



Raman spectroscopy investigations of functionally graded materials and inter-granular mechanics

Maher S. Amer *

Department of Mechanical and Materials Engineering, Wright State University, 3640 Col. Glenn HWY, Dayton, OH 45435, USA

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Abstract

The recent evolution of micro-Raman spectroscopy as micro-mechanical experimental technique had a profound effect on the field of solid mechanics. Micro-Raman spectroscopy (MRS) is the only technique capable of measuring local stress in a wide range of materials with a spatial resolution of 1 μm . With the current trend of near-field Raman, such spatial resolution is expected to increase down to few tens of nanometers. In addition, the technique is capable of interrogating chemical and structural changes in the materials, hence, for the first time, direct correlation can be identified in-situ by means of the same technique. Such capabilities have been previously utilized in the field of fibrous composites to provide accurate measurements of axial and interfacial stress distributions along individual fibers and at fiber/matrix interface. Such experimental measurements shed light on and strengthened our understanding of crucial events taking place during composite loading such as damage initiation, propagation, and resulted in more accurate models capable of predicting composite behavior and lifetime. In this paper we demonstrate the power of MRS in investigating functionally graded joints for carbon–carbon composites and its ability to provide the necessary data for the correlation of chemical changes with mechanics of the joint. In addition, our recent demonstration of the ability of the technique to measure inter-granular stress fields in polycrystalline materials will be reviewed.

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1. Introduction

Since the discovery of the Raman phenomenon in 1929, it has been mainly used by chemists to investigate molecular symmetry and physicists to investigate vibration modes in crystals. In early 1970's Anastasakis and other investigators pointed out the importance of Raman spectroscopy in investigating morphic effects in crystals (Maradudin et al., 1969). A number of studies have been devoted to measure the phonon

* Corresponding author. Tel.: +1 937 775 5095; fax: +1 937 775 5009.

E-mail address: maher.amer@wright.edu.

deformation potentials (PDP) of single crystal materials of academic and applied interest (Herman, 1970). Such PDP determination enabled stress measurements in a number of single crystal materials. In the late eighties, (Galiotis and Batchelder, 1988) reported experimental Raman measurement for a “quasi” phonon deformation potentials for a 6- μm -diameter carbon fiber under axial tensile strain. The value reported was the slope of the linear relationship between Raman peak positions for different Raman active modes in the carbon fiber and the applied axial strain and the authors referred to it as the “Raman frequency gage factor”. This enabled the measurement of local fiber strain in composites and initiated a new era of experimental composite mechanics (Amer, 2000). The technique enabled for the first time experimental investigation of crucial phenomena in composites such as the stress concentration phenomenon (Amer and Schadler, 1997; Wagner et al., 1996; van den Heuvel et al., 2000) and also allowed fundamental understanding of other phenomena such as interfacial durability (Amer et al., 1996; Amer and Schadler, 1998) and creep behavior (Larsen et al., 1999; Beyerlein et al., 2003).

2. The Raman technique

Micro-Raman spectroscopy (MRS) is the only technique capable of mapping the distribution of stresses in different materials with a spatial resolution of 1 μm . The evolution of MRS as a technique to investigate composite micro-mechanics has made a profound effect on the field (Melanitis et al., 1994; Young et al., 1995). Only one other technique provides comparable special resolution. This is a piezospectroscopic technique based on chromium luminescence in alumina and can be used to investigate the mechanics of alumina based ceramics and composites only (Ma and Clarke, 1993; Ma et al., 1995). The Raman technique, however, is superior due to its applicability to different materials even those that are not Raman active as we will discuss in coming sections.

The Raman phenomenon is an inelastic scattering of light. If monochromatic light with frequency ν_o is scattered by molecules or a crystal, much of the scattered light will have the same frequency as the incident light (elastic or Rayleigh scattering), but a small fraction will experience a change in frequency and will have a frequency $\nu_o \pm \Delta\nu$ (inelastic or Raman scattering). This change in frequency ($\Delta\nu$) is equal to the frequency of the natural vibrational modes in the scattering material (Woodward, 1967). In crystalline materials and highly oriented polymers, any change in the crystal symmetry due to an applied strain is reflected as a change in the Raman peak position of the material. The Raman peak position tends to shift linearly to lower wave-numbers under tensile strains (higher frequencies) and to higher wave-numbers under compressive strains (lower frequencies). Fig. 1 shows the dependence of one of the Raman active modes of single crystal alumina on the applied strain in the C-axis direction. Such a calibration curve enables measuring of

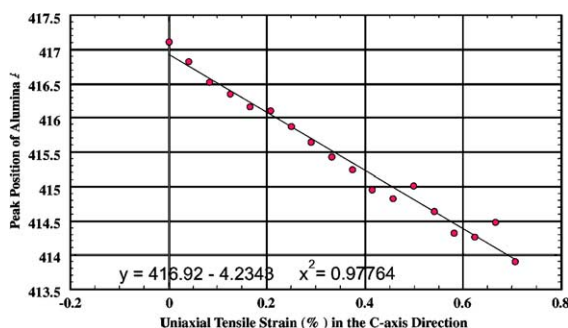


Fig. 1. Raman peak position versus axial strain in the C-axis direction for a single crystal alumina.

strain based upon peak position. It is important to note that peak position can also be calibrated versus applied stress to produce a similar curve with a different slope, of course. Comparing the equations describing the two curves yields a stress/strain relationship from which the elastic modulus of the material can be calculated. Such techniques have been used to investigate different treatment effects on elastic modulus for a number of carbon cellulose, and polymeric fibers (Eichhorn and Young, 2001; Sirichaisit et al., 2003). Because the Raman technique probes the vibrational frequencies of the material it also is a powerful tool for identification of the material chemistry and structure. Each chemical moiety has a Raman fingerprint spectrum that identifies it, and each crystal structure of the same material also can be identified based upon its Raman features associated to the symmetry of that particular structure. For example, amorphous, cubic, and hexagonal forms of silicon can be differentiated based upon their Raman spectra (Amer et al., 2002a,b). This adds a new dimension to our ability to investigate crucial solid mechanics phenomena. Using Raman mapping, maps of local stresses, chemical composition and/or crystal structure can be created and correlated together to investigate stress distribution resulting from, per say, phase transformations. Or it can be used to investigate the correlation between chemical composition and residual stresses in a functionally graded joint as we will discuss in the following section.

3. Functionally graded materials

The micro-Raman spectroscopy technique with its ability to measure local stresses and identify local materials structure was shown to play a major role in investigating mechanics of functionally graded materials (FGM) (Amer et al., 1999). It was found that some ternary carbide (titanium silicon carbide, Ti_3SiC_2) reacted with carbon under certain conditions and gradually transformed into a TiC/SiC composite. Micro-Raman spectroscopy technique proved to be a powerful tool in identifying the composition gradient of the resulting FGM. Fig. 2 shows the concentration of the ternary carbide as a function of distance away from the reaction surface between the ternary carbide and the carbon in a carbon/carbon composite. The graph shows that the ternary carbide has been totally transformed into TiC/SiC composite up to 22 μm , as indicated by the zero concentration of the ternary carbide. SiC was observed as isolated particles in a continuous TiC phase. The concentration of the ternary carbide is then shown to increase linearly over a distance of 18 μm to 100%. This indicates that over the 18 μm distance a functionally graded region has been created within which the chemical composition is changing linearly from Ti_3SiC_2 into TiC. Analysis of the ternary carbide peak position (Fig. 3) shows that tensile stresses are being built-up towards the reaction surface. It is clear that the rate of stress build up is higher within the pure ternary carbide than that within the FGM.

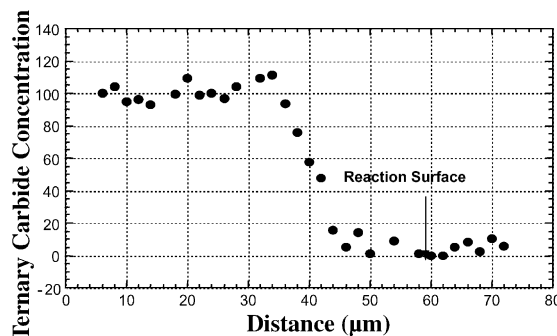


Fig. 2. Ternary carbide concentration in a FGM as measured by micro-Raman spectroscopy.

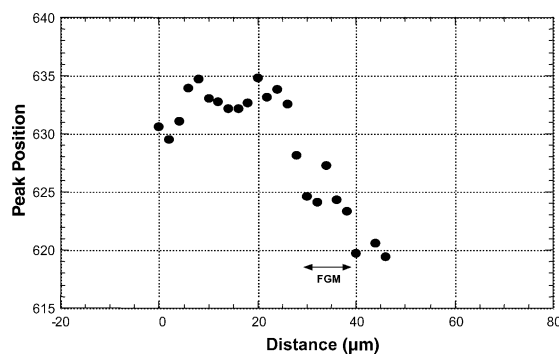


Fig. 3. Peak position (linearly proportional to stress) in the reaction area. total tensile stress created was estimated by 500 MPa.

The total tensile stress created in the joint was estimated to be 500 MPa based upon measurements conducted on the carbon side of the joint.

This shows the power of MRS in investigating functionally graded systems and in correlating composition gradient to induced stresses. It is important to note that the high spatial resolution of the MRS technique is a key issue in acquiring such valuable experimental data. The ability to measure stress gradient within a 18-μm layer in the FGM is crucial to understanding the mechanics of such important class of structural materials.

4. Mesoscopic stress fields in polycrystalline materials

The unique capability of MRS technique to map local stress with 1-μm spatial resolution also enabled mapping local stress distribution in polycrystalline and granular materials under stresses. Inter-granular stresses could be mapped for some Raman active materials such as polycrystalline diamond films (Lucazeau, 2003). Local stress distributions in Raman active materials such as silicon were also mapped under local indentation, and correlations between local stresses and local phase transformations were observed (Orlovskaya and Gogotsi, 2002; Galanov et al., 2003). Local stresses and associated phase transformations in silicon due to laser machining were also investigated (Amer et al., 2002a,b). All such studies provided unique and important information regarding fracture mechanics of very important structural class of matter, that is, polycrystalline materials. The technique, however, was limited to Raman active materials. This puts metals beyond our ability to investigate using such powerful technique. In year 2000, however, Amer and Maguire (2000) developed a new technique to enable mapping of inter-granular stress fields in non-Raman active materials by using Raman active nano-strain gages. The power of the new technique lies in its applicability to non-Raman active materials. A new era of experimental solid mechanics can be started. Such measurements are clearly essential in that they provide the experimental results against which the necessity or reasonableness of the mathematical approximations can be tested. As a practical matter, the results of such measurements could also be used to design polycrystalline and granular media to minimize unfavorable local stress concentrations or to assess the design and engineering performance of the next generation of micro-electrical and mechanical systems (MEMS) (Starman et al., 2003). The technique was used to measure inter-granular stresses in polycrystalline system and monitor the evolution of such stresses upon sample loading until failure. Fig. 4 shows the stresses measured and their correlation to grain size and shape at a global applied tensile stress of 80 MPa. The evolution of mesoscopic stresses and their correlation to the grain structure of the system was also investigated and addressed (Amer and Maguire, 2000).

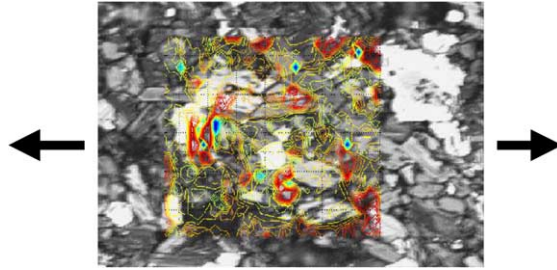


Fig. 4. Optical micrograph showing grain structure in a polycrystalline sample with an overlaid Raman measured mesoscopic stresses field contours. Red indicates high tensile stresses while blue indicates high compressive stresses.

5. Grain orientation and inter-granular stresses in thin films

The effect of local grain orientation and mismatch of grain orientation on the mechanical behavior of polycrystalline materials is widely known. Local non-homogeneities in stiffness due to non-uniform orientation of the grains (of course for non-isotropic materials) lead to local stress concentrations at grain boundaries upon loading. Such phenomena are crucial in thin films. It has been shown that such phenomena in some high temperature superconducting ceramic thin films cause high enough stresses to induce local phase transformations at the grain boundaries that destroy the functionality of the film (Ovid'ko, 2001). The ability to map local grain orientation as well as local stress in polycrystalline thin films adds a powerful experimental means for deeper fundamental understanding of the mechanics and failure of such important classes of matter. Our group (Amer et al., 2001, 2002a,b) has shown that micro-Raman spectroscopy can be used to map the in-plane local grain orientation and measure the grain boundary mismatch angle in thin ceramic films. Local strains were also mapped and correlated to grain boundary mismatches. Fig. 5a shows a $30 \times 30 \mu\text{m}$ Raman map of local grain orientation in a 250 nm thick ceramic film deposited on single crystal substrate. The film shows a single-crystal-like nature with a clear twin band across it. Fig. 5b shows the Raman measured strain map of the same area. It is clear that strain is very uniform in the film with small fluctuations around the twin band. Fig. 6a, on the other hand, shows a $20 \times 20 \mu\text{m}$ Raman map of the local grain orientation in a similar film with high grain boundary angle mismatch. It is clear that regions with high grain boundary angles (upper left and right corners in the figure) are correlated with higher stresses in the film. Such ability to measure both local grain orientation and inter-granular mesoscopic stresses

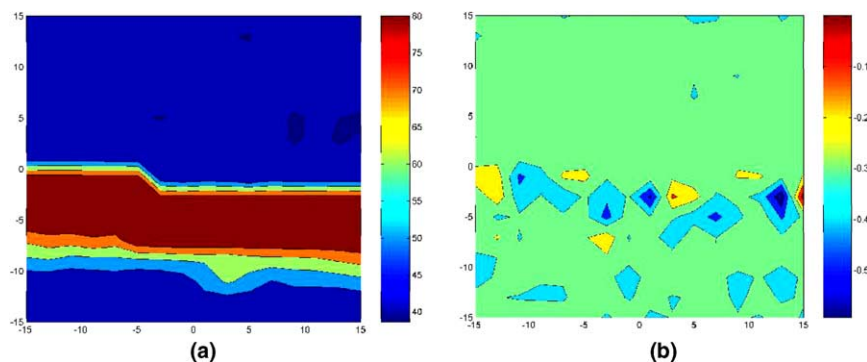


Fig. 5. (a) Raman measured Grain orientation map of a $30 \times 30 \mu\text{m}$ area in a thin ceramic film deposited over a single crystal substrate. (b) Corresponding Raman measured strain mapped over the same area.

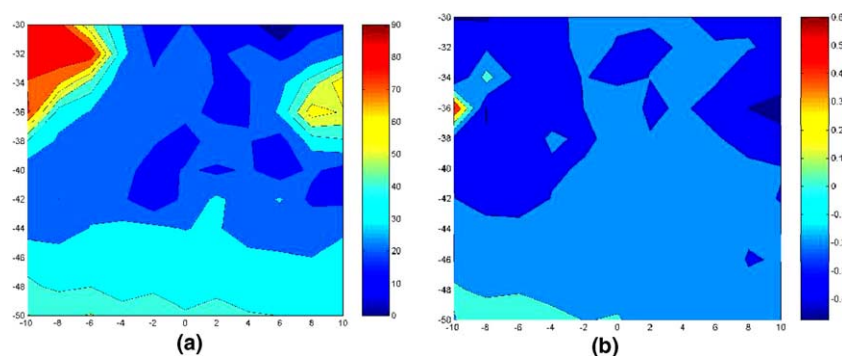


Fig. 6. (a) Raman measured grain orientation map of a $20 \times 20 \mu\text{m}$ area in a thin ceramic film deposited over a bi-textured Ni substrate. (b) Corresponding Raman measured strain mapped over the same area.

and to correlate them to each other by means of a simple spectroscopic technique such as Raman spectroscopy is a key development in experimental mechanics and will definitely lead to better understanding of the mechanical behavior of thin films.

6. Conclusions

It can be concluded that micro-Raman spectroscopy is a very useful micro-mechanical measuring technique. The technique not only proved to be very powerful in investigating composites micro-mechanics in the past decade but also showed recently its tremendous potential as an experimental mechanics technique to investigate functionally graded materials, MEMS, granular bulk materials, and thin films. The ability of the technique to measure local stress, chemical composition, crystal structure and orientation with excellent spatial resolution in the range of $1 \mu\text{m}$ and without sample special preparation requirements represents an opportunity for experimental mechanics investigators that, in spite of current excellent investigations, has been virtually overlooked. In addition, development trends in the Raman technique are heading towards increasing the spatial resolution into the nanometer scale. Several successful studies have been reported (Fokas and Deckert, 2002; Prikulis et al., 2003) and the potential of the technique to contribute to fundamental nano-mechanics studies is very promising.

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