A DIFFRACTOMETER FOR X-RAY STUDIES OF TBC BOND COATS BENEATH ZIRCONIA TOP COATS

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ABSTRACT

Commercially important thermal barrier coatings (TBCs) contain a protective vapor-deposited yttria-stabilized zirconia ceramic layer, over a nickel-aluminum bond coat and a nickel-based superalloy. The thinner high performance coatings typically fail due to mismatch strain at the ceramic/metal interface. We have constructed a laboratory diffractometer with which we have measured diffraction lines of bond coats lying underneath a 125-µm thick thermal barrier coating, without using a rotating anode x-ray source. The diffractometer utilizes a niobium (Nb) target x-ray tube in Seeman-Bohlin geometry with fixed sample position, where a very large Johannson bent crystal is used for gathering and focusing x-rays to the sample.

1. INTRODUCTION

Thermal barrier coatings (TBC) have been used to protect structural turbine components employed in hot section areas, for the last two decades. Typically, TBCs consist of three layers: a ceramic topcoat, a bond coat and a nickel-based superalloy. The thermally protective, top coat layer is nominally 125 or 200 micron thick 7-8 wt.% Y2O3 stabilized ZrO2 (YSZ), deposited via electron beam vapor deposition (EB-PVD) or plasma spray, respectively. Bond coats improve adhesion between the ceramic and the superalloy and typically oxidize in service. Although bond coat compositions vary, they mainly consist of nickel, other first row transition metals (TMs), aluminum, and in some instances platinum or traces of yttrium. Given the interest to employ TBC's at ever increasing service temperatures, development of experimental tests which aid in understanding and predicting failure is needed [1,2].

The ability to characterize TBC's intact is often desired or required. To date, laser fluorescence methods have been a method of choice for characterization of TBC assemblies due to the high spatial resolution and rapid data collection, particularly for stress measurements on cross sections. However, this method can only probe the thermally grown oxide [3]. While slower, x-ray diffraction (XRD) is not so limited and can provide a wealth of crystallographic information including phase identification, lattice constants, stress, and texture before and after service. Recently, Gell et al [2,4] suggested that alloy phase formation at the YSZ-bond coat interface during thermal exposure could effect the coating performance [4]. Therefore, development of an XRD method for probing stresses and structures at the bond coat with the TBC intact is of interest.

Obtaining meaningful x-ray diffraction patterns from the bond coat underlying these thick layers is a formidable challenge. One approach to this experimental problem would be to use

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synchrotron based apparatus of some sort. Such an approach precludes development of a general testing method, and we therefore discuss the development of a laboratory diffractometer made especially for diffraction experiments on bond coats within typical TBCs.

2. EXPERIMENTAL PROCEDURE

2.1. Choice of Incident Radiation

The large absorptive power of the thick YSZ top coats preclude using the standard x-ray tube anodes, other than Mo, for bond coat diffraction studies. In addition to the absorption problem, the TBCs add to the difficulty of bond coat diffraction studies because of interference from YSZ diffraction peaks. The EB-PVD TBC microstructure presents somewhat less of an experimental obstacle than plasma sprayed composites, not only because of the thinner TBC layer (~125 µm versus ~200 µm) but because of the pronounced preferred orientation of the EB-PVD TBC columns [2]. This preferred orientation results in less interference between TBC diffraction peaks and underlying weak bond coat peaks. One does not have this advantage with the plasma sprayed TBC overlayers. We find that there is a region between the EB-PVD TBC diffraction peaks, corresponding to bond coat peaks of usable intensity, in the region of reciprocal space corresponding to twice Bragg angle in the 50° to 60° range, using a Mo or Nb x-ray anode sources. We therefore now highlight this range of Bragg angle and incident x-ray energy.

Although a Mo anode is the most advantageous of the standard x-ray tube anodes, there is an advantage in using a Nb anode instead. The Nb Kα energy is just less than the K shell binding energy of the Y dopant, whereas the Mo Kα energy is maximally efficient at exciting Y K shell electrons. Although Y is only 7 to 8% of the TBC composition, the reduced absorption of Nb relative to Mo radiation becomes quite significant for the large TBC thickness. In addition, for reasons discussed below, we prefer not to use a graphite monochromator as part of the detector assembly but use instead a large Johannson bent crystal to condition the beam impinging on our samples. We then obtain the expected large Y fluorescence signal if Mo Kα radiation is used, but not if Nb Kα radiation is used. Fortuitously, any fluorescence excited from the TM elements in the bond coat is completely absorbed in the TBC. Therefore, we have obtained a specially manufactured Nb anode sealed diffraction tube that is compatible with a standard tube tower, for less expense than a peltier cooled energy dispersive detector. We operate this Nb tube at approximately 55% of the power rating of a corresponding Mo diffraction tube. Thus, the intensity of the diffuse scattering from the TBC, which interferes with the weak bond coat peaks, is diminished along with the bond coat peak intensity by about 55%. Because of the enhanced bond coat diffraction relative to the TBC diffuse scatter intensity, the Nb anode is advantageous over a tube with a Mo anode.

For the standard Bragg-Brentano diffraction condition, in which the incident and exit angle are equal, one has the shortest total path through the TBC to the bond coat and back to the detector. In Table 1 below are tabulated the calculated attenuation factors through the TBC corresponding to incident x-rays, for various incident angles (chi), thickness of TBC, and x-ray anode materials. For simplicity we assume equal angles for both incident and diffracted beams. The 20 µm TBC at a chi angle of 2° would correspond to a glancing angle study of bond coat diffraction under a partially polished off but structurally intact TBC layer. One concludes that such studies are impossible using Cu radiation, and that Nb is preferable to Mo.
Table 1: Attenuation factor for different x-ray sources.

<table>
<thead>
<tr>
<th>TBC Thickness (µm)</th>
<th>Chi Angle</th>
<th>X-ray Anode Type</th>
<th>Attenuation Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>30°</td>
<td>Cu</td>
<td>$3.52 \times 10^9$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mo</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nb</td>
<td>19</td>
</tr>
<tr>
<td>100</td>
<td>15°</td>
<td>Cu</td>
<td>$3.90 \times 10^9$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mo</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nb</td>
<td>49</td>
</tr>
<tr>
<td>200</td>
<td>30°</td>
<td>Cu</td>
<td>$1.24 \times 10^9$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mo</td>
<td>967</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nb</td>
<td>370</td>
</tr>
<tr>
<td>20</td>
<td>2°</td>
<td>Cu</td>
<td>$1.70 \times 10^{14}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mo</td>
<td>167</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nb</td>
<td>82</td>
</tr>
</tbody>
</table>

2.2 Seeman-Bohlin Geometry: Advantages for the Present Application

Although the usual Bragg-Brentano (BB) configuration has many advantages of convenience and relative ease of alignment, for measurements restricted to the back reflection region, there are advantages to the Seeman-Bohlin (SB) arrangement. An excellent review of the relative merits of these two diffractometer configurations is given by King et al [1]. The schematic of the SB geometry is shown in Figure 1. We point out that the optics developed by Schuster and Gobel [6], whereby a parabolic multilayer yields a parallel x-ray beam from a line source, is not presently commercially available for short wavelengths such as is obtained from a Mo or Nb anode. Were a parabolic focusing mirror available for Mo radiation, one would not need to depend on the parafocusing condition. However, in the absence of such a device, one can make use of the fact that in the Seemann-Bohlin arrangement parafocusing can be satisfied for incident and exit angles, measured relative to the sample surface, that are unequal. This feature enables stress measurements to be performed without sacrificing either intensity or resolution. In addition, King et al [5] have pointed out that the source aperture of the SB diffractometer is significantly smaller than that of the BB diffractometer in the back reflection region, so that for the same intensity the SB diffractometer is capable of greater angular resolution [5]. We are unable to utilize here another potential advantage of the SB geometry, which is that one can replace parafocusing with perfect focusing in the diffraction plane if the sample can be formed to the SB focusing circle [7]. The TBC samples we test are inherently flat, resulting in some intensity loss [7]. The effect of divergence out of the diffraction plane is lessened in the back reflection region, and therefore we use a "loose" soller slit arrangement with a spacing to plate thickness ratio of about five to one. We use two rotation stages of different rotational radii to maintain the focus of the silicon crystal, the sample, and the detector axis on the same circle. A standard, low noise scintillation counter was used to detect the diffracted rays.

2.3 Johannson Focusing Monochromator

Bent focusing crystals have been placed between the x-ray source and diffractometer for several reasons. Asymmetric focusing crystals can have the advantage of maintaining a short distance and enhanced acceptance angle relative to the x-ray source, while the distance from the center of the monochromator to the focus may be lengthened to accommodate experimental apparatus of
large radius. Such monochromators are often designed to have sufficient resolution so that only the K\textsubscript{a1} line of the K\textsubscript{a1,2} doublet pair is transmitted. This type of monochromator has been used in combination with a SB diffractometer in a commercial device for studying surfaces by glancing-angle diffraction. Our focusing monochromator is a much larger variant of the commercial device. We use a symmetric Johannson ground and bent silicon (111) monochromator that is 12 cm in length and 4 cm high. The crystal grinding radius of 1 meter is chosen so as to produce enough mosaicity to completely accept the entire Nb K\textsubscript{a1} peak and remove most, but not all of the K\textsubscript{a2} peak. The relationship between brightness and bending radius was based on theoretical results of Suortti et al [8], which show that a reflectivity of between 50% and 70% can be obtained over the angular width corresponding to the Nb K\textsubscript{a1} line. A previous application of this crystal is discussed by Canistraro et al [9], and made use of the fact that the focused image is quite sharp (a line source ~ 400 \textmu m in width). The Si(111) monochromator removes the Nb K\textsubscript{b} line and also Bremsstrahlung except for the small band of continuum radiation lying in the energy range encompassed by the Nb K\textsubscript{a1} peak.

3. EXPERIMENTAL RESULTS

The top trace in Figure 2 illustrates a diffraction scan taken with a “state of art,” commercial diffractometer, on a flat TBC specimen consisting of ~ 125 \textmu m TBC, overlying a bond coat which largely consists of a \textbeta phase Ni(Pt,Al) alloy. The Bragg-Brentano mode is chosen, and a molybdenum anode x-ray tube is used. The stationary anode x-ray tube was operated at 45 kV and 40 mA beam current. The diffractometer is operated with a slit of 0.25 mm between the sample and the detector. The lower trace in Figure 2 is a diffraction scan taken under the same conditions, on a sample having a similar history, except that now the TBC layer is polished down to a thickness of 10 \textmu m. The doublet peaks indicated by the symbol T come from the TBC and are reduced in intensity in the polished specimen. The doublet peaks indicated by B come from the bond coat and are clearly visible in the polished specimen but completely invisible in the scan of the unpolished TBC specimen. We attempted to observe the bond coat peak doublet through the unpolished TBC by step scanning this angular region over a time period of hours, but were unable to detect the bond coat peak.

Figure 3 shows a scan on a similar unpolished specimen using our spectrometer. To minimize absorption in the top coat, we use an incident angle such that exit and incident angles are about the same. The Nb tube was operated at 50 kV and 20 mA. The slit positioned on the focusing circle, between the sample and the detector, had a width of 0.3 mm. In Figure 3 the central member of a "triplet" TBC peak (labeled TT) is centered on twice the Bragg angle of 61° for the specialized diffractometer data, whereas the triplet maximum is centered on about 59.5° for the data taken with a commercial diffractometer. The displacement to a higher angle for the data shown in Figure 3 is due to the use of Nb as opposed to Mo radiation for the anode material. The intensity of peak TT is about ten times as much using our diffractometer as obtained using the commercial instrument (peak T). The full width at half maximum (FWHM) of this peak is about 1.5 times the FWHM for the corresponding peak observed using the Bragg-Brentano instrument as shown in Fig. 1. The peak to the right of the central TT maximum is the K\textsubscript{a2} portion of the K doublet. Its intensity is diminished relative to the central peak maximum more in Figure 3 than in Figure 2, due to the diminishment of the K\textsubscript{a2} peak by the silicon monochromator for the Figure 3 data.
The TBC doublet peak centered at about $53^\circ$ is not as enhanced in intensity for the data in Figure 3, relative to the corresponding peak at slightly greater than $52^\circ$ in Figure 2, as is peak TT relative to peak T (a factor of $\sim 2.6$ instead of $\sim 10$). There can be differences in preferred orientation of the TBC between specimens. The diffuse background scattering intensity for Figure 3 is about five times what was observed in Figure 2. The most significant observation, however, is that in Figure 3 one observes a weak doublet at somewhat less than $56^\circ$, corresponding to the polished specimen bond coat doublet observed in Figure 2 at about $54.5^\circ$. We refer to this doublet as peak BB. We are clearly observing a bond coat diffraction peak through the unpolished TBC barrier, without using either a synchrotron source or rotating anode x-ray tube.

4. SUMMARY AND CONCLUSIONS

The diffuse scatter intensity with our SB diffractometer is five times that of the BB diffractometer, despite the fact that our Nb x-ray tube is operated at about half the power of the Mo tube used with the BB diffractometer. This implies that an order of magnitude intensity gain is possible using our arrangement relative to the BB diffractometer. If large area powder samples were used, which could be bent to coincide with the focusing circle, the intensity and resolution could be further enhanced. One could monochromatize the Bremstrahlung with our large bent crystal, use a rotating anode tube and perform diffraction studies using continuum radiation. The resulting intensity would be only an order of magnitude less than that obtained with a stationary anode tube and BB geometry using $K_{\alpha}$ characteristic radiation [10]. We therefore suggest the possibility of a laboratory facility for diffraction studies on concentrated samples using anomalous scattering, making use of x-ray energies tunable between elemental absorption edges.

5. Acknowledgments

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References

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Figure 1: Schematic of the diffraction geometry in the Seeman-Bohlin diffractometer. The sample may be placed closer to the focus of the bent crystal than to the focus of the x-ray tube, therefore increasing the solid angle for accepting x-rays. There is no divergence slit between the crystal focus and the sample.

Figure 2: Results from Bragg-Brentano diffractometer, polished versus full-thickness TBC specimen, using the Mo Kα radiation.

Figure 3: Results from Seeman-Bohlin diffractometer, full-thickness TBC specimen, using the Nb Kα radiation. The bond coat peak (BB) can be seen through the full thickness. Notice also, how the diffraction peaks from Kα2 can be suppressed relative to Kα1.