# Stress-Relaxation and Creep Behavior of Heat-Treated Stand-Alone Plasma-Sprayed 7 wt.% $Y_2O_3$-$ZrO_2$ Coatings

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## *Abstract*

Plasma-sprayed 7 wt.% $Y_2O_3$-$ZrO_2$ (YSZ) stand-alone coatings were subjected to 10, 50 and 100-hr heat-treatments at 1200°C, followed by mechanical testing in compression at 25°C, 1050°C, and 1200°C. The mechanical tests performed on the samples included cyclic loading/ unloading, stress-relaxation, and creep. In cyclic compression tests at 25°C, it was observed that the YSZ coating that had been heat-treated for 50-hr at 1200°C demonstrated a higher modulus and more strain hysteresis as compared to an as-sprayed sample. As heat-treatment time increased, the YSZ stand-alone coating demonstrated less relaxation of the initial applied stress for stress-relaxation tests run at 1050°C and 1200°C. The steady-state creep rate was observed to decrease with increasing heat-treatment time prior to testing; as expected, the steady-state creep rate increases when the testing temperature was increased from 1050°C to 1200°C. Density (via Archimedes') and phase analysis (via X-ray diffraction) were performed on YSZ coatings before (i.e. as-sprayed) and after heat-treating at 1200°C. Porosity was observed to decrease only slightly (~1%) after a 100-hr heat-treatment at 1200°C as compared to the as-sprayed porosity. The high-yttria metastable tetragonal phase observed in the as-sprayed coatings was observed after a 100-hr heat-treatment at 1200°C. The same metastable tetragonal phase was also observed after a 100-hr heat-treatment at 1200°C followed by a 3-hr stress-relaxation test at 1200°C.

## *1. Introduction*

Thermal barrier coatings have significantly increased the working efficiency of turbine engine and diesel engine systems. The basic thermal barrier coating system is made up of the metal substrate, a bond coat like PtAl or MCrAlY (where M stands for Ni, Co, Mo or Fe), and a ceramic topcoat, usually a 6-8 wt.% yttria-stabilized zirconia, or YSZ. The YSZ layer is particularly effective at insulating the underlying metallic structure; for example, a 0.13 mm thick YSZ layer can create a temperature drop of 189°C across its thickness.[1] The decrease in temperature at the metal substrate allows engines to operate at higher, more efficient temperatures. YSZ coatings are currently produced by two methods, electron beam physical vapor deposition (EB-PVD) and plasma spray. EB-PVD uses a high energy electron beam to vaporize the feed stock ceramic powder, which then condenses on the substrate atom by atom. The plasma-spray process feeds the stock powder into high velocity arc plasma, which melts the powder while propelling it toward the substrate.[1]

Plasma spraying of YSZ powders results in a very unique microstructure[2,3,4,5]. As droplets of molten YSZ strike the substrate, they spread to form a pancake or lamellar structure; coatings are made of multiple stacked lamellae. During the plasma-spray process, porosity is incorporated in the microstructure, both between and within lamellae, forming respectively interlamellar and intralamellar pores. The total porosity of the as-sprayed microstructure is typically 5-20 %[3], with the majority of this porosity comprised of interlamellar pores [6]. Upon cooling, intralamellar cracking occurs due to the thermal stresses induced within the plane of the coating. These cracks are generally parallel to the spraying direction. As each lamella solidifies, a thermal gradient develops between the relatively cool substrate and the newly sprayed lamellae. This gradient orients the YSZ grains in a direction parallel to the spraying direction, forming a columnar grain structure inside the lamellae which appears clearly on TEM micrographs[4].

As the coating is exposed to temperatures simulating the service conditions in an engine (800°-1400°C), the microstructure undergoes several morphological changes that affect its thermal and mechanical properties[5, 7]. Using small angle neutron scattering (SANS), Ilavsky et al.[6, 8] analyzed the shape of the defects in the microstructure as a function of temperature. Healing of intralamellar cracks was found to begin at temperatures as low as 800°C; these cracks continued to close as the temperature was further increased, and were fully closed at 1000°C. Ilavsky also noted that the total specific surface area of the voids decreased by about 33% for coatings heated below 1000°C[8]. The SANS results further showed that interlamellar pores begin to shrink at temperatures near 1000°C, and that shrinkage of the pores is enhanced at higher temperatures. This was confirmed through observation of specimens held at 1200°C and 1400°C for 50-hr[4].

Failure in TBC systems is generally a result of the thermal expansion mismatch between the superalloy substrate, bondcoat and the ceramic topcoat, as well as the large temperature gradient in the system during initial heat-up. Upon heating, the YSZ coating would expand if not for being constrained by the relatively cooler substrate. The resulting compressive stress state in the YSZ coating causes compaction and sintering of the coating, all of which is accelerated by the high temperatures on its surface. Upon cooling, the thermally expanded substrate returns to its original dimensions, but the ceramic coating, due to compaction and sintering, is now shorter compared to its original length. The result is that the coating develops significant in-plane tensile stresses. These tensile stresses are relieved by crack growth and crack link-up through the thickness of the coating. Failure ensues when micro-cracks link to a length great enough to result in coating spallation from the substrate.[2] The amount of sintering that takes place during heating is proportional to the magnitude of tensile stress and, therefore, the amount of cracking observed in the coating during cooling. Stress relaxation of the coatings in compression can thus be used to model the stress state experienced by the coating during the heating stage. To study the nature of these porous coatings at high-temperatures, creep tests were

also conducted on the stand-alone YSZ coatings.

Previous work by Dickinson et al. [9] has investigated the stress relaxation behavior of as-sprayed YSZ stand-alone coatings. The purpose of our present work is to study the effect of long heat-treatment times, and the concomitant change in microstructure, on the time-dependent mechanical behavior of stand-alone YSZ coatings at elevated temperatures. Our approach was to heat-treat samples at 1200°C for times of 10, 50 and 100-hrs and then subject them to stress-relaxation and creep tests at 1050°C and 1200°C. Allowing microstructural changes (such as closure of pores and microcracks) to occur prior to testing will aid in the differentiation of deformation mechanisms contributing to the coating's time-temperature properties.

## *2. Experimental Procedure*

7 wt.% $Y_2O_3$-$ZrO_2$ (YSZ) powder[a] with a particle size of 22.5±6 μm was used to fabricate the coatings. The coatings were sprayed at Ames National Laboratory[b] using the conditions listed in Table 1. The coatings were sprayed onto 250 mm long cylindrical copper substrates with an outer and inner diameter of 12.7 mm and 10.2 mm, respectively. The rod was rotated at 200 rpm during which forty vertical strokes were applied, where a stroke equals one pass down and one pass up. After spraying, the coated rods were mounted on a lathe and sectioned into 15-18 mm lengths using a diamond cutting bit, discarding 12 mm from both ends of the rod. The copper substrate was next etched from the YSZ coating with nitric acid to leave the stand-alone YSZ coating. These coatings were then heat-treated at 1200°C for 10, 50 and 100-hrs. As-sprayed coatings were also tested as a control group to compare to the heat-treated samples.

**Table 1. Parameters for Plasma-Sprayed Coatings Used in this Study.**

| | |
|---|---|
| Current | 900 Amps |
| Volts | 40.9 V |
| Stand-off Distance | 102 mm |
| Arc gas pressure | 0.21 MPa (Ar) |
| Aux gas pressure | 1.1 MPa (He) |
| Powder carrier gas | 0.35 MPa (Ar) |
| Powder feed rate | 1.5 r.p.m. |

The height, thickness and outer diameter of the stand-alone tubes were measured using a digital caliper. The bulk density, as well as total porosity was determined using Archimedes' method. [10] The theoretical density for fully dense YSZ was taken to be 6.08 g/cm$^3$. Coatings were characterized both before and after heat-treatments to monitor changes in density and total porosity.

X-ray diffraction (XRD) was used to monitor phase changes induced during heat-treatment and/or mechanical testing. XRD measurements were recorded using the Siemens Diffraktometer, Kristalloflex D500 and the Bruker-AXS GmbH 2000 software Topas. The radiation used was the average of Cu-$K_{\alpha 1}$ and Cu-$K_{\alpha 2}$. A scanning rate of 0.6°/min was used in the 2θ range from 72-76°. This range was

[a] H.C.-Starck Amperit 825.0

[b] Praxair SG-100 gun with a 730 anode, a 729 cathode and a 113 gas injector.

chosen to differentiate between the non-equilibrium tetragonal (designated currently as *t*'-$ZrO_2$) and cubic zirconia phases.[11] Sodium chloride was used as a standard with the YSZ scans to make certain any shifts associated with diffraction peaks were not the result of improper sample alignment.

The coatings were subjected to axial compressive loading using a standard load frame[c] equipped with a clam-shell type furnace[d]. Strain at 25°C was measured using strain gages[e], while high temperature strain measurements were acquired using a special extensometer[f] that had a resolution of 1 μm.

The primary compression-loading profile used to test YSZ coatings at 25°C and 1050°C was cyclic loading, with monotonically increasing peak stresses. It should be noted that for all elevated temperature mechanical tests samples were allowed to equilibrate at the desired temperature 15 minutes prior to application of any load. Stress relaxation experiments were conducted by loading the YSZ coating to 20 MPa under stroke control. The strain resulting from the applied stress, as measured by the extensometer, was then held constant for the duration of the 3-hr test. The transfer from stroke control to strain control was performed by the computer controlling the experiment and occurred in a matter of seconds after reaching 20 MPa. A 20 MPa stress corresponds to an applied load of approximately 450 N; the calibration of the load cell to 2 N was verified by hanging dead weights from the load cell. In the present work, stress relaxation results at 1050°C and 1200°C are reported. 5-hr creep tests on stand-alone YSZ coatings were also performed at temperatures of 1050°C and 1200°C under a constant stress of 20 MPa.

## 3. Results and Discussion

### 3.1 Physical Properties

The YSZ coatings were typically 15-18 mm tall, with an outer diameter of ~13 mm and a thickness of ~500μm. The density and total porosity of the coatings as a function of heat-treatment time are shown in Table 2. While a minor increase in density was observed after a 100-hr heat-treatment at 1200°C, there was not a substantial statistical difference between the as-sprayed and 100-hr heat treatment conditions.

**Table 2. Measured Density and Porosity of Samples Studied.**

| Condition | Density (g/cm$^3$) | % Total Porosity |
|---|---|---|
| As-sprayed | 5.51±0.11 | 9.3±1.9 |
| 10-hr at 1200°C | 5.53±0.09 | 9.0±1.5 |
| 50-hr at 1200°C | 5.57±0.09 | 8.4±1.6 |
| 100-hr at 1200°C | 5.60±0.08 | 8.0±1.2 |

The XRD results from 004/400 tetragonal reflections as a function of heat-treatment time are shown in Figure 1. No *c*-$ZrO_2$ phase was observed after 100-hr at 1200°C, however, some increase in the tetragonality is evident by 100-hrs. Also, no *m*-$ZrO_2$ was observed after 100-hr at 1200°C (data not shown).

[c] MTS 810 Material Test System
[d] Applied Test Systems furnace series 3320
[e] Vishay Micro-Measurements EA-06-125BZ-350 strain gages
[f] MTS series 632 High Temperature Extensometer

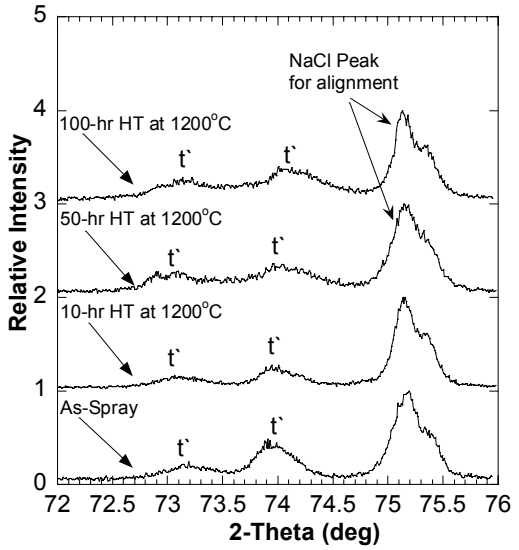


**Figure 1. Plot of the relative intensity of the YSZ samples versus 2θ in the as-sprayed and heat-treated condition. t'-$ZrO_2$ is the metastable high-yttria tetragonal phase. Note that no c-$ZrO_2$ phase was observed even after 100-hr at 1200°C.**

### 3.2 Cyclic Compression Testing

Cyclic compression tests were carried out on samples at room temperature in the as-sprayed condition and after a 50-hr heat-treatment at 1200°C to observe the stress-strain behavior of the material. Samples were taken to a maximum compressive stress of 320 MPa, or an applied force of approximately 7170 N. Figure 2 and Figure 3 presents these results. Both samples demonstrated elastic and permanent deformation with each loading/unloading cycle. Permanent deformation is attributed to compaction of the porous coating. Both samples were ~180 μm shorter in height after the experiment.

Inspection of the overall shape of the stress-strain curve in Figure 2 reveals approximately two different moduli. For example, From 0 MPa through ~160 MPa the apparent elastic modulus is 20 GPa; from 160-320 MPa, the elastic modulus is 31 GPa. This increase in modulus is attributed to densification of the coating (via microcrack closure) under larger applied loads. Similar behavior was observed during monotonic loading of YSZ by Levin et al.[12] Similar trends were observed for the sample heat-treated for 50-hr at 1200°C prior to cyclic compression testing (see Figure 3). However, the 50-hr heat-treated sample does demonstrate a higher modulus in both regimes as compared to the as-sprayed sample. This increase in both moduli can be explained by the observed increase in the densification of the coating after heat-treating (see Table 2). It should be noted that the compliance of the load frame was not subtracted from these results, and thus the modulus data presented in Figure 2 and Figure 3 is an apparent modulus. The true modulus values of the YSZ coating will be slightly higher (~5%) when the elastic strains contributed by the load frame are removed.

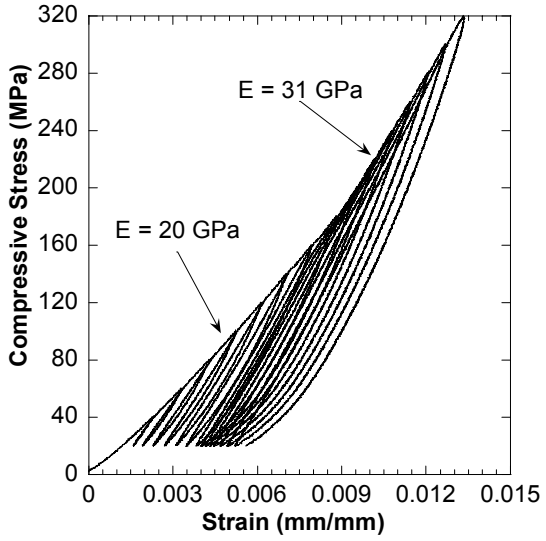


**Figure 2. Plot of compressive stress versus strain of an as-sprayed sample subjected to axial cyclic compression at room-temperature.**

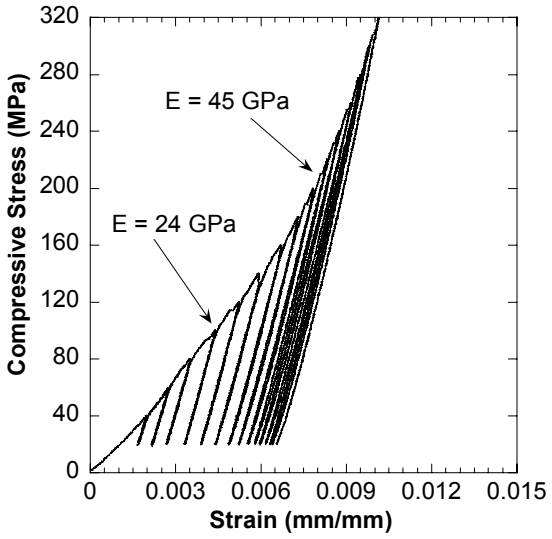


**Figure 3. Plot of compressive stress versus strain of a specimen heat-treated for 50-hr at 1200°C then subject to axial cyclic compression at room-temperature.**

### 3.3 Stress-Relaxation Behavior

Figure 4 shows the stress relaxation behavior at 1050°C of heat-treated YSZ stand-alone coatings subjected to a constant strain. The initial applied stress was 20 MPa; the strain (~0.002 to 0.008) was held constant throughout the test. The stress relaxation behavior of the YSZ coating can generally be split into two regimes: a fast relaxation regime and slow relaxation regime. For example, the as-sprayed sample shown in Figure 4 relaxed a total of 18 MPa during the 3-hr test, with ~11 MPa of the relaxation occurred within the initial 10 minutes and the remaining ~7 MPa relaxing during the remainder of the test (~170 minutes). It was observed that as heat-treatment time increased the magnitude of the relaxation of the coating decreased both in the fast and slow regime. For example, the coating heat-treated 100-hr at 1200°C prior to testing at 1050°C relaxed ~4 MPa in the fast relaxation regime and ~4 MPa in the slow relaxation regime. Thus, this coating only relaxed 8 MPa during the 3-hr hold.

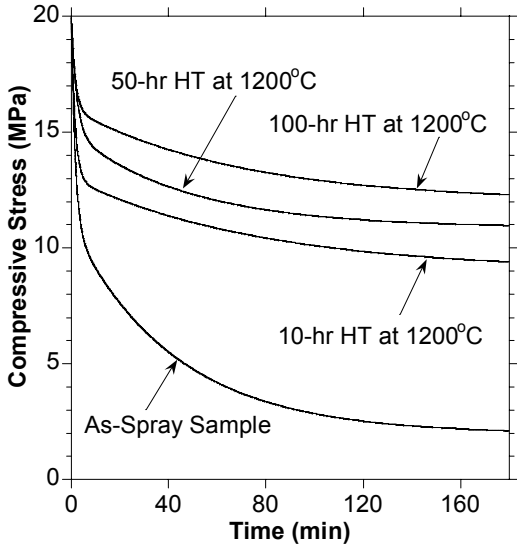


**Figure 4. Stress-relaxation response of YSZ tubes at 1050°C in the as-sprayed condition and after 10, 50, and 100-hr heat treatments at 1200°C.**

Figure 5 plots the compressive stress versus time for coatings heat-treated at 1200°C for either 10 or 50-hrs, then stress-relaxed at 1200°C from 20 MPa. For the same coating starting condition, more relaxation was observed for YSZ samples tested at 1200°C than 1050°C. For example, the as-sprayed coating fully relaxed (relaxed 20 MPa of its 20 MPa applied load) at 1200°C in 70 minutes, while at 1050°C the as-sprayed coating relaxed 18 MPa in 180 minutes. The 10-hr and 50-hr heat-treated samples relaxed 19 MPa and 18 MPa of their initial 20 MPa applied stress at 1200°C. While a 10-hr and 50-hr heat-treated sample only relaxed 9 MPa and 11 MPa at 1050°C. Similarly to the data presented in Figure 4, less relaxation of the initial stress was observed as the

heat-treatment time increased for the samples tested at 1200°C.

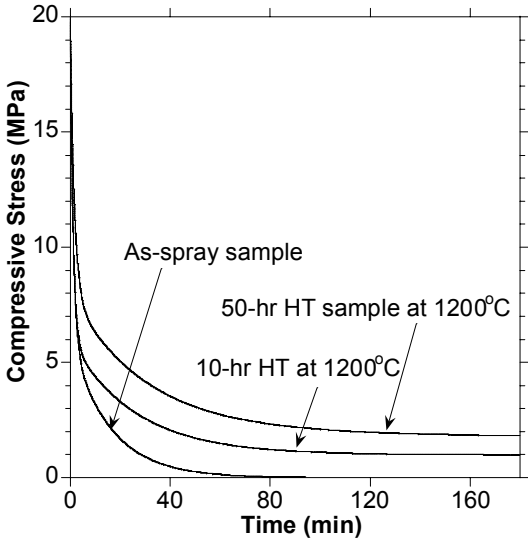


**Figure 5. Stress-relaxation response of YSZ tubes at 1200°C in the as-sprayed condition and after 10, and 50-hr heat treatments at 1200°C.**

XRD investigations were performed on the samples after stress relaxation to monitor any phase evolution that may have been caused by mechanical loads straining the lattice. These results are shown in Figure 6. Like the samples heat-treated for 50-hrs at 1200°C (i.e. no stress was applied), no c-$ZrO_2$ was observed as a result of stress relaxation from either 1050°C or 1200°C. Thus, for the time scale of the tests studied presently, the application of strain did not hasten the decomposition of the metastable tetragonal phase nor further increase the tetragonality of the *t'*-$ZrO_2$.

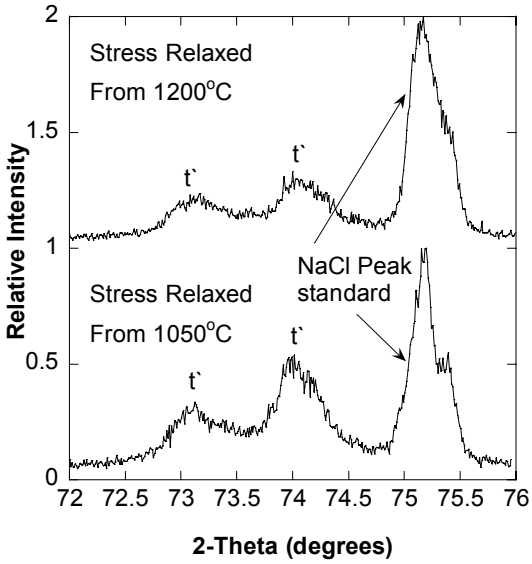


**Figure 6. X-ray data of the samples heat-treated for 50-hrs at 1200°C, then stress relaxed from 20 MPa at either 1050°C or 1200°C. The applied strain did not appear to hasten the decomposition of the metastable tetragonal phase.**

### 3.4 Creep Behavior

Creep tests were also performed on plasma-sprayed YSZ to further investigate its time-temperature dependent deformation behavior. Figure 7 shows the strain versus time results for a 5-hr test run at 1200°C under a 20 MPa applied compressive stress. Steady-state creep is reached after ~3-hrs. Similar to the stress-relaxation results, increased heat-treatment time decreases the amount of deformation that occurs in the material. The activation energy for both the 10-hr and 50-hr heat-treated samples was calculated to be ~280 kJ/mol using the steady-state creep rates at test temperatures of 1050°C and 1200°C.

The effect of increasing the heat-treatment time at 1200°C on steady-state

strain rate at 1050°C and 1200°C is presented in Figure 8. The strain rate at 1200°C is strongly affected by prior heat-treatments, decreasing from $2.6x10^{-7}$ $s^{-1}$ for samples heat-treated 10-hrs at 1200°C as compared to $1.9x10^{-7}$ $s^{-1}$ for samples heat-treated 50-hrs at 1200°C.

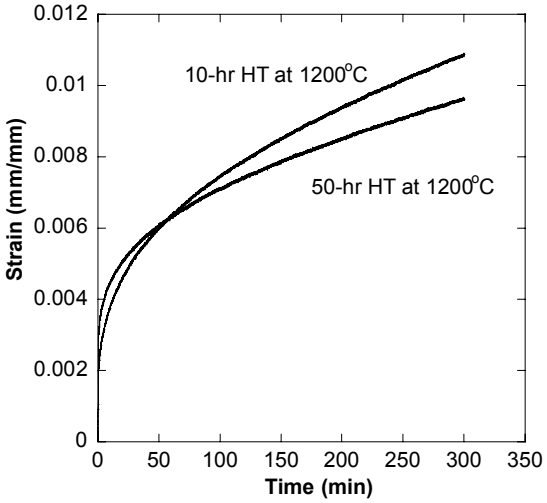


**Figure 7. Creep results for coatings heat-treated at 1200°C for 10-hr or 50-hr, then tested at 1200°C under a constant stress of 20 MPa.**

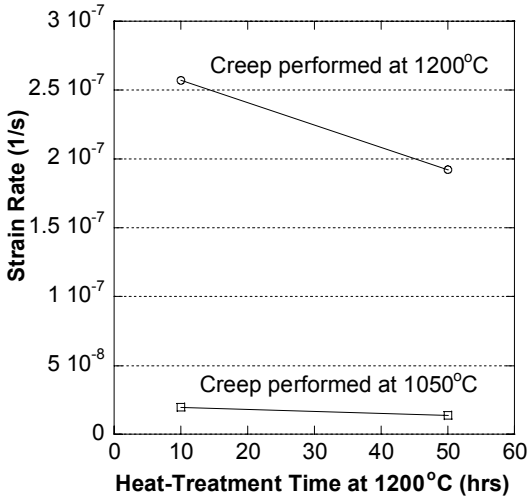


**Figure 8. Steady-state strain rates for creep tests performed at 1050° and 1200°C versus the sample heat-treat time at 1200°C.**

## *4. Conclusions*

7 wt.% $Y_2O_3$-$ZrO_2$ stand-alone coatings were heat-treated for 10, 50, and 100-hrs at 1200°C, then subject to a variety of mechanical tests at 25°, 1050°, and 1200°C. YSZ coatings were observed to densify after a 10-hr heat-treatment at 1200°C. The elastic modulus of samples heat-treated for 50-hrs at 1200°C prior cyclic compression tests increased over that of as-sprayed samples subject to identical cyclic compression testing. The increase in modulus was attributed to densification of the coating as a result of the heat-treatment. YSZ coatings that were heat-treated at 1200°C prior to stress relaxation testing relaxed far less than as-sprayed coatings. As the heat treatment time at 1200°C was increased, less relaxation of the coating was observed. Initial creep testing on plasma-sprayed YSZ demonstrated that the steady-state creep rate decreased with an increase in heat-treatment time prior to testing or a decrease in testing temperature. Overall, increasing heat-treatment time on the materials resulted in increasing resistance to deformation under applied loads at room and high temperatures. The increased resistance to deformation is likely linked to microstructural changes occurring during heat-treatment, such as microcrack healing and small pore sintering. SEM work is needed to accurately ascribe which sintering mechanisms are playing the largest roles in the overall time-temperature behavior of the material.

## 5. Acknowledgements

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