XRD STRAIN AND STRESS DETERMINATION IN NANOSTRUCTURED FILMS AND COATINGS

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1. Abstract

The residual stress determination of nanostructured films and coatings is reviewed. A method of measuring the depth dependence of the stress profile using energy dispersive x-ray diffraction with a high-energy "white" beam synchrotron radiation source is presented. The profiling is accomplished with the aid of a highly collimated incident and scattered x-ray beams and with micro positioning of the sample-interface. The depth of the profiling is on the order of mm and the resolution of the profiling is on the order of a few microns. The technique allows the three dimensional profiling of the stress distribution in these materials.

2. Introduction

X-ray diffraction has of course been the central technique for nearly a century for determining interatomic distances in solids. Applications of this technique to profiling residual strains, as a function of depth from a surface, have also been developed on a more limited basis. Such conventional residual surface strains analysis has utilized the "sin 2Ψ" diffraction method [1], where the varying penetrating power of the x-rays with varying incident angle is exploited. This technique is limited both by the rather broad convolution of scattering depths via the exponential penetration function, and by the limitation of the penetration length to a few microns.

At the nanoscale level Tsakalakos has worked extensively on stress distribution around interfaces of similar or dissimilar multilayered materials using advanced x-ray methods [2,3]. Earlier work [4] on fatigue, corrosion-fatigue and stress-corrosion-cracking demonstrated the ability to measure excess dislocation densities near the surface by x-ray rocking curve analysis. This method, however, failed to quantify the residual stress as a function of distance because it relied on successive removal of surface layers, which resulted in redistribution of the stresses in the remaining material.

In this paper we review some aspects of the energy dispersive diffraction technique as a nondestructive method from which the three dimensional state of stress

G.M. Chow et al. (eds.), Nanostructured Films and Coatings, 223–230.

can be deduced. We also report some new results on WC/Co nanostructured coatings prepared by plasma spraying coating methods.

The expansion of the availability of high-energy synchrotron "white beam" sources (20-100 keV) has led to the expansion of the use of energy dispersive x-ray diffraction. This technique (see Fig. 1. for a schematic) has several unique advantages: these x-rays penetrate deeply; the data collection geometry is extremely stable with stationary incident/diffracted-beam paths; this stability and the high intensity of the synchrotron beam allow extremely high incident/diffracted beam collimation thereby defining very small highly position-specific diffraction volumes; the data collection is very efficient/rapid allowing good signal-to-noise diffraction spectra to be taken quickly on small volumes; and finally, recent advances in precise sample micro positioning allow precision scanning of the diffraction volume laterally and as a function of depth through the sample.

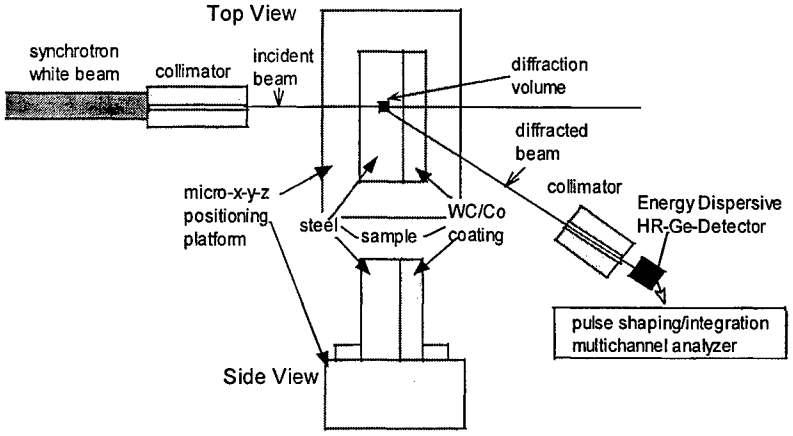

Fig. 1. A schematic of the experimental geometry for energy dispersive x-ray diffraction for WC/Co coatings on steel.

This energy dispersive x-ray diffraction (EDXRD) technique has been widely used for many years for high-pressure diffraction measurements on the small diffraction volumes inside diamond anvil high-pressure cells. The use of this technique for profiling strains in engineering materials has more recently evolved [1,5]. In this section of paper we will note some aspects of applying the energy dispersive diffraction technique to probing the three-dimensional homogeneity and state of stress in WC/Co wear resistant coatings on steel.

It is of great technological importance to be able to predict the failure of materials subjected to static stressing in aggressive environments or dynamic or repeated loading in mechanical and structural applications. This ability is often hindered when inhomogeneous distributions of residual, interfacial or other type of elastic

stresses due to the processing or manufacturing conditions, are present. Thus, for deformation processes which are known to be highly sensitive to preexisting large elastic stresses, the evaluation of these inhomogeneous stresses with respect to depth from the surface or interface is equally essential to the comprehensive characterization of deformation induced damages. Because the EDXRD method is nondestructive, it represents an ideal tool with which to elucidate structural changes, and the degradation in mechanical performance such as fatigue failure and fracture.

3. Energy dispersive technique

Energy dispersive x-ray diffraction involves considering the traditional Bragg equation (1) at a constant scattering angle, 2θ, (usually a few degrees) as a function of the x-ray energy.

$$E_{hkl} = \frac{hc}{\lambda} = \frac{hc}{2 \sin \theta} \frac{1}{d_{hkl}} \qquad (1)$$

Here the interatomic plane spacings, d_{hkl}, are uniquely related to the energies at which the corresponding Bragg reflections occur, E_{hkl}. Since the scattered x-ray energies are typically measured by Ge-detector (see Figure 1) calibrated in units of keV, a more useful version of this equation is

$$E_{hkl} \text{ [in KeV]} = \frac{6.22}{d_{hkl} \sin \theta}. \qquad (1a)$$

With this technique [1] the strain (ε), related to the shifts in the plane spacings (Δd_{hkl}), is determined by the energy-Bragg-line shifts (ΔE_{hkl}).

$$\varepsilon = -\left(\frac{\Delta d}{d}\right)_{hkl} = -\left(\frac{\Delta E}{E}\right)_{hkl} \qquad (2)$$

The strain-resolution that this technique has can be estimated from the differential of equation (2).

$$\left|\left(\frac{\delta d}{d}\right)_{hkl}\right| = \left|\left(\frac{\delta E}{E}\right)_{hkl}\right| + |ctn\ \theta|\ \Delta\theta \qquad (3)$$

For a typical scattering geometry (2) $\Delta\theta$ can be about 2 mrad with θ in the 2° to 8° range, however, substantial improvements on these figures have been and are being made. The δE is the limit of our ability to determine the shift in the centrum of the Bragg-energy peak. Although energy resolution of the cryogenically cooled Ge-detector is only on the order of 0.2 KeV at 60 KeV (or better) the detectable shift in the peak centrum position of such peaks (fitted to Gaussian line shapes) can be far higher. Indeed with such methods Kuntz et. al. [1] has emphasized that the strain requiring sensitivities of 10^{-4} can be obtained. Kuntz et. al. [1] profiled and separated stress and strain variations in the radial and "hoop strain" directions for cylindrical composite materials.

Here we report some preliminary EDXRD measurements on small diffraction volumes in a WC/Co coating on a high-strength-steel base micro-positioned to separately probe the base and coating. These measurements were carried out on Beam Line X17C at the National Synchrotron Light Source at Brookhaven Lab with the indispensable aid of Dr. J. Z. Hu. The enhanced high energy white beam on this line is supplied by a superconducting wiggler insertion device. A schematic of the typical geometry for these preliminary measurements is shown in Fig. 1.

The standard columniation slits on this beam line allow aperturing of the incident beam down to 10 microns. The diffracted beam columniation depends on the variable detector distance from the fixed scattering volume. The existing micro-positioning stage on the line was also utilized. The sample used consisted of a 100 micron WC/Co coating plasma sprayed onto a 2-mm thick steel base.

In Fig. 2, the diffraction pattern for a small volume in the steel is shown along with its bcc indexing. This pattern was collected over just a couple of minutes in the geometry shown in the schematic Fig. 1. This spectrum emphasizes the utility of this hard radiation for collection of high quality diffraction data on small volumes even when buried beneath a high-Z coating.

In Fig. 3, EDXRD pattern for the WC/Co coating is displayed along with the WC indexing. The weal W_2C impurity lines labeled are typical for such materials. The W-K and W-L fluorescence lines are also noted.

Figures 4 and 5 demonstrate the applicability of the method in terms of strain resolution, which is about 10^{-4} and the penetration depth, which reaches 3 mm depth with a diffracting volume size of about 5 μm [1]. The measurements were performed on controlled samples of Al_2O_3 cylindrical fibers embedded in CP Titanium matrix composite. The solid lines represent the theoretically obtained stress distributions from the interface showing the excellent agreement between theory and experiment.

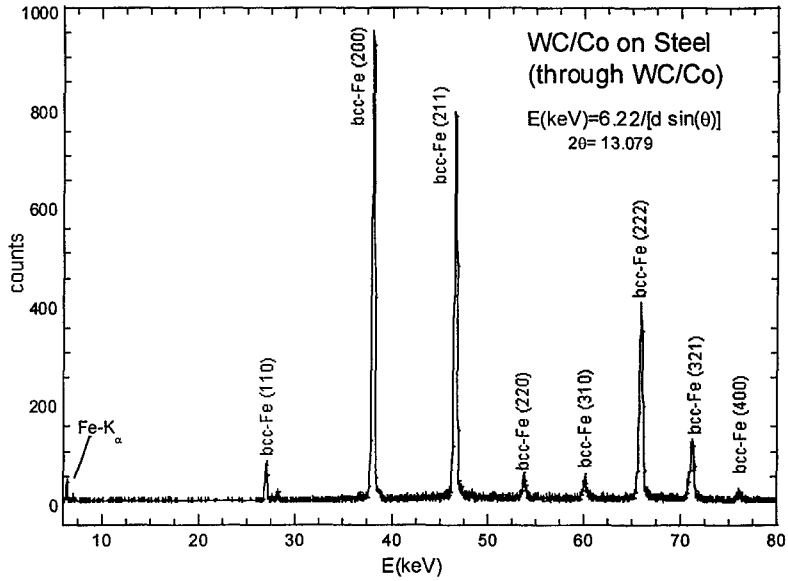

Fig. 2. The EDXRD from the steel layer of a WC/Co on steel sample. Note that this pattern was taken in the geometry where the entered the steel surface normally and the diffracted beam exited the coating surface at an angle 2θ to the normal (as in the schematic).

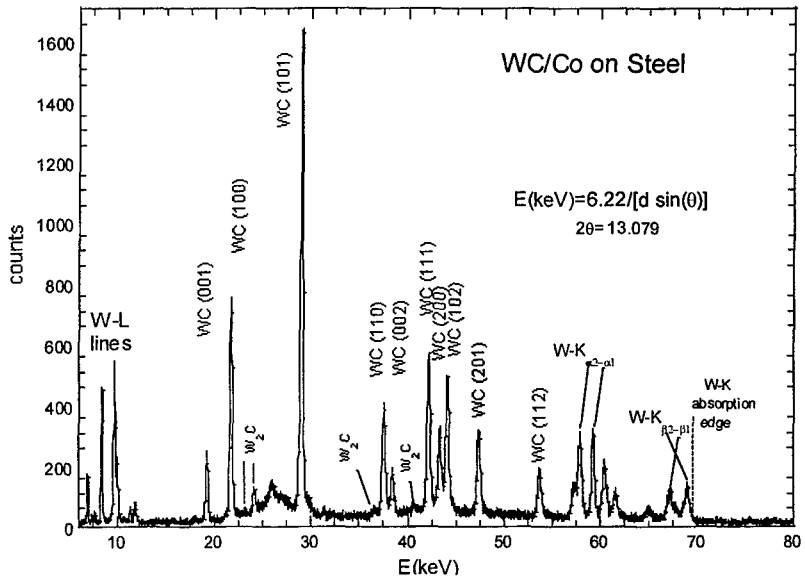

Fig. 3. The EDXRD from the WC/Co layer of a WC/Co on steel sample. Note that this pattern was taken in a reflection the geometry to obtain a high quality near surface pattern for the coating.

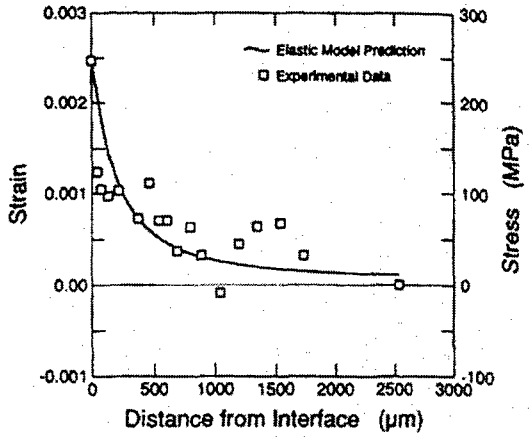

Fig. 4 - Hoop residual strain profile for the CP titanium/Al_2O_3 (HIPO) sample

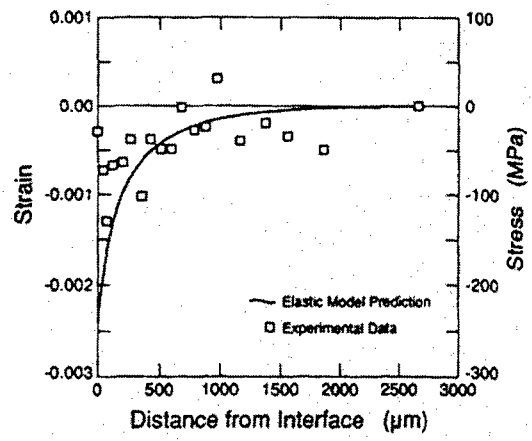

Fig. 5 - Radial residual strain profile for the CP titanium/Al_2O_3 (HIPO) sample

4. Discussion and Conclusions

In this paper we have reviewed a new technique for measuring residual stresses in nanostructured films and coatings using energy dispersive x-ray diffraction. The scattering volume was scanned through this interface of substrate/coating via micro positioning of the sample. The samples were placed into a geometry that allowed x-ray access in various orientations. Lateral profiling of the strains, approaching the edges, were also possible to be performed to probe for strain relief effects at such surfaces.

These experiments were carried out on beam lines at the National Synchrotron Light Source at Brookhaven Lab.

A key factor for the accurate measurement of the residual and interfacial stress distribution is the ability to penetrate the coating and the substrate sufficiently to allow for long range stress relaxation from the surface and interface of the nanostructured coatings.

The energy dependence of the absorption length (1/e decay length) for x-rays in WC/Co is shown in Fig.6. Note that the density of commercial WC/Co of 15 g/cm^3 was used. The effective penetration lengths in the 30 -150 keV range are sufficiently large to allow the proposed diffraction profiling. Indeed, as shown in Fig. 6, the penetration depth for WC/Co is in the range of a few mm for the working energy conditions.

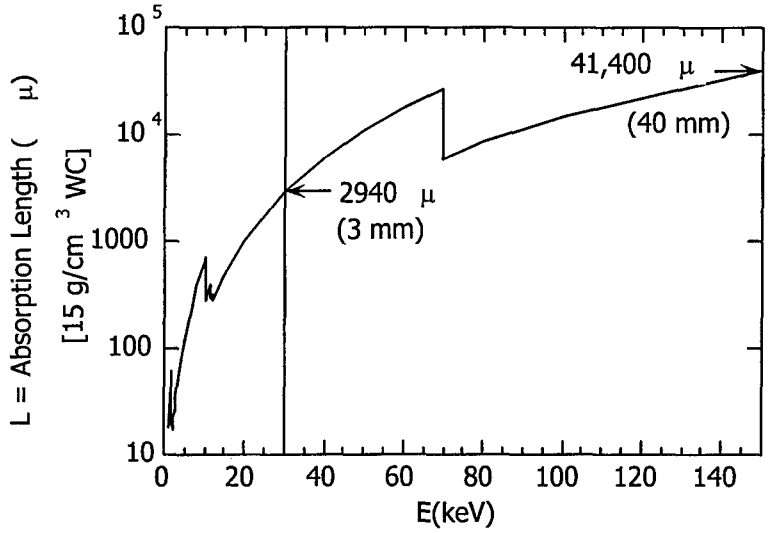

Fig. 6. The energy dependence of the absorption length (1/e decay length) for x-rays in WC/Co.

The detected volume is determined by the intersection of the collimated beam and the diffracted beam. Incident beam columniations of down to 5 μm have been reported as possible both at NSLS [6] and CHESS [7]. Additional incident and diffracted beam aperturing will be used.

The diffraction experiments proposed utilize a constant incident and diffracted beam positions. Thus positioning of the diffraction volume is determined by the translational positioning of the sample. Sample micro positioning is typically available on beamlines (e.g. 2.5 μm step size reported for X23A3 Beamline at NSLS). For additional required accuracy Newport Corporation produces a wide range precision positioners (e.g. 0.1μm repeatable positioning with 400 mm travel).

In summary, for nanostructured films and coatings with thickness in the range of 100 μm we can measure the stress distributions with spatial resolution down to 1 μm due to new developments in beam aperturing and micro-position devices. We can measure strains down to 10^{-4} with accuracy of about 2 to 5 % (as determined by the peak position described above). Our original control experiments of WC/Co coatings demonstrated the feasibility of the method and revealed some of the expected working conditions for the stress determination. For films of larger thickness, a better resolution can be obtained by increasing the diffracted volume.

In the future, it is hoped that this approach to the problem of the residual stress distribution can eventually transcend the laboratory research stage and be used directly as a diagnostic tool for technological applications. For example, an in-situ fatigue stage development in conjunction with the EDXRD technique could provide invaluable information on the determination of prefracture damage, crack initiation and the remaining lifetime of the materials.

Acknowledgments

The Authors gratefully acknowledge the support of the Office of Naval Research under contract ONR N000149910424- 99PRO4801-00. These measurements were carried out on Beam Line X17C at the National Synchrotron Light Source at Brookhaven Lab with the indispensable aid of Dr. J. Z. Hu.

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6. see Microbeam Diffraction at NSLS (July 97 NSLS Newsletter).
7. see CHESS B1 Beamline Facilities Description.