Unveiling Residual Stresses in Air Plasma Spray Coatings by Digital Image Correlation

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Abstract

We report a new three-dimensional digital image correlation (3D-DIC) based method for *in-situ* probing of the residual stresses in air plasma spray (APS) coatings. The inherent surface texture and coloration of APS coatings enabled extraction of surface profiles with accuracies of better than $\pm 8.8 \mu\text{m}$. The residual stress history of a three-layer thermal barrier coating system (TBC) was obtained experimentally by 3D-DIC curvature measurements from 22 to 800°C coupled with a newly developed residual stress model for multilayered TBC systems. The residual stress in TBC systems was released in an observed linear trend through 800°C. Anomalous increases in curvature and residual stress upon heating between temperatures of 800°C and 900°C were partially caused by expansive tetragonal to monoclinic ($t \rightarrow m$) phase transformation within the partially stabilized zirconia top coat. A coupled stress-temperature dependent mechanism was used to uncover the phase transformation induced stresses. The technique opens up new opportunities for monitoring the residual stress development in manufacturing and operation of coatings, thin films, and structures of dissimilar materials.

1. Introduction

Thermal spray coatings are used in a wide variety of applications to improve surface thermal, mechanical, and chemical properties [1,2]. While the function and durability of coatings depend on many parameters including coating thickness, roughness, and residual stress [3,4], these properties, and stress in particular, are difficult to ascertain in real time during coating preparation and application. Indeed, the most widely accepted residual stress evaluation techniques are *ex-situ* and frequently destructive, such as Raman spectroscopy [5] or X-ray diffraction (XRD) [6] of cross sectioned samples. A robust monitoring technique that could evaluate some these properties in real time would have positive implications for coating durability and consistency and eliminate the need of destructive testing which is not eco-friendly. In this work, we demonstrate digital image correlation (DIC) enabled methods for in-process monitoring of thermal spray systems that are able to probe coating surface profile and residual stresses.

Residual stress, caused by nonuniform heating and thermal expansion and lattice mismatch between substrate and coating, is often measured in laboratory settings by Raman spectroscopy [5] or XRD [7,8] techniques, although neither are suitable for in-process applications in harsh manufacturing environments. An alternative method of measuring residual stresses by specimen curvature during processing was first introduced by Matejicek [9] and used by many others [10,11], although this required prior knowledge of mechanical properties for the substrate and coating. In this method, a beam is supported on one or both ends, and curvature is measured with displacement sensors affixed to the back of the specimen as the front is coated [9], or with various non-contact optical or laser techniques [12,13]. In particular, the non-contact methods have demonstrated surface-profile measurements to accuracies on the order of 10-100 μm , although they may struggle to provide full-field surface measurements [12,13]. The

tediousness and difficulty of mounting wired sensors to coating samples limit widespread use. Measured curvature may be coupled with deformation models to provide residual stress contours throughout the sample thickness. In this work, this model is extended from bi-layer coating systems to arbitrarily multilayered coating systems as described in Section 1.1. Implementation of the curvature method with non-contact, full-field surface profile measurements would enable simultaneous, real-time measurement of coating curvature and thus residual stress and also eliminate the requirement for wired sensors, improving upon existing methods.

Curvature methods have proven effective in holistically measuring residual stress gradients but fail to capture microscopic mechanisms that alter residual stresses. For instance, the tetragonal to monoclinic ($t \rightarrow m$) phase transformation within yttria-stabilized zirconia (YSZ) thermal barrier coatings (TBC) results in volume expansions and may significantly alter residual stress [14]; this transformation has been observed after aging at temperatures above 1300°C for several hundred hours [6,15]. Low temperature $t \rightarrow m$ transformation below 425°C has been observed in 5 mol %YSZ (5-YSZ) [16], although not for the higher concentration 8 mol% YSZ (8-YSZ) commonly used in TBC systems and tested in this study; however, after annealing at high temperatures, the metastable 8-YSZ t' phase segregates into yttria-lean and yttria-rich t phases [17], of which the lean phase may undergo the $t \rightarrow m$ transformation at lower temperature. Complementary XRD [6] or Raman spectroscopy [15,16] studies are therefore essential to identify the $t \rightarrow m$ transformation within the TBC systems.

Initially developed in the field of experimental mechanics, the three-dimensional DIC (3D-DIC) technique is an optical non-contact measurement procedure that processes stereoscopic images of specimens to extract surface profile and deformation information [18]; full-field measurements are obtained by dividing a larger area of interest in the images into small subsets

and matching surface features of each subset in images acquired throughout the experiment through numerical optimization algorithms [19]. For any given pair of images in which the surface coating is perturbed (such as during coating deposition), surface contour, curvature and position can be extracted; on the other hand, if the surface pattern remains unperturbed, deformation measurements may also be obtained. Under ideal conditions with appropriate lighting and high contrast surface patterns, 3D-DIC methods measure surface profiles to an accuracy of $1/20,000^{\text{th}}$ of camera-object distance [20,21]; for a reasonable camera-object distance of about 500 mm, this corresponds to an accuracy of approximately 25 μm . Thus, 3D-DIC presents a novel route for residual stress measurement; the DIC-obtained curvature may be converted to residual stresses. Due to the versatility of the 3D-DIC method, residual stress measurements are demonstrated at temperatures up to 800°C.

1.1. Curvature-based residual stress measurements for multi-layered coatings

The theoretical and experimental basis for studying residual stresses of bilayered plasma-sprayed coatings is well established (e.g., [9,22,23]); however, these models are deficient for complex multi-layered coating systems that are widely employed in industry, such as thermal barrier coating systems with top coat, bond coat, and substrate layers, or other functionally graded coating systems. Here, a curvature-based residual stress model for arbitrarily multi-layered coating systems is derived from Euler-Bernoulli beam theory. For this work, the multi-layered model is reduced to $n = 3$ layers to extract residual stress data for a thermal barrier coating system with top coat, bond coat, and substrate layers. Although elementary, this derivation is presented in brief due to the importance of residual stresses in the performance of multi-layer coating systems and the absence of such models in the literature.

First, the geometry of an arbitrarily-layered beam (Fig. 1) is assumed. Using the Euler-

Bernoulli beam theory conventions, a linear and continuous strain distribution is assumed in the form [9,10]:

$$\varepsilon_{xx}(z) = c_1 z + c_2. \quad (1)$$

Given this deformation gradient, force and moment equilibria conditions are satisfied with the following

$$\sum_{i=1}^n E_i \left(\begin{bmatrix} \frac{z_{i+1}^2}{2} & z_{i+1} \\ \frac{z_{i+1}^3}{3} & \frac{z_{i+1}^2}{2} \end{bmatrix} - \begin{bmatrix} \frac{z_i^2}{2} & z_i \\ \frac{z_i^3}{3} & \frac{z_i^2}{2} \end{bmatrix} \right) \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \sum_{i=1}^n E_i \alpha_i \Delta T \left(\begin{bmatrix} z_{i+1} \\ \frac{z_{i+1}^2}{2} \end{bmatrix} - \begin{bmatrix} z_i \\ \frac{z_i^2}{2} \end{bmatrix} \right), \quad (2)$$

where E_i and α_i are the elastic modulus and coefficient of thermal expansion for the i^{th} layer and ΔT is the deviation from equilibrium temperature. The strain gradient parameters c_1 and c_2 are easily determined with this relationship given the mechanical properties of each layer. Using linear-elastic and isotropic relationships within each layer, the residual stress at a given point in the i^{th} layer is found in terms of mechanical properties:

$$\sigma_{xx}^{Residual}(z) = E_i \times (\varepsilon_{xx}(z) - \alpha_i \Delta T). \quad (3)$$

By geometric inspection, it can be shown that the unknown parameter c_1 is equivalent to the specimen curvature

$$c_1 = \frac{1}{\rho} = C_{xx}, \quad (4)$$

where ρ is the surface's radius of curvature.

This set of equations may be used to extract residual stresses by three different means. First, the stresses may be solved theoretically only in terms of mechanical properties and specimen dimensions. Second, experimental curvature measurements may provide c_1 , enabling the solution of c_2 using one of the equilibrium conditions in Eq. 2. Finally, if DIC strain measurements are obtained at the equilibrium temperature, surface strain measurements may be converted directly to residual stresses after subtracting thermal expansion strains.

Fig. 1. N-layered composite beam model for residual stress calculations.

2. *Research Methods*

2.1. *Establish accuracy of 3D-DIC curvature measurements for APS coatings*

The accuracy of 3D-DIC techniques for curvature measurements on a sample of APS coating was first verified. Experiments involved a thermal barrier coating (TBC) specimen of 8-YSZ with a bond coat of NiCoCrAlY on a HR 224 nickel alloy substrate. For validation, sample curvature was measured using a tribometer as a surface profiler by scanning a sharp indenter tip over the surface profile (UMT 3, Bruker Nano). The profiler applied a constant contact force of 1 N, sufficient force to maintain probe contact without deforming the sample. Height and spatial accuracy on the profiler were found to be better than 1 μm .

As intrinsic DIC surface patterns generally possess inferior contrast to artificially generated patterns (e.g., spray paint application), the influence of various experimental imaging parameters was assessed to optimize the use of 3D-DIC for surface profile measurement.

First, optimal camera-object distance was determined experimentally by adjusting camera-sample distance and comparing extracted surface profiles to reference profile measurements. The TBC sample was imaged at distances between 300 and 900 mm and analyzed with 3D-DIC to compute the apparent surface profile. Multiple images were captured at

each camera distance without moving the sample, and artificial displacements between images at each distance were used to quantify the in-plane and out-of-plane accuracies of each measurement. Comparison in measured sample height between the DIC and reference profiles was used to holistically prove convergence of the 3D-DIC measurements. Average curvatures were computed and compared from the 3D-DIC and reference data by fitting circular profiles to the data using a least-squares method.

As summarized in Table 1, all DIC experiments used dual 5 megapixel CCD cameras (PointGrey Research) with 50mm compact lenses (Schneider Kreuznach). The 3D-DIC setup was configured to increase depth of field as well as minimize noise and distortion from convective currents by using small apertures, relatively long exposure times and low-heat LED lighting. It was determined qualitatively that oblique flood lighting at angles of approximately 30° improved correlation results by exaggerating shadows caused by coating surface roughness.

Table 1. 3D-DIC parameters

Imaging Parameters	
Cameras	5 megapixel CCD (PointGrey)
Lenses	50 mm compact lens (Schneider)
Exposure	5 ms
Aperture	f/8
Stereo angle	~25°
3D-DIC Analysis	
Subset Size	41 px
Step Size	7 px
Software	Vic-3D

2.2. Influence of phase transformation and temperature on residual stress

Residual stress of the TBC sample was obtained by the non-contact 3D-DIC curvature method at temperatures between 22°C and 900°C after repeated annealing cycles to induce a phase transformation within the top coat. Curvature was first obtained after two three-hour

annealing treatments at 1200°C (totaling 6 hours) in ambient conditions, which established an equilibrium temperature for thermal expansion and relieved quenching-based residual stresses in the NiCoCrAlY bond coat [8]; the sample was exposed to 900°C for approximately 20 minutes in subsequent annealing treatments¹. *In-situ* curvature measurements were obtained during subsequent heatings up to 800°C and 900°C as outlined in Table 2. The 3D-DIC curvature measurement method is depicted in Fig. 2. The TBC specimen was mounted at one end to an alumina plate with high temperature cement (Omega Engineering) to minimize artificial curvature constraints. After heating to a designated temperature in a box furnace (MTI Corporation), the sample was allowed to equilibrate for 15 minutes, and the furnace door was gently opened to acquire images. Approximately 30 images were captured at each temperature over a period of 10 seconds, and the furnace was subsequently closed and heated to the next temperature. Heating and cooling rates were less than 5°C/min.

Image distortion due to mixing of air at the furnace threshold was controlled in two ways. First, the specimen was positioned at the front and bottom of the furnace to minimize the amount of air mixing between the samples and camera, and a fan forced air upwards across the furnace opening to promote even and faster mixing [24]. Second, all images at each temperature were averaged on a pixel basis to eliminate distortion caused by random convective currents. Y-direction curvature was extracted by fitting circular profiles to the surface profiles obtained at each temperature using a least-squares scheme. X-direction curvature was ignored due to relatively small dimension and complex boundary conditions imposed by the cement base (Fig. 2).

¹ Notation is developed for this paper to concisely describe annealing state. A description of “2x1200°C” indicates two annealings at 1200°C, while a description of “2x1200°C + 1x900°C” indicates an additional annealing to 900°C.

Table 2. Curvature Test Matrix. DIC measurements acquired throughout entire temperature range unless otherwise noted.

Starting Anneal state	Temperature Range	Curvature measurements during:	
		Heating?	Cooling?
2x 1200°C	22-800°C	✓	
2x 1200°C	22-900°C	✓	
2x 1200°C, 1x 900°C	22-800°C	✓	✓
2x 1200°C, 1x 900°C	22-900°C	✓ (at 25°C)	✓ (at 25°C)
2x 1200°C, 2x 900°C	22-900°C	✓ (22-800°C)	✓ (22-800°C)

Fig. 2. Experimental setup to measure curvature. Sample is 12 x 25 mm in size.

XRD patterns of the top coat were obtained at various stages of annealing using a powder diffractometer (X'Pert Panalytical Pro MPD, Philips) with monochromatic copper radiation at 45 kV and 40 mA. Diffraction measurements were obtained at $2\theta = 5 - 80^\circ$ in 0.05° steps, which enabled identification of phase content within both the $28^\circ < 2\theta < 32^\circ$ and $72 < 2\theta < 76^\circ$ regions. Results from 3 scans at each annealing state were averaged to reduce noise. A Reitveld refinement scheme was performed with monoclinic, tetragonal, and cubic phases using the

Profex-BGMN software package to determine composition and lattice parameters.

Residual stress was computed from the curvature measurements using Eqs. 1-3. The TBC sample had nominal top coat thickness of 198 μm , bond coat thickness of 230 μm , and substrate thickness of 1000 μm . While thin (<5 μm) oxide layers were observed on the exposed back surface of the superalloy substrate as well as at the interface between the top coat and bond coat, the contribution of these layers to bending stiffness was considered negligible compared to the much thicker primary constituent layers.

Computations used experimental values for elastic moduli and literature values for thermal expansion coefficients. High-temperature nanoindentation (NanoTest Vantage, Micro Materials) with a cubic boron nitride (cBN) Berkovich indenter and microindentation (UMT 3 tribometer, Bruker Nano) with a Sapphire Vickers indenter were used to probe the temperature dependence of elastic moduli of the top coat, bond coat, and substrate in the TBC sample at temperatures between 22°C and 900°C. Stiffness information of each layer was extracted from the nanoindentation force-displacement curves with the Oliver-Pharr method [25]. Calculations assumed temperature-insensitive elastic modulus and Poisson's ratio of 800 GPa and 0.12 for the cBN indenter and 375 GPa and 0.24 for the Sapphire indenter [26] and Poisson's ratios of 0.31, 0.31, and 0.3 for the top coat, bond coat, and substrate of the TBC sample [8,27]. Nanoindentation load was 50 mN to produce deep indents that sampled material across many grains, and microindentation load was 3 N. Coefficients of the thermal expansion of 12.0, 17.9 and 18.0 $\mu\text{ε}/^{\circ}\text{C}$ were obtained from the literature for the top coat, bond coat, and HR-224 substrate [28,29].

3. *Accuracy of 3D-DIC for APS coatings*

The surface profile of the TBC sample was obtained by 3D-DIC at different camera

distances, as plotted in Fig. 3a. It was found that for camera-sample distances below 600 mm, the observed surface profiles converged toward an identical, approximately parabolic profile. For unknown reasons, the profiles obtained at higher camera-sample distances possessed exaggerated curvature. Profiles obtained from larger camera-sample distances displayed pronounced local and systematic deviations from this profile. These profiles were compared to tribometer measurements (solid line in Fig. 3a) and showed that the 3D-DIC measurements at camera distances less than 600 mm indeed converged toward the actual surface profile.

The accuracy of 3D-DIC profile measurements was further quantified by computing phantom displacements between images captured without moving the sample or camera. Errors associated with in-plane and out-of-plane position were separately computed and are plotted in Fig. 3b. Positional error demonstrated similar trends as a function of camera-sample distance, with best performance at distances less than 600 mm, although error associated with out-of-plane measurements was consistently higher. The standard deviation associated with in-plane position was less than $2.4\ \mu\text{m}$ for all camera-sample distances less than 600 mm and thereafter increased to $5.6\ \mu\text{m}$ at a distance of 910 mm. Standard deviation of the out-of-plane position was less than $6.8\ \mu\text{m}$ for distances less than 600 mm and increased to $39\ \mu\text{m}$ at distance of 910 mm.

Fig. 3. Assessment of 3D-DIC surface profile measurement accuracy as a function of

camera distance. (a) Comparison of measured surface profiles as a function of camera distance (colored circles). The surface profile obtained by profilometer is displayed as a solid black line. (b) Standard deviation in in-plane position (blue circles) and out-of-plane position (red squares) measurements.

Of particular relevance to the computation of residual stress, average curvatures were extracted from the profilometer and 3D-DIC (distance = 600 mm) surface profiles. These two methods produced radii of curvature equal to 347.3 ± 8.6 and 361.9 ± 1.4 mm, respectively; the difference between these measurements was 4.2%. Since residual stress in plasma sprayed coatings was a linear function of curvature, this measurement suggested that 3D-DIC measurements may be used to compute residual stresses to similar accuracy.

Several important trends emerged from these results. Most obviously, there existed a limit to the accuracy of 3D-DIC profile measurements such that further improvements could not be achieved with reductions in camera-sample distance. Accuracy plateaued at values of 8.8 μm (based on vector addition of in-plane and out-of-plane accuracies) for camera distances below 600 mm. Since the DIC method computed surface profiles by averaging the location of micro-scale textural features (i.e., surface roughness) within a subset, it was concluded that *surface roughness physically governed the accuracy of 3D-DIC measurements* on the plasma sprayed coatings. This finding contrasted with conventional DIC experiments that use artificially generated surface patterns, in which both camera-sample distance and feature size may be reduced to improve accuracy.

Second, the accuracy of the 3D-DIC APS measurements compared favorably with other measurements in the literature. Using a 99% confidence level on total positional error, these results suggested a maximum error of 22.6 μm , or $1/26,500^{\text{th}}$ of camera-sample distance. This

value was slightly better than found in the literature [20] and emphasized that the surface profile of APS coatings may be accurately measured with 3D-DIC without artificial surface patterns. Based on the limitations imposed by surface roughness, it was anticipated that rougher coatings would demonstrate slightly worse performance.

4. *Residual Stress Measurements of TBC sample*

Non-contact residual stress values on the TBC sample were obtained via 3D-DIC and compared to the Euler-Bernoulli model for residual stress. The TBC sample was heat treated at 1200°C for 6 hours to establish an equilibrium temperature, at which temperature creep eliminated residual stresses and curvature [8]. Upon cooling the specimen demonstrated pronounced convex curvature on the top coat surface due to thermal expansion misfit.

4.1. *Curvature measurement by 3D-DIC*

TBC curvatures at elevated temperatures after different annealing treatments are reported in Fig. 4, which showcases a complex relationship between temperature and curvature. Most obviously, the curvatures exhibited primarily linear decreases with temperature from 22-800°C regardless of heat treatment; slope of this relationship remained unchanged for all heat treatments at $-2.43 \pm .141 \times 10^{-6} mm^{-1} C^{-1}$. Extrapolation of the linear curvature trends suggested an equilibrium temperature of above 1500°C that was well above the initial annealing temperatures, which hinted at either nonlinearity in material properties above 900°C or permanent deformation.

However, treatment above 800°C enhanced room-temperature curvature. This repeatable effect was demonstrated by three annealings at 900°C, which resulted in increases in room temperature curvature of 4.2, 1.1 and $1.0 \times 10^{-4} mm^{-1}$, and measurable increases in curvature did not occur when heated to only 800°C. We note that although the last two increases were less

than the 4.2% measurement error determined in Section 3, the increases in curvature were persistent at all temperatures and verified by profilometer. More precise identification of the critical temperature associated with this increase in curvature was somewhat hindered by measurement error, although examination of the green 2x1200°C trial in Fig. 4 suggested this increase occurred above 850°C, as curvature jumped to be in line with the 2x1200°C + 1x900°C treatment curve. In contrast, after heating to only 800°C (Table 2), no measureable increase in curvature at any temperature between heating and cooling curves was observed for the blue 2x1200°C + 1x 900°C trial.

Fig. 4. 3D-DIC enabled curvature measurements of TBC sample at various stages of annealing. Solid circles indicate measurements obtained during heating, and open circles indicate measurements obtained during cooling.

4.2. High Temperature Mechanical Characterization of TBC sample

The calculated elastic moduli were determined based on the unloading curves obtained from indentation according to the Oliver-Pharr method [25], as shown in Fig. 5 and are presented

in Fig. 5c as a function of temperature up to 900°C. The three constituent materials demonstrated approximately linear softening trends up to 900°C, which was consistent with findings for 8-YSZ in the literature [27]; the average moduli decreased from 54.9 to 43.5 GPa in the top coat, from 222.1 to 181.3 GPa in the bond coat, and from 111.2 to 86.2 GPa in the substrate. Error in these measurements was about 9% for each measurement, as indicated by error bars in the figure. The jump of the substrate average modulus at 400°C remained within the deviation of the observed trend. The impact on the moduli due to phase transformation and yielding was considered. Although the γ to β phase transformation has been observed in NiCoCrAlY bond coats between 600°C and 800°C [8], no effect on material stiffness was observed. This softening trend has important implications in explaining residual stress relaxation at elevated temperatures, which is discussed further in Section 4.4. Furthermore, Fig. 5a shows an increasing amount of yield within the 8-YSZ top coat at greater temperatures. The yield as indicated by the initial step of the loading curve, which occurs at greater depths with greater amounts of yield [30]. In contrast, Fig. 5b exhibits creep within the bond coat occurring around 800°C. As a result of this trend, creep within the TBC at higher temperatures could induce increased curvature upon cooling and counter any relaxation due to top coat yielding.

Fig. 5. Determination of high-temperature TBC mechanical properties via indentation. Selected indentation loading curves from (a) the top coat and (b) the bond coat at temperatures that demonstrate reductions in stiffness and yield stress with temperature.

(c) Elastic moduli of the three constituent layers up to 900°C.

4.3. Phase Composition Evolution of TBC

Phase content within the top coat was determined using XRD over diffraction angles $2\theta = 5^\circ$ to 80° , and a narrow region of these patterns is shown in Fig. 6a to highlight the growth of monoclinic phases during heat treatment. Phase composition for corresponding heat treatments determined using Reitveld refinement methods are presented in Table 3. The deposited coating was somewhat impure, containing measureable amounts of both cubic c and monoclinic m phases in addition to tetragonal phases. Monoclinic content within the top coat increased from 1.59% in an untreated state up to 2.79% after 2x1200°C and 2x900°C annealing treatments, indicating a $t \rightarrow m$ transformation; at the same time c content diminished with increasing heating to trivial amounts. Trends in t were unclear, possibly due to strong overlap between these peaks. Monoclinic content decreased after mechanical removal and pulverization of the top coat.

The peak locations shifted subtly to smaller 2θ with increasing heat treatment. Since XRD measurements were obtained on the planar top surface of the TBC sample, the decrease in 2θ indicated tensile lattice strains in the coating thickness direction; these effects could be construed as Poisson's ratio effects due to in-plane *compression* with increasing heat treatment. By tracking the combined $t(1\ 0\ 1)$, and $c(1\ 1\ 1)$ peaks at $\approx 30.2^\circ$, out-of-plane strains of $\epsilon_{zz} = 0.16\%$ and 0.25% were obtained for the 1x1200°C and 2x1200°C+2x900°C treatments. Assuming a Poisson's ratio of 0.31 for the top coat (Section 0) and linear elasticity, these would correspond to in-plane surface compressive strains of $\epsilon_{xx} = 0.51\%$ and 0.80% . Using the beam curvature model outlined in Section 1.1 and room temperature mechanical properties outlined in Section 4.2, these surface strains would correspond to changes in curvature of .0074 and .012;

these curvatures were larger than those measured in Section 4.1 by a factor of 2.6. Moreover, the XRD-measured surface compression strains were larger than could simply be explained by the small volume fraction of m phase. Thus, it was concluded that in addition to the $t \rightarrow m$ transformation, other mechanisms contributed to changes in curvature.

Fig. 6. Phase composition analysis by XRD. (a) XRD patterns between 20° and 40° at various stages of heat treatment, with m (1 1 $\bar{1}$) and m (1 1 1) peaks marked at $2\theta = 28.2^\circ$ and 31.5° by vertical lines.

Table 3. XRD computed phase composition

Annealing State	t	c	m
Untreated	$93.2 \pm .55\%$	$5.15 \pm .52\%$	$1.59 \pm .20\%$
1x1200°C	$97.93 \pm .26\%$	$.33 \pm .17\%$	$1.74 \pm .19\%$
2x1200°C, 2x900°C	$94.61 \pm .44\%$	$2.59 \pm .37\%$	$2.79 \pm .23\%$
1x1200°C, Pulverized	$84.58 \pm .60\%$	$14.61 \pm .60\%$	$.81 \pm .46\%$

4.4. Residual Stress Calculations

Residual stress was determined by two different methods. First, the Euler-Bernoulli

model derived in Section 1.1 was solved using a system of linear equations to identify the unknown coefficients C_1 and C_2 in Eqs. (1-3). Second, 3D-DIC-derived curvature data was used to directly calculate the unknown coefficient C_1 within the model and then the residual stress. “Theoretical” residual stresses from the beam model were compared to the curvature-based experimental results (Fig. 7). The compressive residual stress determined by the Euler-Bernoulli model was linear with temperature and indicated that all residual stress would be relieved by 1200°C. Residual stresses computed by 3D-DIC curvature followed a similar linear trends and showed slight increases in residual stress with increasing heat treatment that closely matched changes in curvature (Fig. 4). By this calculation, the residual stresses within the coating would be fully relieved at 1200°C, which was caused by the assumption of equilibrium temperature; in contrast, curvature measurements demonstrated no such trend.

Fig. 7. The compressive residual stress determined based on a Euler-Bernoulli model and with 3D-DIC curvature data of a TBC specimen over repeated heating and cooling treatments. The solid black line is the trendline associated with the Euler Bernoulli

theoretical data.

5. Discussion

We have demonstrated the unique capability of 3D-DIC as a system for obtaining curvature measurements and conducting residual stress calculations in harsh plasma spray coating environments. These achievements have many implications for spraying applications and understanding of TBC mechanical behavior at high temperatures.

5.1. Accuracy of measurements

The 3D-DIC system demonstrated repeatable and facile surface profile measurements, with curvature measured within 4% of tribometer profile measurement. While the profile measurements obtained by 3D-DIC were comparable to those of the profilometer methods, the 3D-DIC method demonstrated a key advantage in speed of acquisition. After camera setup, only a single pair of images was required for profile extraction. In contrast, measurement with alternative profilometer or confocal microscope techniques would demand multiple line scans to inspect similarly sized regions of interest. For specific applications that demand only $\sim 10\text{ }\mu\text{m}$ precision, such as determination of macroscopic surface contours of thermally sprayed systems, 3D-DIC inspection would serve as a high-throughput, high-accuracy alternative. On the other hand, 3D-DIC measurements were limited by camera resolution and intrinsic spatial averaging of surface profiles over subset domains and would therefore be infeasible for measurements of microscopic roughness. These encouraging results complement studies by McNeill et al. [20] and others [18,19,20] who have demonstrated the potential of DIC for reliable surface profile measurements. Based on these promising findings, 3D-DIC techniques could be reliably applied to a wide variety of APS coatings.

5.2. Temperature and Phase-transformation induced curvature

As discussed in Section 4.1, anomalous increases in TBC curvature occurred upon heating above 800°C. XRD measurements provide evidence of the expansive $t \rightarrow m$ transformation within the top coat that partially explained curvature evolution. However, complementary mechanisms are required to fully explain these changes.

One possible but unlikely cause for increases in curvature was growth of oxide layers at elevated temperatures; if these oxide layers formed on a curved sample, they could contribute to progressive increases in curvature. However, the constituent materials, being designed for operation at 1200°C, were mostly stable at the experimental temperatures. Weight measurement before and after heating to 900°C (after the initial 2x 1200°C annealings) revealed weight loss of 0.05%, indicating that the initial annealing treatments had formed stable and fully-developed oxide scales and that only insignificant loss of material was observed. Moreover, the oxide layers would be too small to contribute significantly to curvature; thickness of the TGO layer on the bond coat/top coat interface as well as the oxide scale on the uncoated face of the substrate were less than 5 μm .

As observed by Chen et al., there exists a well-defined γ to β transformation in NiCoCrAlY between 600-800°C that results in expansion of the bond coat upon cooling, and therefore may increase curvature. However, these strains were found to result only after quenching from high temperatures [8]; slow cooling throughout the experiment mitigated this effect by allowing stress release through creep. It is unlikely that this phase transformation had any significant effect on curvature during heating to 900°C.

The key limitation of the theoretical model calculations was the assumption of linear elasticity and absence of stress relaxation at all temperatures. According to more complex material models, regions of the coating under tensile stress could elongate and enhance

curvature. Residual stresses using the linear elastic model with experimental mechanical properties at 900°C and actual sample geometry are calculated and shown in Fig. 8, which revealed average compressive stress of 58 MPa in the top coat and average tensile stress of 57 MPa in the bond coat. In light of the experimental results, stresses in the tension-loaded bond coat are of particular relevance.

Prior work in the literature has shown creep initiation in NiCoCrAlY bond coats at 850°C at stresses below 15 MPa [31]; presumably, the critical creep stress would continue to decrease at higher temperatures. Within the context of this work, tensile residual stresses in the bond coat must exceed the temperature-dependent critical creep stress to initiate this curvature-enhancing mechanism; presumably this criterion was not satisfied at temperatures below 800°C but was satisfied at higher temperatures. Importantly, this mechanism would also explain the diminishing increases in curvature in successive heating to 900°C; creep in the bond coat would reduce residual stresses in the coatings below the critical value, at which point the curvature would no longer increase.

Fig. 8. Estimated residual stress at 900°C using trilayer beam model in Eqs. 1-3.

5.3. *Coupled Stress- and Temperature-induced phase changes*

Experimental results in this work demonstrated that the $t \rightarrow m$ transformation within the 8-YSZ coating occurred with increasing heat treatment above 800°C, and that this transformation was somewhat reversible upon the release of residual stresses. The monoclinic phase content increased to $2.59 \pm .37\%$ after 2x 1200°C + 2x 900°C heat treatment, which was much higher than the $0.50 - 1 \text{ mol}\%$ equilibrium m content reported in other works [32,33], although this current study involved annealing at higher temperatures for shorter duration than in [32] (up to 1200°C for ~6 hours compared to 155°C for 48 hours). A key difference, however, was the much higher residual stresses in the YSZ coating in this current study of $\approx -300 \text{ MPa}$. What was the source of $t \rightarrow m$ transformation?

Since deposition and annealing temperatures remained well below 1300°C with short annealing times, the mechanism of the observed $t \rightarrow m$ transformation was certainly different than equilibration during long (upwards of 1000 hours) annealing times at higher temperatures [6]. In fact, even if the YSZ coating were briefly heated above 1300°C, the $t \rightarrow m$ transformation would occur much more slowly than observed in this work [15].

In other works, the $t \rightarrow m$ transformation has occurred in yttria-lean t phases (4-6 mol% YSZ). Using empirical relationships developed by Ilavsky and Stalik [33], the yttria content within the tetragonal phase may be determined using the lattice parameters:

$$\text{mol}\% \text{YO}_{1.5} = (1.0225 - c/a)/0.001311. \quad (5)$$

The composition of the YSZ coating was determined to be 7.44 mol% and 7.06 mol% in the untreated and 2x1200°C + 2x900°C annealed states, respectively; no $t \rightarrow m$ transformation has been previously reported for this yttria concentration. Additionally, the tetragonal composition in yttria-lean YSZ would be regenerated upon heating above T_0 temperature, and m generation

depends on cooling rate. Since identical cooling rates were achieved and yttria concentration remained high, this mechanism inadequately explains the growth of monoclinic phase.

In summary, these findings suggest an alternative transformation mechanism that may be related to the high residual stresses within the YSZ coating. The complexities of this experiment due to multiple coating layers made it difficult to fully isolate mechanisms of the phase transformation; future studies are required to fully explain this mechanism.

5.4. *Residual stress*

High fidelity, facile curvature measurements enabled accurate measurement of residual strains as a function of temperature. Coupled with independent property measurement at high temperatures, the residual stresses within a TBC sample were determined to 5% accuracy (± 9.3 MPa, based on curvature accuracy at room temperature). In agreement with other studies [32,34], it was observed that the TBC was under a compressive stress in as-deposited condition due to thermal misfit with the substrate. Yang et al. observed a compressive stress of the TBC layer of about 130 MPa, less than the approximately 300 MPa compressive stress observed in this study [34]; however, this difference may be attributed different sample thicknesses and to the reverse phase transformation, $m \rightarrow t$, which was accompanied by a volume shrinkage and reduction of curvature. In contrast, Scardi et al. observed a $t \rightarrow m$ transformation and progressive increase of compressive stress with temperature, but the magnitude of the stress was much lower, about 30 MPa [32]. As previously discussed, this difference in residual stress may be explained by the different monoclinic phase content; however, further scrutiny of the cause of the transformation is needed to identify the source and understand the impact of annealing temperature and duration.

In this study, the linear trend displayed in Fig. 7 suggests that the compressive residual

stress was relieved by 1200°C, as predicted by the Euler-Bernoulli model. While the theoretical model did agree with the initial experimental test using 3D-DIC (within 5% difference), progressive heating, which was observed to lead to coupled phase-temperature induced phase changes, increased the residual stress gradually to values approximately 16% different from the theoretical data. With future studies to enhance understanding of the growth mechanisms of the observed $t \rightarrow m$ transformation, these mechanisms can be addressed within the model to introduce a corresponding corrective term. Although certain assumptions in the model such as linear elasticity were insufficient, the residual stress computations proved instructive and could readily be corrected for more complex material models.

5.5. *Implications*

Several key implications of this study deserve further investigation. The source of the observed $t \rightarrow m$ transformation which initiated the increased curvature with heating may be investigated in order to derive an appropriate residual stress model, building off the Euler-Bernoulli model presented in this study. Furthermore, this understanding of the phase transformation would enable greater understanding of the residual stress evolution above 800°C.

Curvature and residual stress within the top coat were measured to 800°C, and linear extrapolation of these trends predicted full curvature release above 1500°C, which was well above the maximum annealing temperature. The DIC-curvature method could be extended to much higher temperatures with appropriate UV illumination and narrow-bandpass filters, as per [35], enabling direct measurement of nonlinear curvature behavior. Indeed, time-dependent curvature and strain related phenomena such as creep and diffusion-based kinetics could be observed in real time.

Importantly, the capability of 3D-DIC to provide a holistic understanding of APS residual

stresses in real time has important implications for coatings manufacturing and operation. Real time stress measurements may empower customized manufacturing and operation adjustments to minimize stress within the coating layers. Such capability may provide more reliable APS coatings while reducing manufacturing costs and waste. The impact of 3D-DIC residual stress monitoring on manufacturing and the spraying process will be explored in future studies.

6. Conclusion

3D-DIC was studied in detail as a method for in-situ, real-time evaluation of APS coating curvature and residual stress. The inherent texture of APS coatings enabled the direct measurement surface profile during exposure to high-temperature environments. It was found that accuracy of the 3D-DIC measurements was limited by surface roughness, which governed the minimum feature size available for surface profile measurement. With appropriate lighting and camera-sample distances, the 3D-DIC measurements demonstrated positional accuracy of 22.6 μm , or $1/26,500^{\text{th}}$ of camera-sample distance, which compared favorably available values in the literature. A residual stress model for multilayered coatings was derived using Euler-Bernoulli beam theory and linear-elastic material models to predict residual stress within superalloy, NiCoCrAlY bond coat, and YSZ top coat TBC system up to 800°C, and results were compared to experimental curvature measurements obtained by 3D-DIC. The model compressive stresses matched within 5% of experimental results after initial heat treatment at 1200°C but could not capture increases in curvature after subsequent annealing treatments above 800°C. The increases in curvature were attributed to both creep in the bond coat as well as $t \rightarrow m$ phase transformation within the top coat. The $t \rightarrow m$ transformation were unexpected and were suspected to be induced by both stress and temperature.

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