STRESS RELAXATION OF MCrAlY BOND COAT ALLOYS
AS A FUNCTION OF TEMPERATURE AND STRAIN

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ABSTRACT
The tensile stress relaxation behavior of two NiCoCrAlY bond coat alloys was examined at several temperatures between 25 and 899°C (1650°F) and at 0.1, 0.3, 0.5, and 0.8% strain. One alloy was made from Praxair's CO211 powder and served as the reference alloy, while the other was a Westinghouse-developed, oxide-dispersion-strengthened alloy. The specimens were loaded to the desired tensile strain at a constant strain rate, and the elastic modulus, yield strength, and yield strain were determined as a function of temperature for the two alloys using the stress/strain information from this loading segment. There was not a statistically significant difference in the high temperature elastic properties between the two alloys, although the oxide-dispersion-strengthened alloy tended to exhibit larger yield strengths. The relaxation data for both alloys were reduced into a form in which instantaneous stressing rate during relaxation was examined as a function of stress and temperature using an Arrhenius power-law model. The oxide-dispersion-strengthened alloy exhibited a larger stress exponent and activation energy than the reference alloy between 677-899°C (1250-1650°F), and was generally more creep resistant. The results from this study demonstrate that bond coat relaxation should occur during engine operation. Bond coatings fabricated from the oxide-dispersion-strengthened alloy have the potential to reduce residual stresses in the TBC ceramic top coating.

INTRODUCTION
The operating temperatures of air-cooled superalloy hardware in land-based gas turbine engines can be effectively reduced by application of plasma-sprayed thermal barrier coatings (TBCs). These bi-layer coating systems consist of an oxidation-resistant metallic bond coating overlaid with a thermally-insulating ceramic top coating. A typical bond coat consists of an MCrAlY alloy (where M = Ni and/or Co) applied by plasma-spraying, with NiCoCrAlY being the most commonly used bond coat alloy due to its good ductility [Stringer and Viswanathan, 1994]. The bond coating is intended to provide oxidation protection, hot corrosion resistance and, for plasma-sprayed top coats, a rough surface to which the ceramic top coat can bond. The plasma-sprayed top coat increases the durability of superalloy components by reducing their operating temperature, but these ceramic layers are susceptible to failure by spallation (due to stresses resulting from oxidation and thermal cycling).

Degradation of plasma-sprayed TBCs is a complex problem and the factors which dictate the stress state of the ceramic layer are not yet fully understood. It is generally agreed that stresses generated during engine operation are primarily due to (1) thermal expansion mismatches between the metallic and ceramic components during heating and cooling, and (2) oxidation along the metal-ceramic interface [Miller, 1987]. There are also indications that the high-temperature mechanical properties of the bond coat can play an important role in determining TBC durability [Wortman, et al., 1989, Brindley and Whittenberger, 1993, and Brindley, 1997]. Since the MCrAlY bond coat alloys become very ductile at temperatures above 700°C [Hillery, 1988], they typically relax thermally-induced stresses imposed by the superalloy substrate and ceramic top coat, which can alter the stress state of the coating system. Furthermore, it has been recognized that bond coat mechanical properties affect adhesion of the thermally grown oxide layer [Evans, 1995].

Several factors provided motivation for the present study. First, it appears that the stress relaxation behavior of the bond coat alloy exerts a strong influence on the residual stress state of the ceramic top coating. Relaxation of the bond coat at elevated temperatures results in an effective increase in the stress-free temperature, which subsequently induces larger compressive stresses in the ceramic top coat during cooling to ambient temperature. Increased stresses can accelerate fracture and spallation of the top coat. Second, the thermally-induced strains...
in the TBC system arise from thermal expansion mismatches between the three components of the TBC system; this subsequently sets up constraint-controlled (or strain-controlled) deformation. It was of interest to perform stress relaxation testing at constant strains (i.e., not constant load or stress as in a conventional creep test) to most closely mimic service conditions. Finally, incorporating an oxide-dispersion in high-temperature alloys can increase their creep or relaxation resistance [Howson, et al., 1980]. It was the intent of the present study to examine the stress relaxation behavior of a commercially-utilized NiCoCrAlY bond coat alloy (containing no oxide dispersion), and compare its response to that of a Westinghouse-developed oxide-dispersion-strengthened bond coat alloy. If the creep or relaxation resistance of an alloy is increased, then presumably the stress-free temperature and ceramic top coating residual stress will concomitantly decrease (if all other factors are equal).

EXPERIMENTAL APPROACH
Materials and Test Equipment

Two NiCoCrAlY bond coat alloys were tested. One alloy was fabricated from Praxair's CO211 thermal spray powder (nominal wt% composition Co-32Ni-21Cr-8Al-0.5Y), and served as the reference alloy in this study. The other alloy was a proprietary Westinghouse oxide-dispersion-strengthened bond coat alloy, and was designated as “ODS” alloy in the present study. Powders of both alloys were hot isostatically pressed (HIPed) into billets, and were machined into buttonhead tensile specimens. Due to the relatively large size of the buttonhead specimens, HIPing was used to fabricate the needed large billets. However, the grain structure was generally coarser for the HIPed alloys than for low pressure plasma sprayed (LPPS) alloys of the same alloy composition with grain sizes being three to four times larger. The effects of the coarser grain-sized-structure on overall bond coat mechanical performance (compared to LPPS alloys) were not addressed in the present study.

High-temperature contacting extensometers (25 mm gage length) were utilized in electronic-closed-loop strain control with electromechanical testers. Strain control testing is preferred over typical displacement controlled testing because machine compliance does not need to be measured or corrected for (this “correction” can introduce error). The stability of the extensometer (and thermal environment) produced desired setpoint strains within ±10 με at all temperatures, which was better than the ASTM recommended allowable of ± 25 με for stress relaxation testing [ASTM E328, 1993]. Button-head tensile specimens (6.35 mm diameter and 35 mm gage length) were tested. A schematic of the specimen, load train, extensometer, and furnace arrangement is shown in Fig. 1. Approximately twenty specimens of each of the two alloys were strained at a rate of 0.02% s⁻¹ to one of the four setpoint strains; the setpoint strain was then maintained and the stress relaxation was monitored as function of time. This test matrix allowed the stress relaxation behavior to be examined as a function of total tensile strain and temperature. An example of the generated data for a complete test is shown in Fig. 2.

Elastic Property and Stress Relaxation Testing

The elastic modulus, yield strength, and yield strain were determined for each specimen from the monotonically increasing strain segment (see Fig. 2). These properties for the two alloys were determined as a function of temperature using the 0.02% s⁻¹ straining rate. As a supplement, the straining-rate effect on the elastic properties of the two alloys at 788, and 899°C was examined by straining specimens at 0.2 and 0.002% s⁻¹.

Stress relaxation testing was performed at 20 (70°F), 232 (450°F), 454 (850°F), 677 (1250°F), 732 (1350°F), 788 (1450°F), 843 (1550°F), and 899°C (1650°F) at 0.1, 0.3, 0.5, and 0.8% total tensile engineering strains. The majority of specimens were tested at 0.3% strain, so much of the included analysis and interpretation involves stress relaxation at this level. Additionally, 0.8% was also of primary interest because it served as the largest test strain. The relaxation behaviors at 0.1 and 0.5% strains were also analyzed (and provided results for the elastic property determinations), but to a lesser extent.

Figure 1. Schematic of test set up. Feedback signal from the capacitance sensor was used for the strain-control testing.

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1 Tonawanda, NY.
2 Model 1380, Instron Inc., Canton, MA.
Determination of Relaxation Parameters

The deformation behavior during stress relaxation testing of both alloys as examined after the stress relaxation data from each test were reduced into a form which related the instantaneous stress relaxation rate (or a converted "strain rate") to the corresponding instantaneous tensile stress. The employed technique was the same as that described previously [Lee and Hart, 1971]. Scatter in the stress decay / time data hindered the use of common data differentiation techniques (e.g., 7 point differentiation) because it did not yield a continuous function. Therefore, a function comprised of linear exponential terms (whose time constants spanned several decades) was used to fit the experimental stress decay / time data. An example of this fit to the relaxation data is shown in Fig. 3. This function facilitated differentiation of the data and yielded stress relaxation rate as a continuous function of time and stress. The relaxation rate (\(\dot{\varepsilon}\)) was then converted to strain rate (\(\dot{\varepsilon}\)) according to:

\[
\dot{\varepsilon} = -\frac{1}{E} \varepsilon ,
\]

where E was the elastic modulus determined from the monotonically increasing strain segment. The strain rate was then related to the instantaneous stress and temperature according to the familiar Arrhenius power-law relationship

\[
\dot{\varepsilon} = W \sigma^n \exp\left(-\frac{Q}{RT}\right),
\]

where W is a constant, \(\sigma\) is stress, \(n\) is the stress-exponent, \(Q\) is the apparent activation energy, \(R\) is the gas constant, and \(T\) is absolute temperature. An example of the power-law fit is shown in Fig. 4 (temperature dependence not included in this because the results from only one specimen are shown). The parameters \(W, n,\) and \(Q\) were determined for both alloys after (1) experimental data at different temperatures were pooled, (2) the natural logarithms of both sides of Eq. 2 were taken, and (3) multi-linear regression performed. This regression analysis assumed there was one rate limiting damage or creep mechanism at all stresses and temperatures for a particular strain during stress relaxation. The values of \(n\) and \(Q\) were indicative of which dominant deformation mechanisms were active, and their dependence on temperature. These parameters for both alloys were determined and compared, and the significance of their relative values was analyzed.

RESULTS AND DISCUSSION

Elastic Properties

The average elastic modulus at room temperature was larger for CO211 than for ODS alloy, but the average moduli of the two alloys at 677°C and higher were equivalent. Comparing the data in Figs. 5 shows that the average elastic modulus of CO211 at room temperature was 200 GPa (29 Msi) while ODS alloy had an average modulus of approximately 165 GPa (24 Msi). However, the average moduli of the two alloys were equivalent at 677°C (≈ 120-140 MPa) and reduced to approximately 50% of their room temperature values at 899°C (≈ 100 MPa). An equivalent drop in elastic modulus has been reported for another NiCoCrAlY

Figure 2. Examples of typical generated stress and strain histories.

Figure 3. Example of a smoothing function used to fit stress decay data during stress relaxation.

Figure 4. Example of the power-law fit used to relate strain rate to stress.
bond coat material over the same temperature range [Strangman, 1977].

The average yield strains of the two alloys were statistically equivalent from 25 to 899°C. They were approximately 0.34-0.38% at room temperature, then dropped to approximately 0.3% at 677°C, and further decreased to approximately 0.1% of their room temperature average yield strain at 899°C, as shown in Figs. 6. The decreases in yield strain were equivalent to those reported for another NiCoCrAlY alloy over the same temperature range [Strangman, 1977].

The ODS alloy tended to have a larger average yield strengths than CO211 (see Figs. 7). The room temperature average yield strength of ODS alloy was approximately 860 MPa (124 ksi) while CO211 had a value of approximately 695 MPa (101 ksi). The yield strengths of ODS alloy remained higher than that of the CO211 at 677 and 788°C (620 MPa (90 ksi) versus 410 MPa (60 ksi), and 340 MPa (50 ksi) versus 210 MPa (30 ksi), respectively). However the average yield strengths of both alloys were equivalent (~30 to 50 MPa or 4-7 ksi) at 899°C. The drop in yield strength through 899°C was greater than that reported for the NiCoCrAlY alloy examined by Strangman [Strangman, 1977]. The yield strengths for a Ni-22Cr-10Al-0.3Y bond coat were reported to be 160 MPa (23 ksi) and 13 MPa (1.9 ksi) at 760°C (1400°F) and 982°C (1800°F), respectively [Hillery, et al., 1988]. The mechanical characterization of these elastic properties provides useful results which could be coupled with thermal conductivity data in finite element analysis to predict elastic stresses and strains in TBC systems as a function of temperature. Of course, the data would only be applicable while the strains in the bond coat alloy were less than the yield point or proportional limit.

All the elastic property data described so far were generated at a 0.02% s⁻¹ strain rate. The elastic properties of both bond coat compositions at 788 and 899°C changed when they were strained at different rates. The average elastic modulus of both bond coat materials decreased when strained at slower rates, as illustrated in Fig. 8 for CO211 at 788°C. The elastic modulus was approximately 120 GPa (18 Msi) when strained at 0.2% s⁻¹, decreased to 93 GPa (13 Msi) at 0.02% s⁻¹, and further decreased to 38 GPa (5 Msi) at 0.002% s⁻¹ (Fig. 8). The moduli similarly decreased at 899°C, with no linearity present at 0.002% s⁻¹. The ODS alloy showed identical trends. This information shows the rate at which the bond coat alloys are strained will affect their stiffness. Additionally, the reader is cautioned to recognize that some other elastic modulus measurement techniques (e.g., resonance excitation) would not be able to identify this elastic modulus dependence on strain rate at elevated temperatures. The investigation of the effect of strain rate on the stress relaxation behavior was not a primary focus of this study, so the stress relaxation data and discussion which follow pertain to specimens only loaded to the setpoint strains at a rate of 0.02% s⁻¹.

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Figure 5. Elastic modulus as a function of temperature for CO211 and ODS alloys. Standard deviation bars shown.

Figure 6. Yield strain as a function of temperature for CO211 and ODS alloys. Standard deviation bars shown.

Figure 7. Yield strength as a function of temperature for CO211 and ODS alloys. Standard deviation bars shown.
Stress Relaxation Behavior

There was a change in the stress relaxation behavior of both alloys tested at room temperature through 454°C compared to temperatures 677°C and above. The alloys showed little stress relaxation up to 454°C, while the stress relaxation was substantial at 677°C and above. An example of this is shown in Fig. 9 for CO211 at 788°C. Both alloys relaxed no more than 10% of the stress which existed at the onset of stress relaxation at ≤ 454°C for a duration to 360 minutes. Both alloys relaxed approximately 70 to 75% of the stress at 677 and 788°C, while almost 100% of the stress relaxed at 843 and 899°C. This information shows that both bond coat alloys are unable to support stresses at isothermal temperatures of 843°C and above for a relatively long duration due to relaxation. If a TBC system comprised of one of these bond coat alloys is subjected to temperatures even as low as 677°C and then cooled below it, then residual stresses will be imposed on the ceramic top coat. Lastly, because the alloys relaxed so much stress at ≥ 677°C, service (or residual) stresses in TBC systems comprising them would be limited by relaxation of the bond coat alloy and not by their elastic properties (mismatches in elastic properties may be more significant at lower temperatures where relaxation is not prevalent).

Any existing differences between the two bond coat compositions were not obvious in the stress relaxation curves (see Fig. 10). However, ODS alloy appeared to relax less than CO211 at equal temperatures (e.g., 677 and 788°C) for a duration less than 100 minutes. This subtle difference was found to be more obvious through the employment of Eq. 2, as will be described later.

The stress exponents and activation energies, described in Eq. 2, were determined for the two alloys using the stress relaxation data for each tested specimen. The stress exponents for both alloys as a function of temperature and 0.3 and 0.8% strain are listed in Tables I and II, respectively. The stress exponents for ODS alloy tended to be larger than for CO211 with the exception of 0.3% strain at 677°C.

The data for 677 through 899°C in Tables I and II were combined and the activation energies and stress exponents were determined after multi-linear regression of Eq. 2. The results of this regression are shown in Table III. Independent of the total strain during stress relaxation, ODS alloy exhibited a larger stress exponent and activation energy. The activation energies and stress exponents for CO211 were equivalent for the 0.3 and 0.8% strains (165 and 142 kJ/mol (39 and 34 kcal/mol) and 2.2 and 2.4, respectively). However they were different for ODS alloy for the 0.3 and 0.8% strains (279 and 508 kJ/mol (67 and 120 kcal/mol) and 3.1 and 4.0, respectively). This shows that the stress relaxation behavior of CO211 was independent of applied strain; however, it was dependent on the applied strain for ODS alloy. Larger stress exponents and activation energies for ODS nickel-based alloys over pure metals and solid solution-strengthened alloys are documented (Howson, et al., 1980), and the differences between CO211 and ODS alloys are consistent with these observations. These quantitative results can be readily coupled with thermal property data and used in non-linear finite element analysis to predict the strains in a ceramic top coat as a function of temperature and time.
Published activation energies and stress exponents for identical NiCoCrAlY alloys examined in the present study were not located; however, published values of these parameters for similar bond coat alloys showed that the determined stress exponents and activation energies in the present study were similar. An activation energy of 290 kJ/mol (69 kcal/mol) and a stress exponent of 3.8 were reported [Hebsur and Miner, 1987] for a Ni-20.3Co-17.3Cr-13.6Al-0.5Y alloy (for 660°C to 850°C), which are values comparable to those of ODS alloy. Brindley and Whittenberger [1993] determined stress exponents ranging from 2.4 to 7.1 and activation energies ranging from 274 to 645 kJ/mol (65 to 154 kcal/mol) for various NiCrAlY alloys tested by compressive stress relaxation tests at 700 to 1000°C (1292 to 1832°F). The activation energy and stress exponent values obtained for CO211 and ODS alloys were bracketed by the values obtained by Brindley and Whittenberger, which values they attributed to solute-controlled glide formation and dislocation-climb being concurrently operative. It is plausible to suggest that these same mechanisms were operative in CO211 and ODS alloys.

Table I. Stress Exponents (n in Eq. 2) at 0.3% Total Strain as a Function of Temperature for Both Alloys.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>CO211 n ± 1 Std. Dev.</th>
<th>ODS Alloy n ± 1 Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>677</td>
<td>4.4 ± 0.1</td>
<td>3.3 ± 0.1</td>
</tr>
<tr>
<td>732</td>
<td>3.3 ± 0.1</td>
<td>5.8 ± 0.1</td>
</tr>
<tr>
<td>788</td>
<td>3.1 ± 0.03</td>
<td>4.8 ± 0.03</td>
</tr>
<tr>
<td>843</td>
<td>2.4 ± 0.04</td>
<td>no test</td>
</tr>
<tr>
<td>899</td>
<td>2.8 ± 0.03</td>
<td>4.1 ± 0.04</td>
</tr>
</tbody>
</table>

Table II. Stress Exponents (n in Eq. 2) at 0.8% Total Strain as a Function of Temperature for Both Alloys.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>CO211 n ± 1 Std. Dev.</th>
<th>ODS Alloy n ± 1 Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>677</td>
<td>no test</td>
<td>5.8 ± 0.1</td>
</tr>
<tr>
<td>732</td>
<td>no test</td>
<td>no test</td>
</tr>
<tr>
<td>788</td>
<td>2.9 ± 0.05</td>
<td>no test</td>
</tr>
<tr>
<td>843</td>
<td>2.7 ± 0.05</td>
<td>no test</td>
</tr>
<tr>
<td>899</td>
<td>2.3 ± 0.10</td>
<td>2.7 ± 0.05</td>
</tr>
</tbody>
</table>

Table III. Stress Exponents and Activation Energies (Eq. 2) for Both Alloys Between 677 and 899°C.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CO211 ± 1 Std. Dev.</th>
<th>ODS Alloy ± 1 Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>n @ 0.3%</td>
<td>2.2 ± 0.1</td>
<td>3.1 ± 0.1</td>
</tr>
<tr>
<td>Q @ 0.3%</td>
<td>165 ± 8 kJ/mol</td>
<td>279 ± 8 kJ/mol</td>
</tr>
<tr>
<td>n @ 0.8%</td>
<td>2.4 ± 0.1</td>
<td>4.0 ± 0.1</td>
</tr>
<tr>
<td>Q @ 0.8%</td>
<td>142 ± 11</td>
<td>508 ± 14</td>
</tr>
</tbody>
</table>

The analysis using Eq. 2 showed significant differences in the deformation behavior which were not obvious in the stress relaxation curves (Fig. 10). These differences in stress exponent and activation energies are graphically illustrated in Figs. 11(a)-(b) for 0.3 and 0.8% strain, respectively. The values of the stress exponents are represented by the relative slopes of the curves (steeper slope - larger valued exponent), while the values of the activation energies were represented by the relative spacing between the parallel curves (larger spacing - larger valued activation energy). Note that there was a stress for a given temperature and strain where the creep deformations of the two alloys were equal. For stresses below this "intersection stress," ODS alloy was more creep resistant. Also note that this "intersection stress" was a function of temperature. A deformation map was constructed from this information which defined stress and temperature domains where CO211 was more creep resistant than ODS alloy and vice versa. For the 0.3 or 0.8% strain curves in Fig 12, ODS alloy exhibited better creep resistance than CO211 for stresses below the shown strain curves (for 677-899°C). This map shows ODS alloy was more creep resistant than CO211 for the typical stresses which were encountered in the present study. Ultimately, a TBC system comprised of ODS alloy is likely to transfer less residual stress onto a ceramic top coat than a TBC system utilizing CO211 assuming both the hypothetical systems have the same stress free temperature.

CONCLUSIONS

The tensile stress relaxation behavior of two NiCoCrAlY bond coat alloys were determined at several temperatures between 25 and 899°C (1650°F) at 0.1, 0.3, 0.5, and 0.8% strain. One alloy was made from Praxair's CO211 powder and served as the reference alloy, while the other was a Westinghouse-developed oxide-dispersion-strengthened alloy. There was no statistically significant difference in the high temperature elastic properties of the two alloys, although the oxide-dispersion-strengthened alloy tended to exhibit larger yield strengths. The elastic modulus for both alloys decreased by about 50% between 25 and 899°C. The yield strengths and yield strains decreased by approximately 90% over the same temperature range. The amount of recovered stress for a duration up to ≈ 6 h increased with higher test temperature for both alloys: less than 10% of the maximum achieved stress was recovered up to 454°C (850°F); approximately 70 to 75% at 677°C (1250°F); and almost 100% between 788°C (1450°F) and 899°C. The relaxation data was reduced into a form in which instantaneous stressing rate during relaxation was examined as a function of strain and temperature using an Arrhenius power-law model. The oxide-dispersion-strengthened alloy exhibited a larger stress exponent and activation energy than the reference alloy between 677-899°C, and was generally more creep resistant.
Figure 11. Comparison of alloy creep or relaxation behavior as a function of temperature for (a) 0.3% strain, and (b) 0.8% strain.

Figure 12. Domains representing where one alloy was more resistant to relaxation than the other.

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REFERENCES