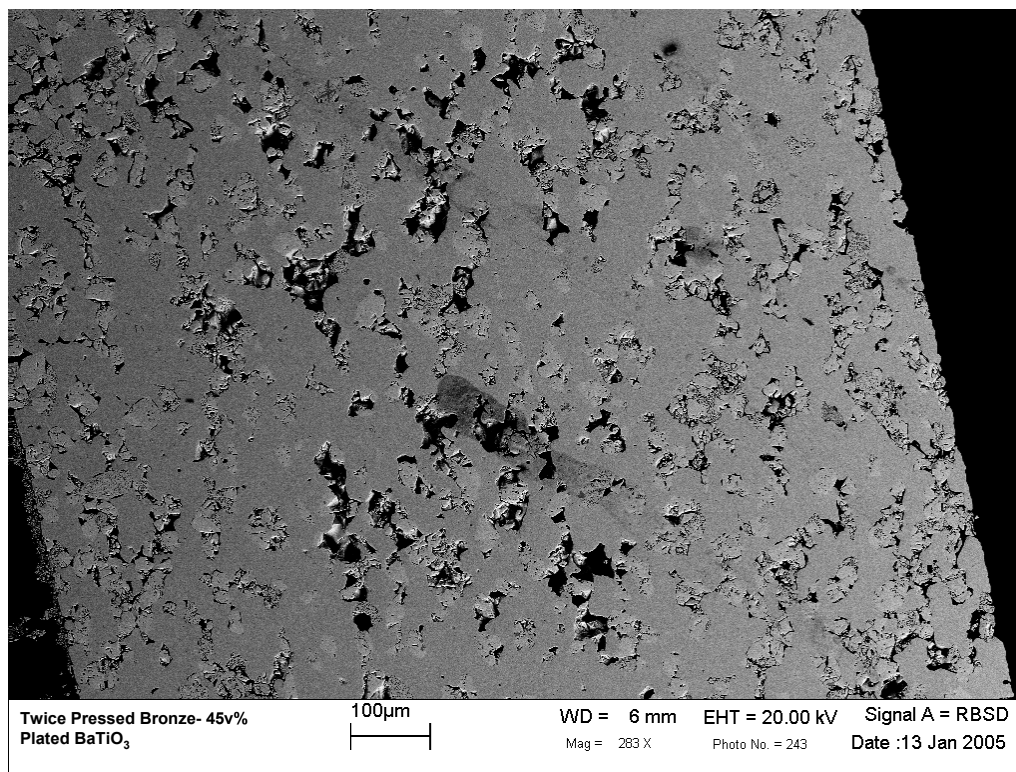
B 20. Bronze- 15v% plated BaTiO₃ pressed twice



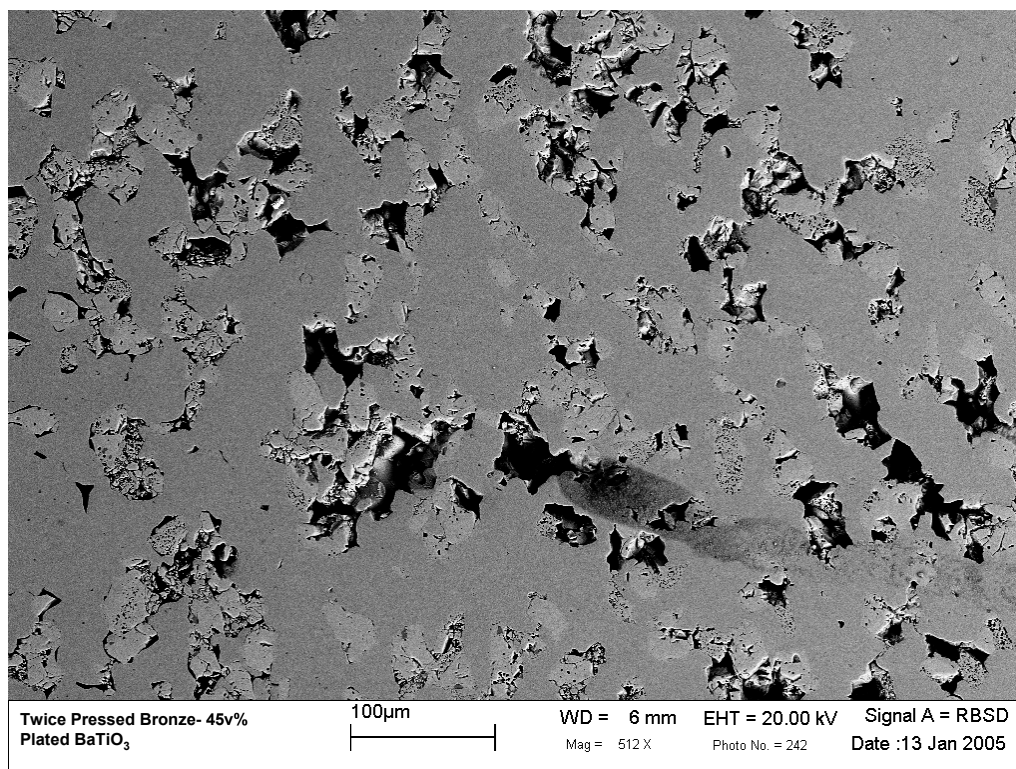
B 21. Bronze- 30v% plated BaTiO₃ pressed twice



B 22. Bronze- 30v% plated BaTiO₃ pressed twice

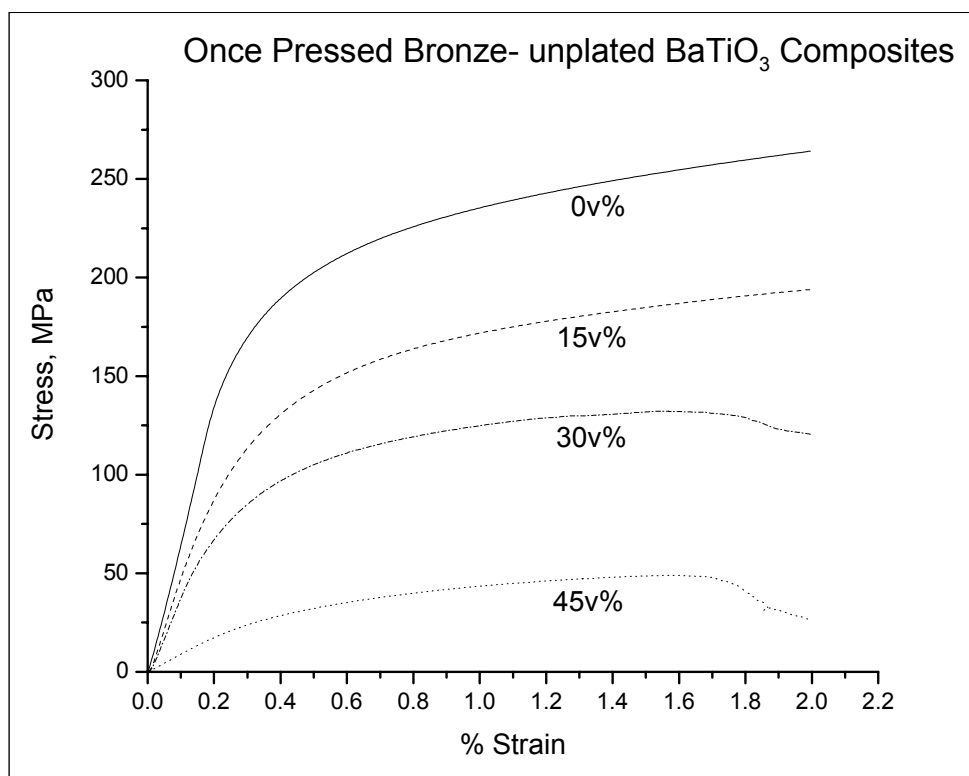


B 23. Bronze- 45v% plated BaTiO₃ pressed twice

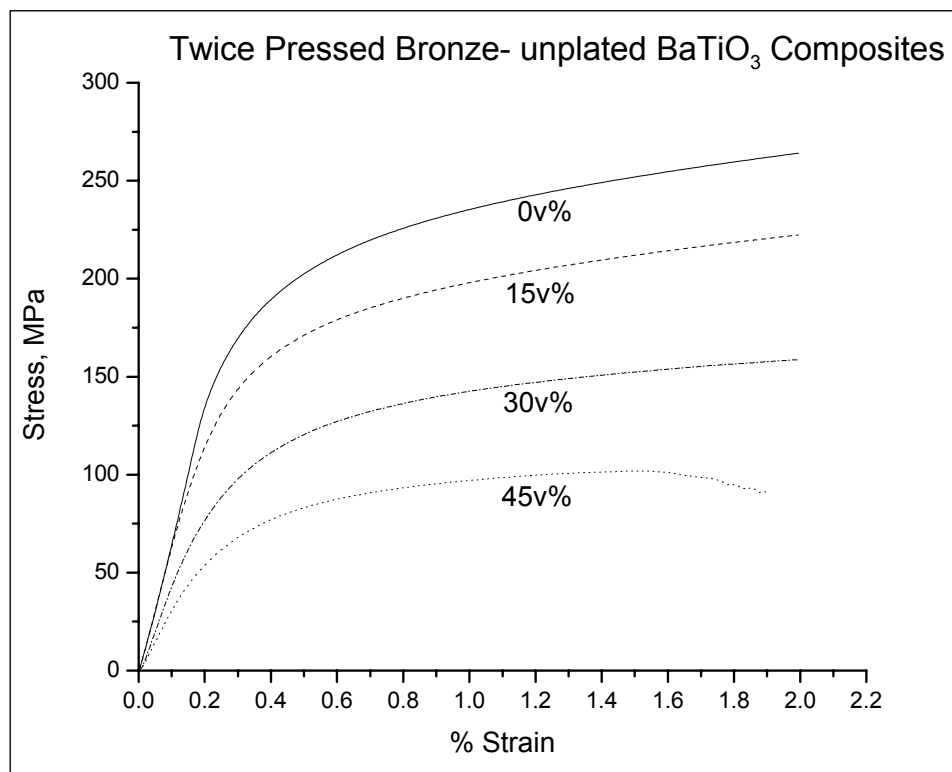


B 24. Bronze- 45v% plated BaTiO₃ pressed twice

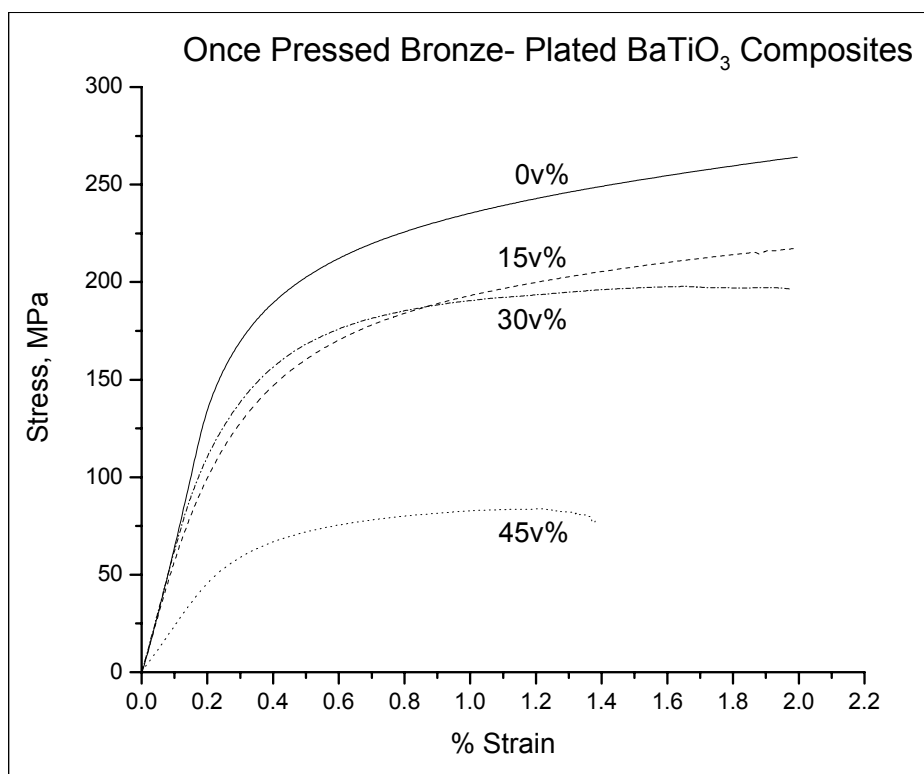
Appendix C: Stress/Strain Curves vs. Volume Percent BaTiO₃



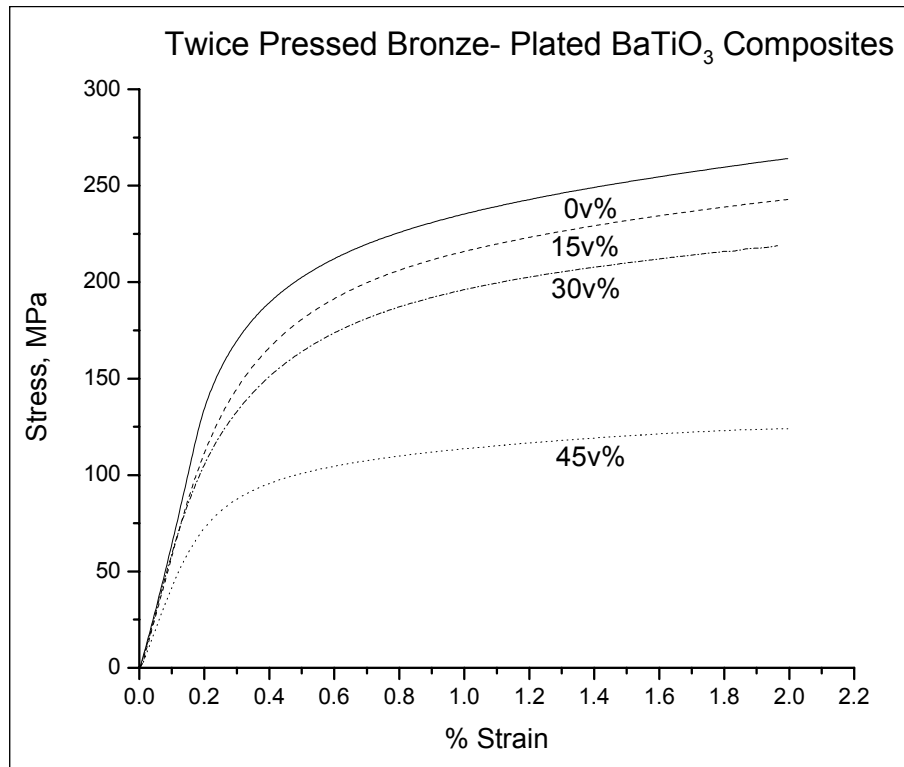
C 1. Stress/Strain curves of once pressed bronze- unplated BaTiO₃ composites of various v%



C 2. Stress/Strain curves of twice pressed bronze- unplated BaTiO₃ composites of various v%

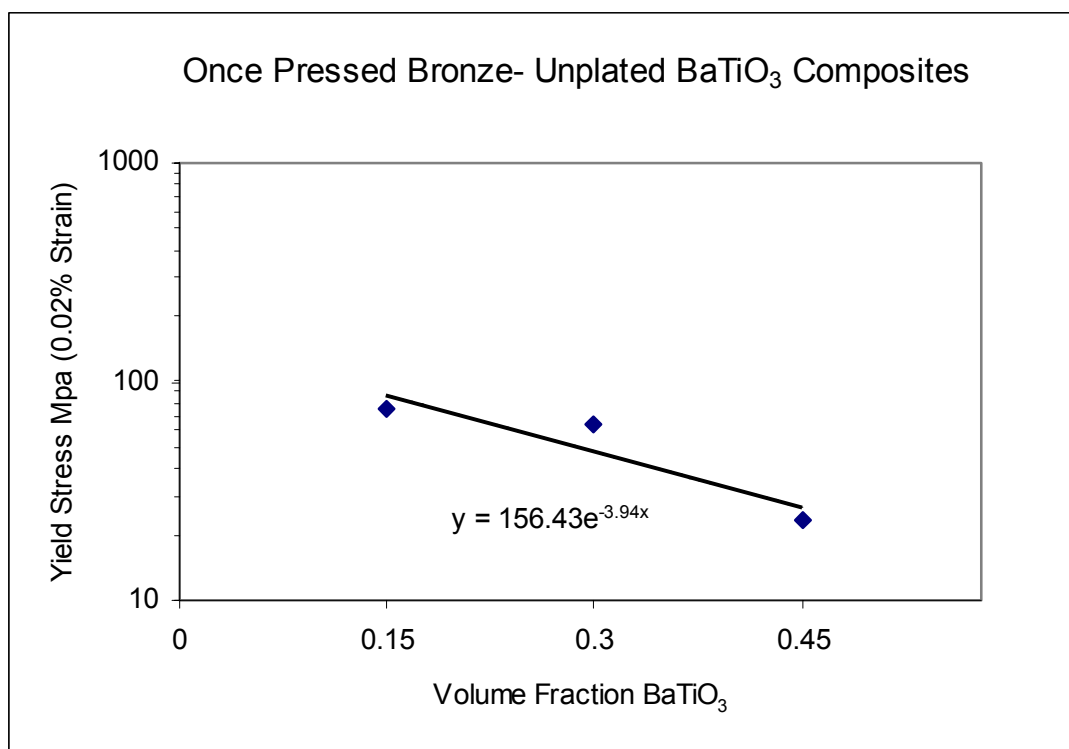


C 3. Stress/Strain curves of once pressed bronze- plated BaTiO₃ composites of various v%

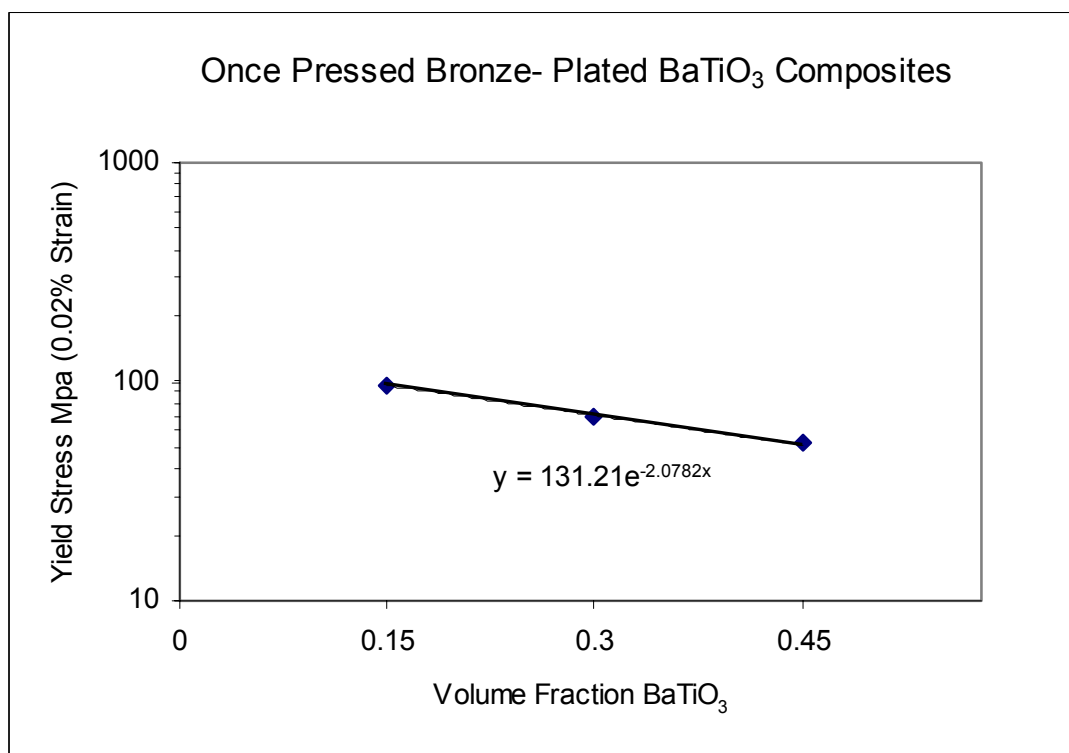


C 4. Stress/Strain curves of twice pressed bronze- plated BaTiO₃ composites of various v%

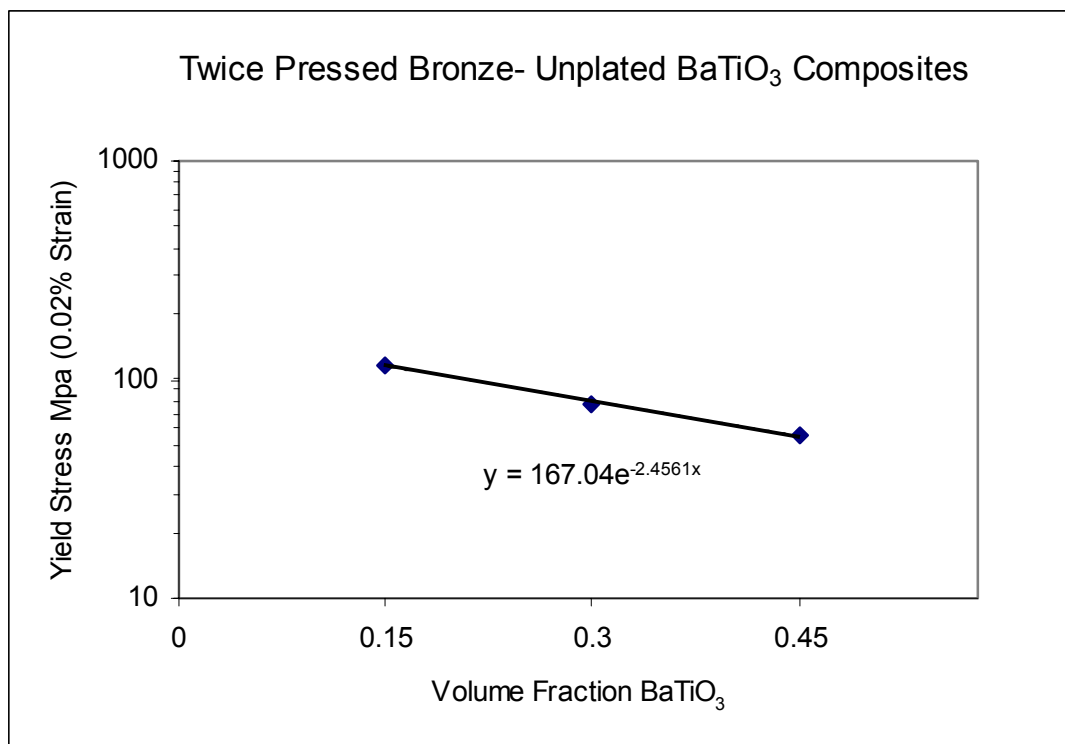
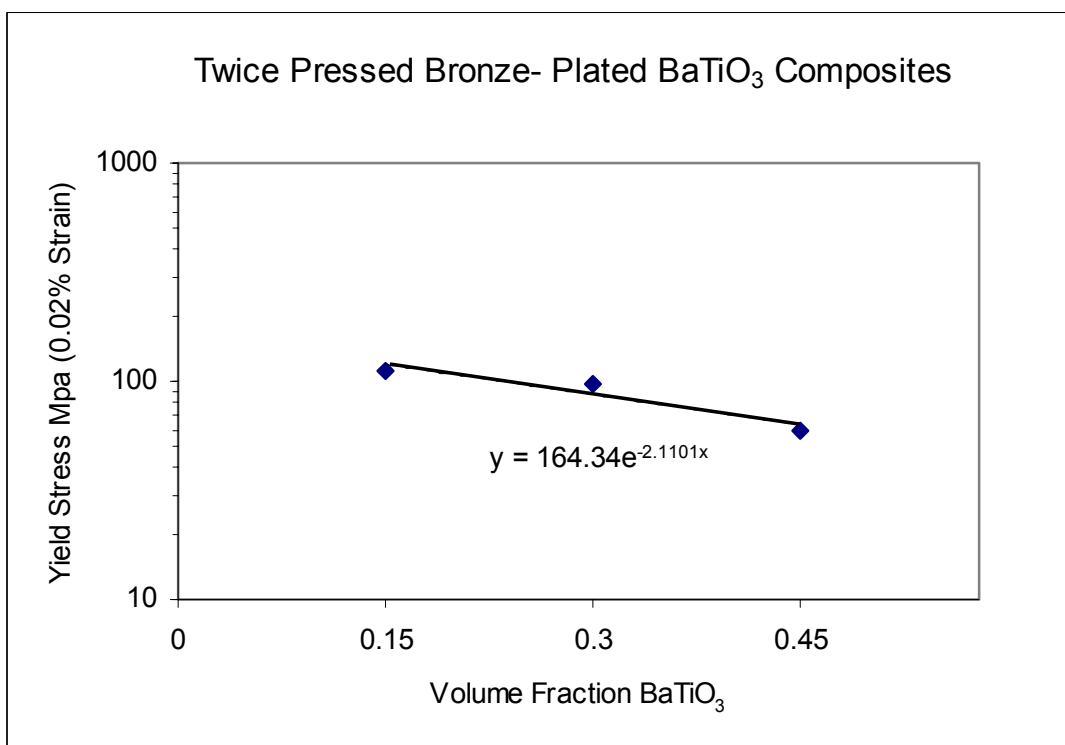
Appendix D: Yield Stress vs. Volume Fraction
BaTiO₃



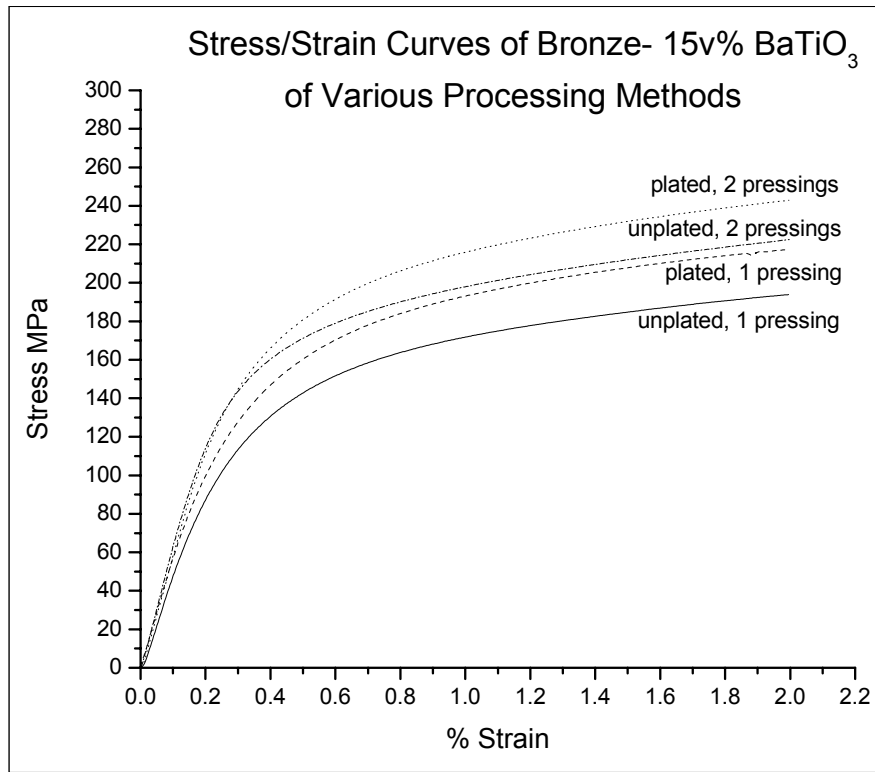
D 1. Yield Stress vs. Volume fraction unplated BaTiO₃ in once pressed composites



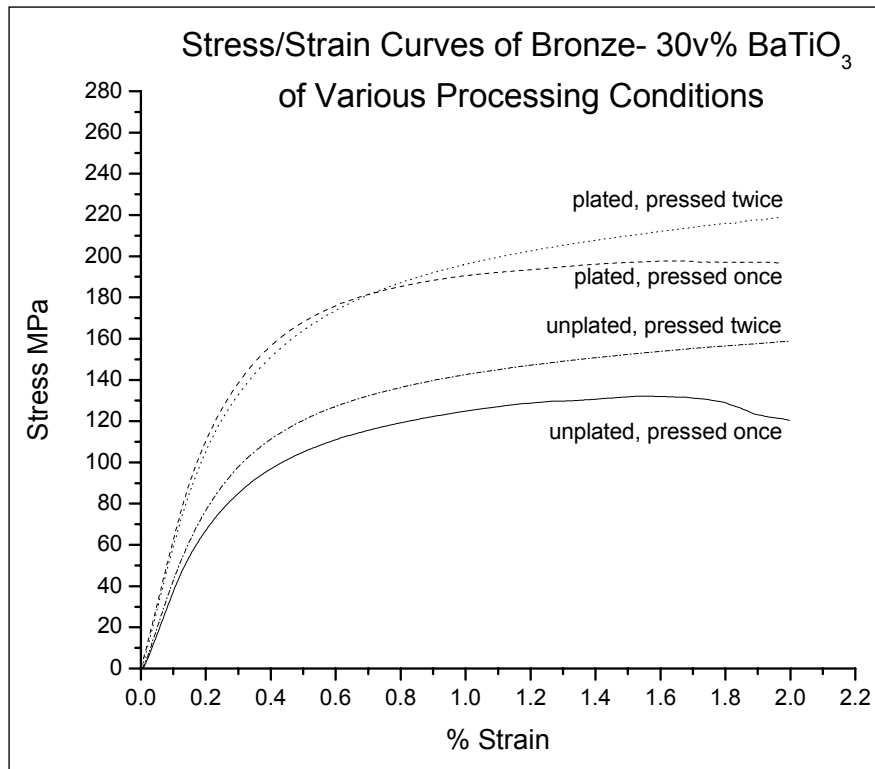
D 2. Yield Stress vs. Volume fraction plated BaTiO₃ in once pressed composites

**D 3. Yield Stress vs. Volume fraction unplated BaTiO₃ in twice pressed composites****D 4. Yield Stress vs. Volume fraction plated BaTiO₃ in twice pressed composite**

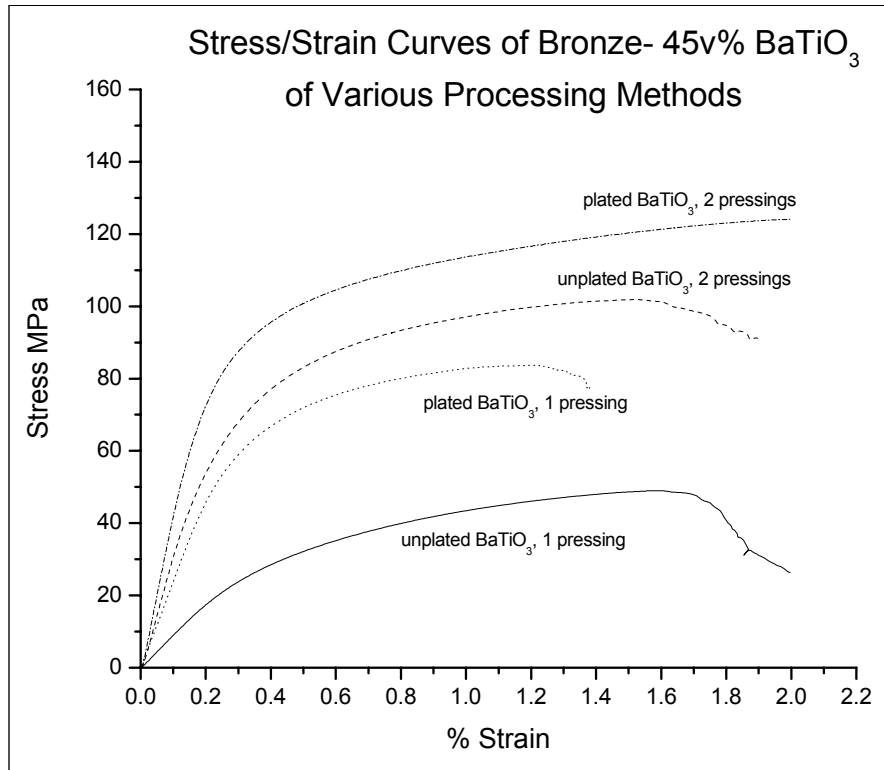
Appendix E: Stress/Strain Curves vs. Composite Processing



E 1. Stress/Strain curves of bronze- 15v% BaTiO₃ composites of various processing methods

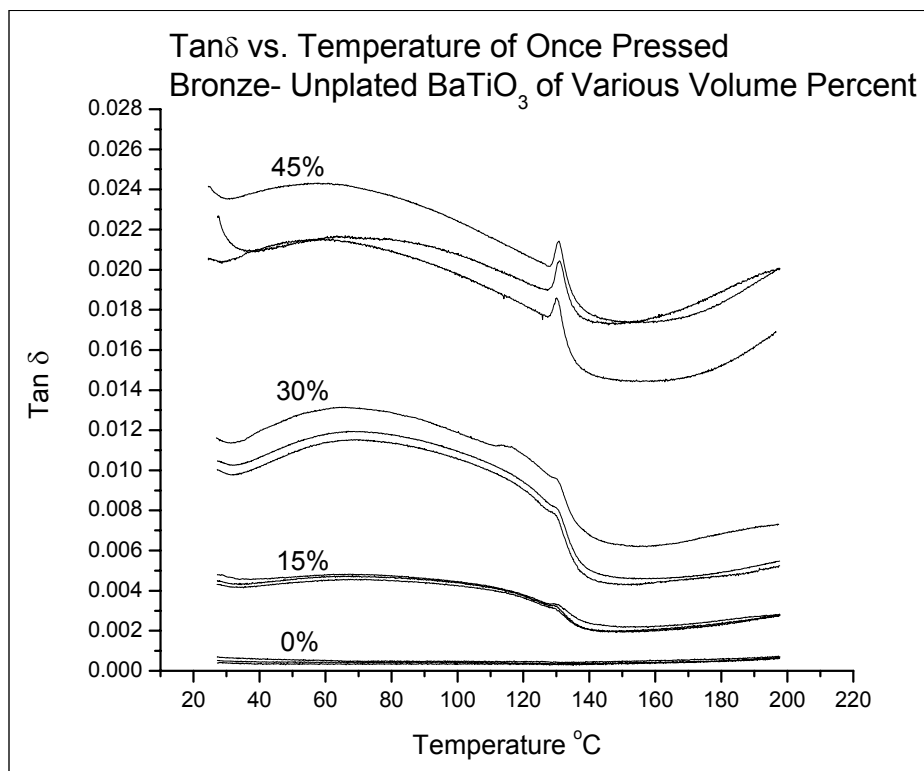


E 2. Stress/Strain curves of bronze- 30v% BaTiO₃ composites of various processing methods

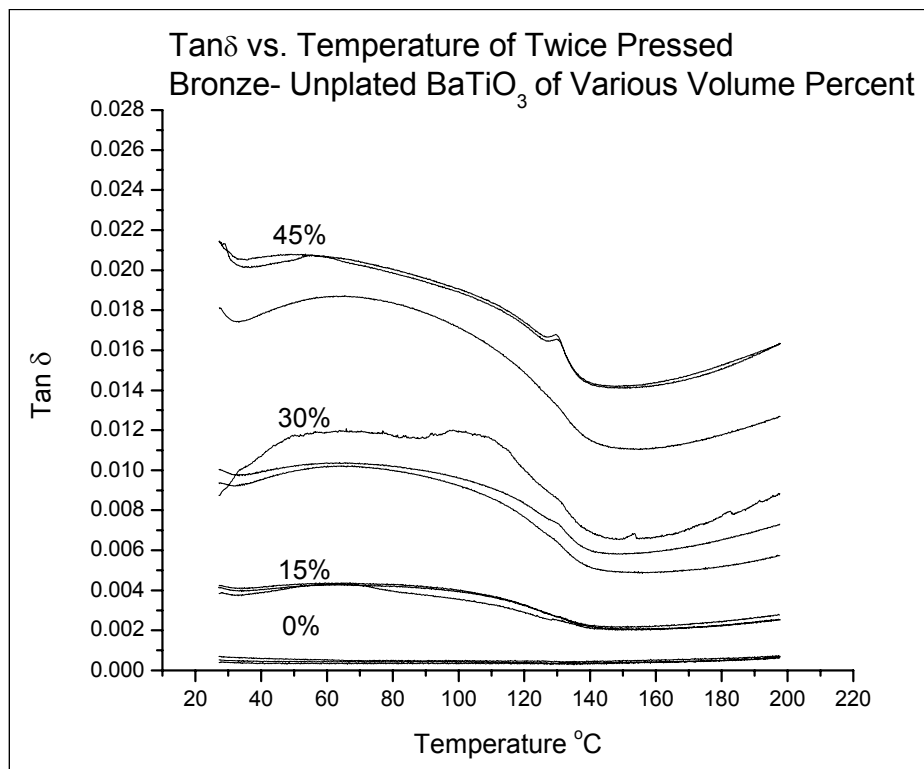


E 3. Stress/Strain curves of bronze- 45v% BaTiO₃ composites of various processing methods

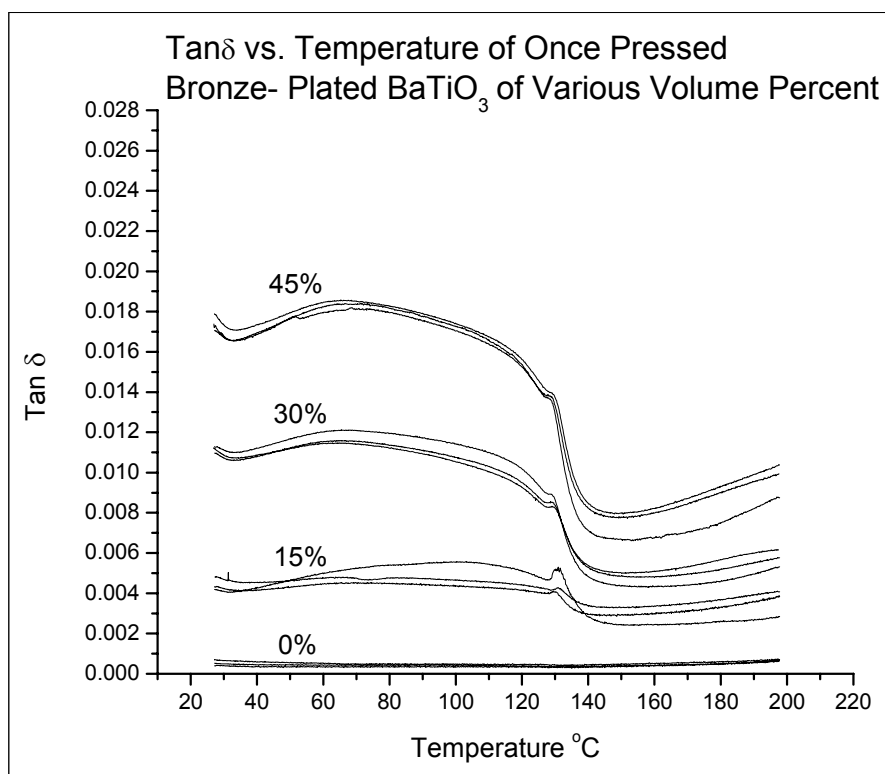
Appendix F: Tan δ vs. Temperature Curves for Various Volume Percent BaTiO₃



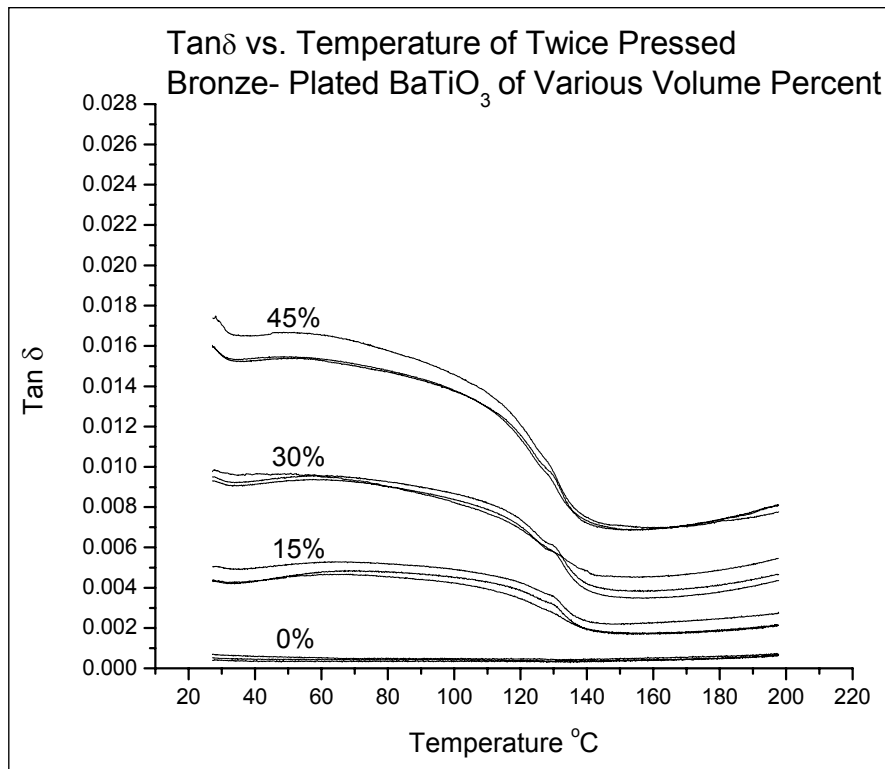
F 1. Tan δ vs. temperature of once pressed bronze- unplated BaTiO₃ composites of various v%



F 2. Tan δ vs. temperature of twice pressed bronze- unplated BaTiO₃ composites of various v%

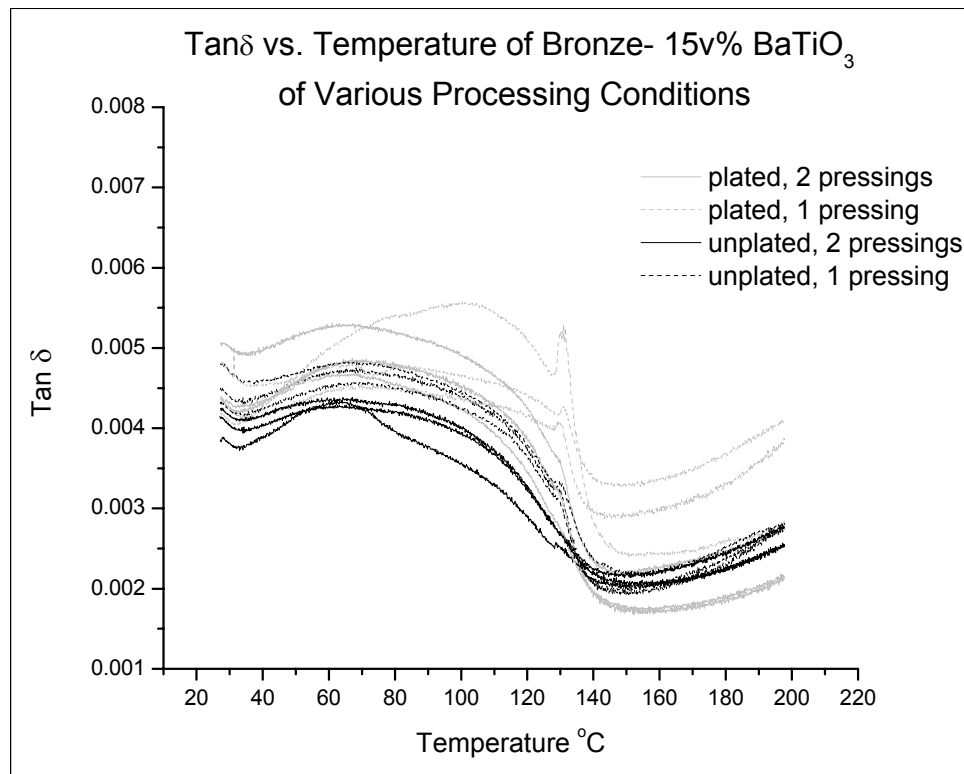


F 3. Tan δ vs. temperature of once pressed bronze- plated BaTiO₃ composites of various v%

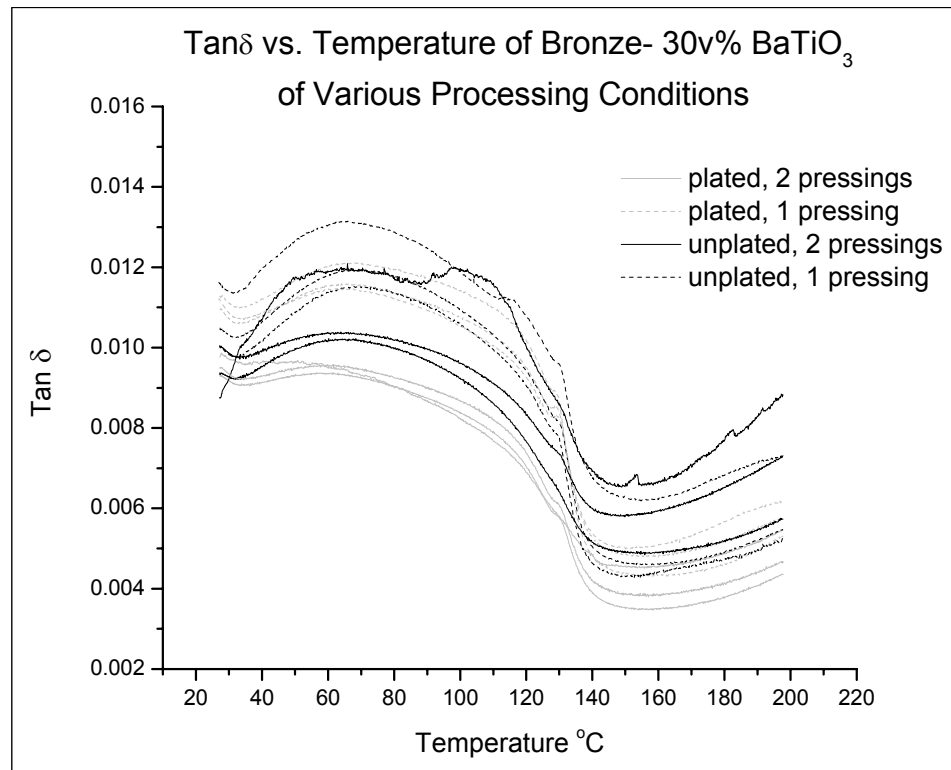


F 4. Tan δ vs. temperature of twice pressed bronze- plated BaTiO₃ composites of various v%

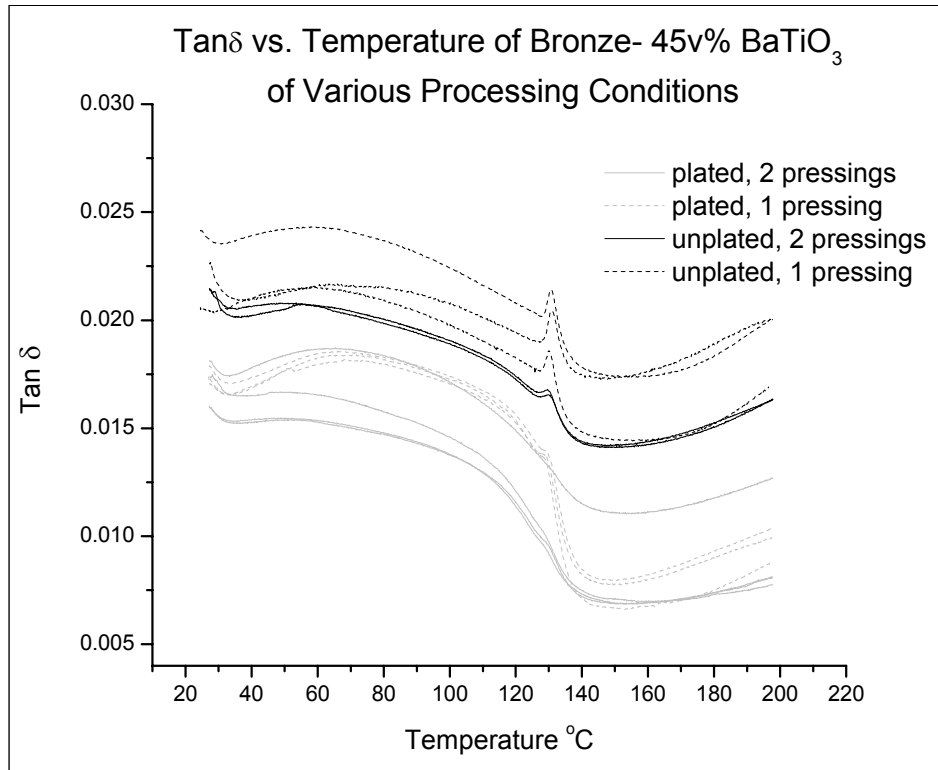
Appendix G: Tan δ vs. Temperature Curves vs. Composite Processing



G 1. Stress/Strain curves of bronze- 15v% BaTiO₃ composites of various processing methods

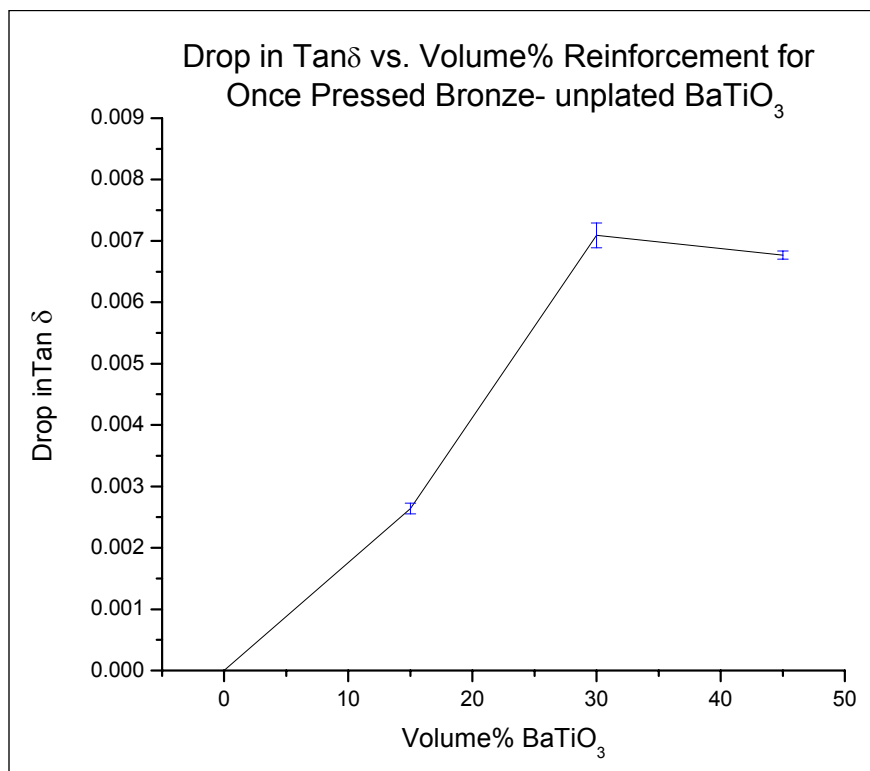
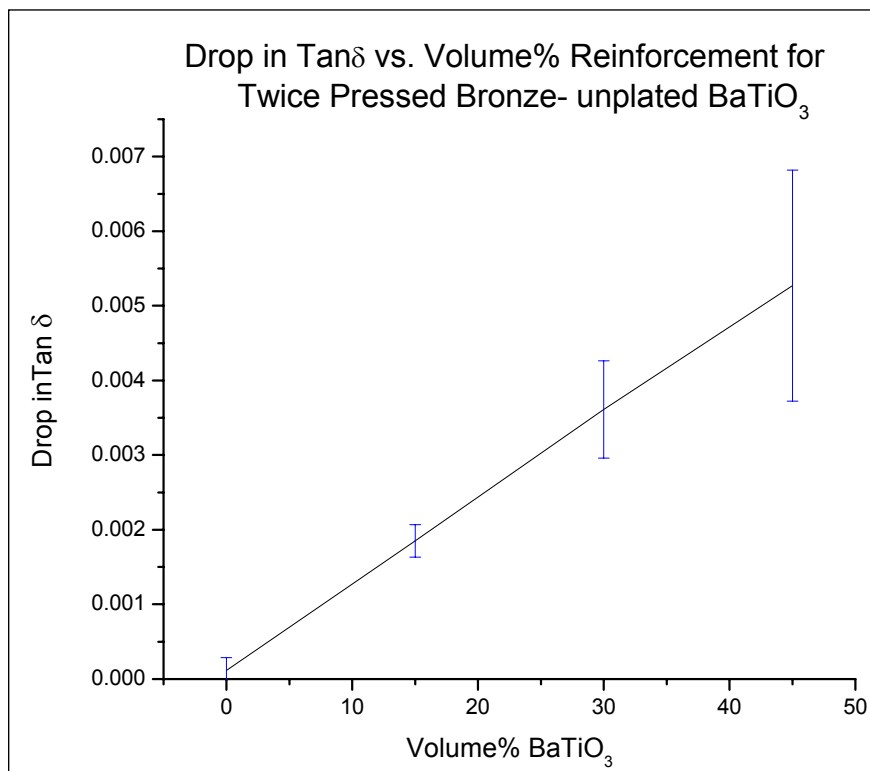


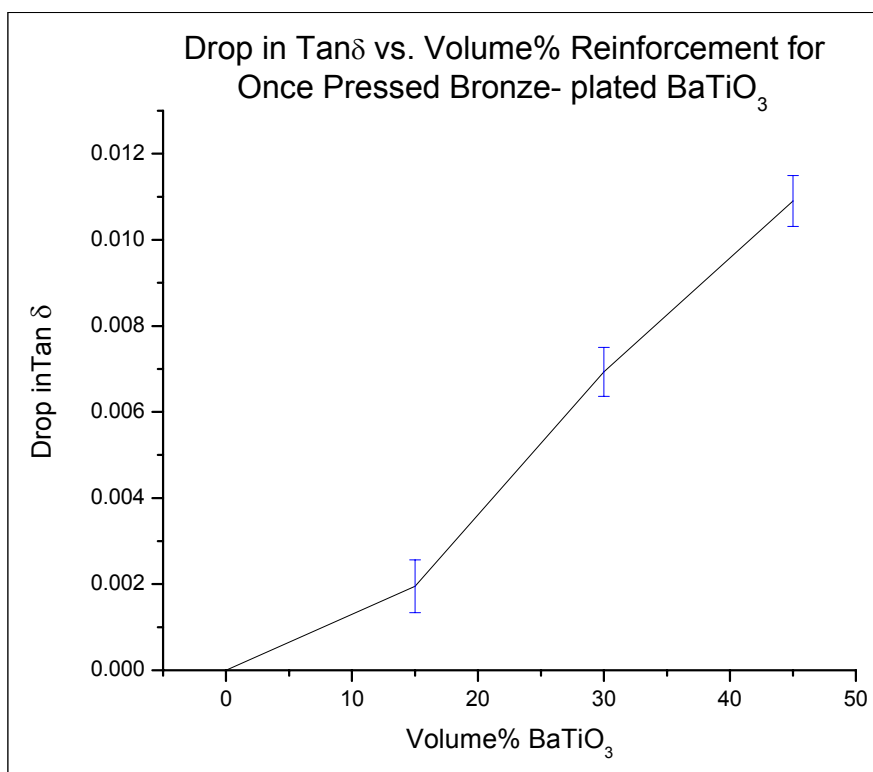
G 2. Stress/Strain curves of bronze- 30v% BaTiO₃ composites of various processing methods



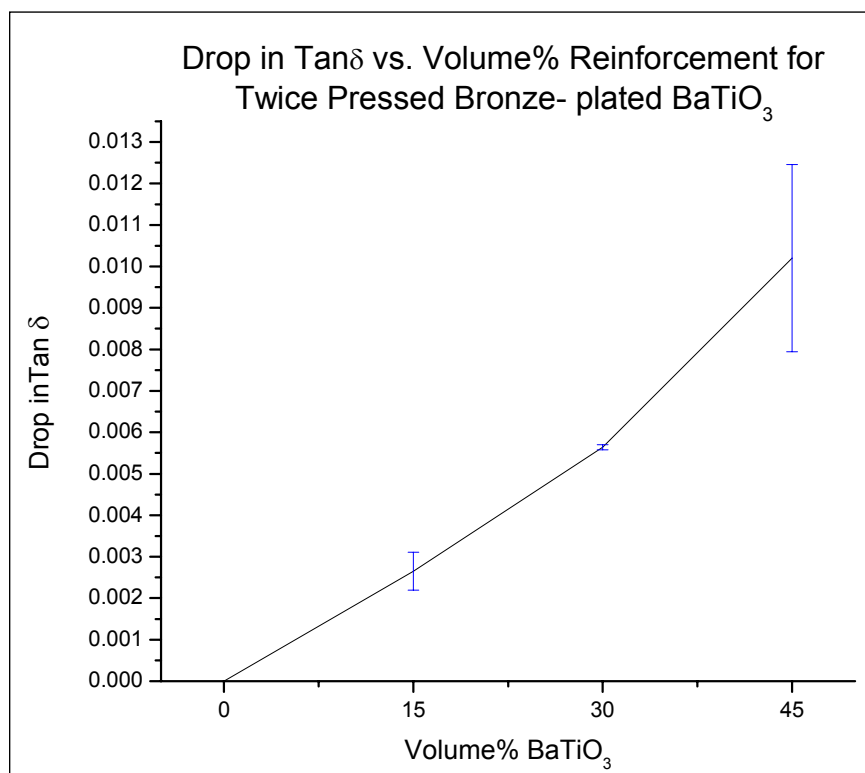
G 3. Stress/Strain curves of bronze- 45v% BaTiO₃ composites of various processing method

Appendix H: Drop in Tan δ vs. Volume Percent BaTiO₃ for Various Processing Methods

**H 1. Drop in $\tan\delta$ vs. volume percent of once pressed bronze- unplated BaTiO_3 composites****H 2. Drop in $\tan\delta$ vs. volume percent of twice pressed bronze- unplated BaTiO_3 composites**



H 3. Drop in $\tan\delta$ vs. volume percent of once pressed bronze-plated BaTiO_3 composites



H 4. Drop in $\tan\delta$ vs. volume percent of twice pressed bronze-plated BaTiO_3 composites

VITA

Ben Poquette was born and raised in and near the U.P. of Michigan, so as he got older it became obvious to attend Michigan Technological University, which was located even further north than his home. During his second year there, he took one year to study abroad in Xalapa, Mexico, where he learned Spanish. After a short bout with almost deciding to change majors, he continued in MSE, and in the Summer before his senior year, had an internship with Alcoa Aluminio in Recife, Brazil. Then in 2002 he received his bachelor's degree in MSE. Since then, he has been attending graduate school in MSE at Virginia Tech.

Ben is an avid skier, and until recently was a member of the National Ski Patrol. He also loves the outdoors and traveling, and he brews a little hard cider on the side.