

Optimization of the NiCrAl-Y/ZrO₂-Y₂O₃ Thermal Barrier System

(NASA-TM-86905) OPTIMIZATION OF THE
NiCrAl-Y/ZrO₂-Y₂O₃ THERMAL BARRIER SYSTEM
(NASA) 24 p HC A02/MF A01 CSCI 11F

N85-15878

Unclas

G3/26 13456

Stephan Secura ✓
Lewis Research Center
Cleveland, Ohio



Prepared for the
Eighty-seventh Annual Meeting of the American Ceramic Society
Cincinnati, Ohio, May 5-9, 1985

NASA

OPTIMIZATION OF THE NiCrAl-Y/ZrO₂-Y₂O₃ THERMAL BARRIER SYSTEM

Stephan Stecura
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

SUMMARY

The effects of bond and thermal barrier coating compositions, thicknesses, and densities on air plasma spray deposited NiCrAl-Y/ZrO₂-Y₂O₃ life were evaluated in cyclic furnace oxidation tests at temperatures from 1110 to 1220 °C.

Thermal barrier system lives are very sensitive to temperature and compositions. A 110 °C temperature increase decreased life by a factor of about 17. Increases of aluminum in the bond coating from about 6 to 11 or 19 wt % were very detrimental to life for bond coatings containing 25 and 35 wt % chromium.

Increase of chromium concentration from about 16 to about 36 wt % in the bond coating was very beneficial. It has been established that yttrium concentration in the bond coating, yttria concentration in zirconia thermal barrier coating, and the densities of both coatings pass through optima while it was not determined whether the thicknesses of both coatings, the chromium and the aluminum concentrations in the bond coatings pass through optima for this particular test.

An empirical relation was developed for the experimental data. The equation gives thermal barrier system life as a function of the parameters studied within the limits imposed in this study.

INTRODUCTION

Development and evaluation of thermal barrier coatings expanded very rapidly after it was shown that a two layer thermal barrier system is feasible (refs. 1 and 2). Since that time, extensive evaluations of NiCrAl-Y/ZrO₂-Y₂O₃ in particular have been carried out (refs. 3 to 18).

Although optimization studies were done on the NiCrAlY bond coatings (refs. 7 and 8), these studies did not resolve whether it would be more beneficial to use high chromium, low aluminum, and low yttrium concentrations in the bond coating or just the opposite. It was suggested in reference 8 that for yttria-stabilized zirconia to have long lives, the bond coating probably should contain more than 20 wt % of chromium, more than 5 wt % of aluminum, and probably less than 0.3 wt % of yttrium. However, such bond coating compositions were not evaluated. In addition, the published data are such that it would be difficult to quantitatively predict the behavior of any thermal barrier system when the temperature, compositions, thicknesses, and densities are changed.

To resolve these problems, an extensive optimization of air-plasma sprayed NiCrAlY bond coating compositions was carried out with ZrO₂-6.1 wt % Y₂O₃ and ZrO₂-8.0 wt % Y₂O₃ thermal barrier coatings. In addition, the effects of bond and thermal barrier coating thicknesses and densities on thermal barrier system

(TBS) life were also determined. All of these evaluations were done in cyclic furnace oxidation tests at temperatures from 1110 to 1220 °C. The data obtained in this study made it possible to develop an empirical relation that can be used to predict changes in TBS life due to changes in the parameters mentioned above.

The late Jack E. Brown's dedication and expertise in plasma-spray deposition made it possible to obtain the reproducibly desired specimens vital to this investigation.

EXPERIMENTAL PROCEDURE

Chemical compositions of NiCrAlY bond coatings and ZrO₂-Y₂O₃ or YSZ thermal barrier coatings are reported in table I. Two kinds of thermal barrier coatings were used, the standard purity denoted by ZrO₂-Y₂O₃ or YSZ, and nuclear grade denoted by ZrO₂-Y₂O₃ (N) or YSZ (N). The nominal particle size distributions in all powders were 90 percent minimum of -200 mesh (74 μ diameter) to 85 percent minimum of +325 mesh (44 μ diameter). Conventionally cast MAR-M-200+Hf was used as a substrate material in all cases and its composition is reported in table I. The values reported in table I are the maximum impurity concentration values that have been detected. All compositions throughout this report are expressed in wt %.

Flat test specimens (about 2.5 by 1.25 by 0.25 cm) with all corners and edges rounded to about 0.25 cm diameter were used. Specimen surfaces were grit-blast cleaned with fresh high-purity alumina. Within 5 min of cleaning, the NiCrAlY bond coating was applied with a Plasmadyne spray gun.¹ The YSZ coating was applied within 20 min of completing the bond coating. All plasma-spray depositions were done in open air. An attempt was made to maintain the plasma-spray gun at 90° to the surface being sprayed where possible. Further plasma sprayed coating deposition details are given in table II. To obtain greater thermal barrier coating thickness uniformities and to make sure that the coatings were of desired thicknesses, specimens were plasma spray coated on only one surface at a time and the thickness measured with a micrometer. Sometimes it was necessary to build up the coating thickness through additional plasma spray deposition. In cases where the bond coating thickness on any surface exceeded 0.023 cm, such specimens were rejected. When the thermal barrier coating thickness exceeded 0.043 cm, the thermal barrier coating thickness on part or all of a particular specimen surface was reduced to between 0.036 and 0.041 cm through grinding with garnet abrasive paper. This approach has been found to be a requirement to obtain acceptable test life reproducibility. Specimens were tested in cyclic furnace in air at test temperatures of 1110, 1160, and 1220 °C. The cycle consisted of a 9-min heat-up, 60-min at temperature, and 60-min of cooling to about 300 °C. The temperature in the furnace, measured with a Pt-Pt/13 percent Rh thermocouple, was estimated to be accurate to about ±10 °C at 1220 °C. Specimens were removed from the furnace between 350 and 400 °C after 1, 2, 3, 4, and 12 cycles and every 12 cycles thereafter for inspection. The specimens were cooled to room temperature, weighed, and

¹Trade names or manufacturers' names are used in this report for identification only. This usage does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

specific weight gains (mg/cm^2) calculated. Whenever the specific weight gain at failure for anyone of the three or more replicate specimens varied by more than ± 6 percent, such a specimen was rejected. Wide variations in specific weight gains at failures are generally due to abnormal variations in coating thicknesses and/or at least partially to variations in the densities of both coatings. Because of their greater ΔT , inspection cycles are more severe than standard test cycles. Tests were continued until failure - the formation of a crack in the YSZ coating visible to the unaided eye.

The densities of the bond and thermal barrier coatings were determined in the following manner. Plasma sprayed sheets (4 by 6 cm) of 0.018 to 0.022 cm thick bond coating or 0.036 to 0.041 cm thermal barrier coating were weighed to the nearest mg. The thickness of the sheet was measured with a pin micrometer at at least 100 places. The area of the sheet was measured with a planimeter and the density calculated by:

$$\rho = \frac{W}{t_{\text{ave}} A} \quad (1)$$

where

ρ density, g/cm^3

W weight of the sheet, gm

t_{ave} average thickness, cm

A area, cm^2

RESULTS

A cyclic furnace was used in this study because the test conditions (temperature in particular) could be rigidly controlled and greater numbers of specimens could be tested under identical conditions. It was already reported (refs. 1, 7 to 9, and 13) that the thermal barrier system that had the longest life in a cyclic furnace also had the longest life in Mach 0.3 and Mach 1.0 burner rigs and the failure initiation is the same in the furnace as in the burner rigs. The data obtained in this study show that it is possible to reproduce thermal barrier system data through control of coating deposition and test parameters. Reproducibility here is defined as percent scatter of the individual results from the average of two or more specimens of the same compositions and condition. The reproducibilities in the number of cycles to failure for sets of three to eight specimens for thermal barrier systems that failed in 100 1-hr cycles or less were about ± 10 percent. For those systems that failed in more than 1000 1-hr cycles, the reproducibilities were about ± 5 percent.

The data in figures 1 to 3 for test temperatures of 1110, 1160, and 1220 $^{\circ}\text{C}$, respectively, show the effects of yttrium concentration on cycles to failure for variations in aluminum and chromium concentrations in the bond coating and yttria concentration in YSZ. The curves in these figures were arbitrarily fit by hand.

Increasing temperature from 1110 to 1220 °C decreased the lives of Ni-35.0Cr-5.9Al-0.95Y/ZrO₂-Y₂O₃ and Ni-25.5Cr-6.2Al-0.75Y/ZrO₂-Y₂O₃ thermal barrier systems by about 17 times. Note that these two test systems have 0.95 or 0.75 Y, about 35 or 25 Cr and about 6 Al in the bond coating, that ZrO₂-6.1Y₂O₃ is superior to ZrO₂-8.0Y₂O₃, and that the test lives for these systems are about three times longer than the test lives for the Ni-16.2Cr-5.9Al-0.15Y/ZrO₂-Y₂O₃ system.

As aluminum concentration in the bond coating of the above two best systems is increased from about 6 to 19 wt %, the system lives are decreased by about 15 times at 1110 °C. On the other hand, at lower bond coating yttrium levels, aluminum content has a much smaller effect. At the low bond coating aluminum level the yttrium effect is much greater than that of chromium (fig. 1) but at higher aluminum levels the benefits of Cr and Y additions tend to be mitigated by aluminum.

The data in figure 1 show that each of the bond coatings in the thermal barrier systems studied has its own optimum yttrium concentration. From the data in figure 1 it may be concluded that the optimum yttrium concentrations in the nominal Ni-16Cr-6Al, Ni-25Cr-6Al, and Ni-35Cr-6Al bond coatings should be in the neighborhood of 0.15, 0.75, and 0.95 wt %, respectively. However, the optimum yttrium concentration values in the Ni-25Cr-6Al and Ni-35Cr-6Al bond coatings could be slightly different if additional data were available for the 0.3 to 0.9 wt % yttrium concentrations in the bond coatings. Finally, it should be noted that the optimum yttrium concentration in the bond coating changes with chromium concentration (figs. 1 to 3).

On the basis of the data in figures 1 to 3 it can be concluded that the 6.1Y₂O₃-stabilized zirconia is slightly better than the 8.0Y₂O₃-stabilized zirconia coating. This is further supported by the data obtained at 1110 °C in figure 4. The data in figure 4 show that the maximum thermal barrier system life is obtained when the concentration of yttria in zirconia is about 6 wt %. The data in figure 4 are similar to those reported in reference 7. However, the data in figure 4 were obtained for the thermal barrier systems whose bond and thermal barrier coatings were plasma-spray deposited at 400 and 600 A while those in reference 7 were deposited at 350 and 550 A, respectively. The data in figure 4 show that ZrO₂-Y₂O₃ thermal barrier coating has an optimum yttria concentration at which the longest life is obtained.

The life of the thermal barrier system is affected by the bond and thermal barrier coating thicknesses. Increasing the thickness of the bond coating from about 0.012 to 0.030 cm in Ni-25.7Cr-5.9Al-0.30Y/ZrO₂-8.0Y₂O₃ or in Ni-16.6Cr-5.9Al-0.07Y/ZrO₂-8.0Y₂O₃ increased lives by about 2.5 times at 1110 °C (fig. 5). The data in figure 5 are supported by the data obtained for Ni-35.9Cr-5.6Al-0.85Y/ZrO₂-8.0Y₂O₃ thermal barrier system. When the bond coating thickness in this last system was increased from about 0.022 to 0.035 cm and then to 0.045 cm, life in 1-hr cycles at 1170 °C increased from 301 to 405 to 440 cycles, respectively. The bond coating thicknesses in figure 5 were selected because it is believed that the thermal barrier systems having bond coatings of less than 0.010 cm should not be used for such systems fail very rapidly and not more than 0.030 cm because of configurational limitations of the engine hot components. The data in figure 5 indicate that it is not possible to determine whether the effect of bond coating thickness on thermal barrier system life passes through an optimum.

14)

The data in figure 5 show that increasing the thickness of the 6.1Y₂O₃- or 8.0Y₂O₃-stabilized zirconia coating from about 0.025 to 0.085 cm in Ni-35.4Cr-6.2Al-0.22Y/ZrO₂-8.0Y₂O₃ system, decreases life by about two times. To determine whether the thermal barrier coating thickness passes through an optimum, additional data between 0.005 and 0.025 cm are required.

The densities of the bond and thermal barrier coatings also have very significant effects on the thermal barrier system life (figs. 6 and 7). Both coatings have optimum densities at which maximum life is obtained. When the bond coating density is increased from the optimum value by about 4 percent, the Ni-35.9Cr-5.6Al-0.85Y/ZrO₂-8.0-Y₂O₃ system life decreased by about 35 percent at 1170 °C while a decrease of about 2.5 percent in the optimum density decreased life by about 30 percent. It was found that when Ni-35.0Cr-5.0Al-0.95Y and Ni-25.5Cr-6.2Al-0.75Y bond coatings are air-plasma-spray deposited, oxygen concentrations increased from about 250 ppm in as-received powders to about 2200 ppm in the deposits. The results from chemical analysis of residues extracted by methanol-5 vol % bromine from plasma-spray deposited bond coatings showed that these residues contained aluminum, chromium, yttrium, and nickel. Since there was no observable increase in nitrogen and carbon during plasma-spray deposition, then the extracted residues were oxides.

The effect of thermal barrier coating density on the thermal barrier system life is not as great as that of the bond coating density. Increasing or decreasing the density of 6.0Y₂O₃- or 8.0Y₂O₃-stabilized zirconia coating in the Ni-35.0Cr-5.9Al-0.95Y/ZrO₂-Y₂O₃ system by about 3 percent from the optimum density value, decreases the life by about 12 percent.

The data in figure 8 show that the densities of the standard and nuclear grade ZrO₂-Y₂O₃ coatings plasma-spray deposited under the same conditions are quite different. The data in figure 8 show that the density increases linearly with the logarithm of current used during plasma spray deposition. The straight lines in figure 8 were drawn according to least squares method. This difference in densities might be due to many factors. The data in table 1 show that the concentrations of Ca, Hf, Fe, Mg, Ni, Si, and Ti in as-received nuclear grade powders are significantly lower than in the as-received standard purity powder. Nuclear grade powders had an average particle diameter of about 45 μ as compared to an average particle diameter of about 60 μ in the standard purity powders (fig. 9). Examination of both powders by scanning electron microscopy showed that the nuclear grade powder particles are more porous than the standard purity particles (fig. 9) although both powders were prepared by the same method. Probably due to these differences between these two powders, the nuclear grade powder particles were more fully melted and were more fluid, consequently higher densities (fig. 10).

The plasma-sprayed nuclear grade coatings had a greater number of very fine cracks (fig. 10) than the standard purity coatings. In fact, a very extensive scanning electron microscopy examination of the plasma-spray deposited standard purity coating had to be done in order to find such cracks. Nuclear grade coatings had more large grains and more columnar structures within the grains than the standard purity coatings.

The effect of plasma-spray powder used during deposition of standard and nuclear grade ZrO₂-Y₂O₃ or the densities of ZrO₂-Y₂O₃ on the thermal barrier system are shown in figure 11. These data show that the standard and nuclear

grade $ZrO_2-Y_2O_3$ plasma-spray deposited coatings of about the same densities have lives that are different by about 15 percent at optimum plasma-spray currents (figs. 8 and 11).

DISCUSSIONS

Statistical regression analysis of the data set consisting of 225 points was used to derive an empirical equation to predict the change in the thermal barrier system life as a function of parameters studied and within the imposed limits. Only the highest and the lowest cycles to failure values for each set of replicate specimens were used in regression analysis. Three equations were applied to experimental data:

$$\ln(C) \propto \ln(X_i) \quad (2)$$

$$\ln(C) \propto X_i \quad (3)$$

$$C \propto X_i \quad (4)$$

where

C cycles to failure

X_i parameter evaluated in this study

Evaluations were done on centered and non-centered data values. The best fit for the data presented in this study was obtained when equation (3) was used. The semilogarithmic equation describing the experimental data is given below:

$$\begin{aligned} \ln(C) = & -39.3970 + 0.02575 (X_1 - \bar{X}_1) + 0.00579 (X_1 - \bar{X}_1)^2 - 0.19732 (X_2 - \bar{X}_2) \\ & - 0.74574 (X_3 - \bar{X}_3) - 1.4614 (X_3 - \bar{X}_3)^2 + 1.3398 (X_3 - \bar{X}_3)^3 \\ & - 0.12605 (X_4 - \bar{X}_4) + 102.602 (X_5 - \bar{X}_5) - 4777.3 (X_5 - \bar{X}_5)^2 \\ & - 487564 (X_5 - \bar{X}_5)^3 - 11.1903 (X_6 - \bar{X}_6) - 3.4239 (X_7 - \bar{X}_7)^2 \\ & - 3.2284 (X_7 - \bar{X}_7)^3 - 3.8467 (X_8 - \bar{X}_8)^2 - 0.07165 (X_1 - \bar{X}_1)(X_3 - \bar{X}_3) \\ & + 0.10492 (X_3 - \bar{X}_3)(X_4 - \bar{X}_4) + 0.02519 [(X_3 - \bar{X}_3)(X_9 - \bar{X}_9)]^2 \\ & - 0.03150 [(X_1 - \bar{X}_1)(X_3 - \bar{X}_3)]^2 + 0.00337 [(X_1 - \bar{X}_1)(X_3 - \bar{X}_3)]^3 \\ & + 729.4 (X_8 - \bar{X}_8)^2 (X_7 - \bar{X}_7) + 52,595.7/T, K \end{aligned} \quad (5)$$

where

- C cycles to failure;
 X_1 concentration of chromium in the bond coating, wt %
 X_2 concentration of aluminum in the bond coating, wt %
 X_3 concentration of yttrium in the bond coating, wt %
 X_4 concentration of yttria in zirconia coating, wt %
 X_5 bond coating thickness, cm
 X_6 thermal barrier coating thickness, cm
 X_7 bond coating density, gm/cm³
 X_8 thermal barrier coating density, gms/cm³
 X_9 concentration of nickel in the bond coating, wt %
T absolute temperature, K

All of the parameters except "Ln (C)" and "T" were centered. The centered values are listed below:

$$\bar{X}_1 \quad 31.3840 \text{ wt \%}$$

$$\bar{X}_2 \quad 7.3032 \text{ wt \%}$$

$$\bar{X}_3 \quad 0.5956 \text{ wt \%}$$

$$\bar{X}_4 \quad 7.1809 \text{ wt \%}$$

$$\bar{X}_5 \quad 0.0197 \text{ cm}$$

$$\bar{X}_6 \quad 0.0404 \text{ cm}$$

$$\bar{X}_7 \quad 6.9955 \text{ gms/cm}^3$$

$$\bar{X}_8 \quad 5.1835 \text{ gms/cm}^3$$

$$\bar{X}_9 \quad 60.7170 \text{ wt \%}$$

The standard deviation in $\ln(C)$ is 0.0949 or approximately ± 10 percent and the R-squared is 99.3 percent. The parameters in equation (5) are centered about their respective means because non-centering brings about high correlation of several terms in the equation and this increases the standard deviation and reduces the R-squared value. The data in figures 12 and 13 show the agreements between calculated and experimentally determined values for the effect of bond coating yttrium concentration and the effects of bond and thermal barrier coating densities on thermal barrier system life, respectively. Disagreement between the calculated and experimentally determined values in these two figures could be due to many factors. For example, in order to be able to plot the experimental data it was assumed that bond coatings with different yttrium concentrations were nominally Ni-35Cr-6Al. The actual chromium concentration ranged between 34.6 and 36.2 wt % and aluminum concentration ranged between 5.8 and 6.6 wt %. It was also assumed that the bond coatings were nominally 0.020 cm thick and the thermal barrier coatings were 0.038 cm. Actually, the bond coating thicknesses ranged between 0.018 and 0.022 cm and thermal barrier coatings ranged between 0.036 and 0.043 cm. Furthermore, the bond and thermal barrier coatings were not of uniform thicknesses. Thus, the presence of locations with thinner bond coatings was very likely. Such a condition would lead to a more rapid failure as the bond coating thickness data in this study suggest. Although an attempt was made to increase the thermal barrier coating thickness uniformity it is believed that areas of thicker coatings than 0.043 cm and thinner than 0.036 cm were present. Nonuniformity in thickness of the thermal barrier coating is also believed to affect the life. Furthermore, since the powders were plasma-spray deposited by hand operation, the distance between the gun and the specimen surface was not constant. Thus, the density of the thermal barrier coating even on the same surface of the specimen could vary at different locations.

Equation (5) can readily be simplified for each thermal barrier system studied in order to show how the three optimum parameters identified in this study affect thermal barrier system life. For Ni-35.0Cr-5.9Al-0.95Y/ZrO₂-6.1Y₂O₃ thermal barrier system, the simplified equations relating: (1) thermal barrier system life to yttrium concentration in the bond coating (eq. (6)); (2) thermal barrier system life to bond coating density (eq. (7)); and (3) thermal barrier system life to thermal barrier coating density (eq. (8)) are:

$$\ln(C) = 6.034 + 1.50621 x_3^3 - 4.55929 x_3^2 + 4.19715 x_3 \quad (6)$$

$$\ln(C) = 941.0512 - 3.22840 x_7^3 + 64.32892 x_7^2 - 425.71115 x_7 \quad (7)$$

$$\ln(C) = -53.5675 - 2.26080 x_8^2 + 23.43862 x_8 \quad (8)$$

The optimum yttrium concentration in the bond coating and the optimum densities of the two coatings in the thermal barrier system can readily be determined by differentiating the above equations and then letting $dC/dx = 0$ or by substituting various corresponding values for "x" in any of the above equations and plotting the data. Using these approaches the optimum values were obtained and are reported in table III. For the Ni-35.0Cr-5.9Al-Y bond coating, the optimum yttrium concentration seems to be between 0.7 and 0.9 wt %. This value is slightly lower than the value one might have been tempted to accept on the basis of the data in figures 1 to 3. There is a very good agreement between

the calculated and the experimentally determined values for the bond and thermal barrier coating densities.

Equation (5) can readily be reduced to an Arrhenius type equation simply by keeping all parameters constant except the temperature. Thus, one obtains:

$$\ln(C) = A + Q/RT \quad (9)$$

where

- A constant
- Q activation energy
- R gas constant
- T absolute temperature

Plotting $\ln(C)$ versus $1/T$, "A" and "Q" can be calculated. In figure 14, "A" is the intercept and "Q/R" is the slope of the line. The values obtained from the slopes of the lines in figure 14 ranged between 50 379.0 and 55 502.0. The lines in figure 14 were drawn according to the least squares method. These "Q/R" values calculated from the data in figure 14 are in agreement with the 52 595.7 value obtained in equation (5). Multiplying of "Q/R" values by "R" (where $R = 1.987$ cal/mole) gives the activation energy for the degradation or failure of the thermal barrier system. One might be tempted to utilize the above activation energy value to predict the process or the failure mechanism of the NiCrAl-Y/ZrO₂-Y₂O₃ system. It is true that this activation energy could principally be associated with the oxidation of the bond coating. In the oxidation of such complex systems as air-plasma sprayed NiCrAlY, a single rate controlling step may not exist. A complex sequence of oxidation steps at various locations is probably involved.

Finally, the data in figure 14 suggest that equation (9) can be used to calculate the life of a thermal barrier system under furnace test conditions as a function of temperature.

CONCLUDING REMARKS

An extensive study has been carried out to determine the effects of temperature and bond and thermal barrier coating compositions, thicknesses, and densities on the life of plasma-spray deposited NiCrAl-Y/ZrO₂-Y₂O₃ thermal barrier systems in air. Small MAR-M-200+Hf coupons, completely coated, were evaluated in cyclic furnace tests between 1110 and 1220 °C. Utilizing the data obtained in this study, it was possible to:

1. Establish that the yttrium in the air-plasma sprayed bond coating, yttria in the thermal barrier coating, and densities of both coatings have optima at which maximum life is attainable. It was not determined whether the thicknesses of both coatings and chromium and aluminum concentrations in the bond coating pass through optima. If these four parameters do pass through optima, then the optimum bond coating thickness is above 0.045 cm, the optimum thermal barrier thickness below 0.025 cm, the optimum chromium concentration is

at or above 35 wt %, while the optimum aluminum concentration is at or below 6 wt %.

2. Develop an empirical equation to predict changes in thermal barrier system life as a function of temperature, and bond and thermal barrier coating compositions, thicknesses, and densities within the ranges studied.

3. Thermal barrier system life is favorably affected by increases of yttrium from 0.15 to 0.95 wt % and chromium from 16 to 35 wt %. Increases in aluminum from 6 to 19 wt % are very detrimental.

4. The thermal barrier system having the longest life is Ni-35.0Cr-5.9Al-0.95Y/ZrO₂-6.1Y₂O₃ closely followed by Ni-35.0Cr-5.9Al-0.95Y/ZrO₂-8.0Y₂O₃ and Ni-25.5Cr-6.2Al-0.75Y/ZrO₂-6.1Y₂O₃ system.

REFERENCES

1. S. Stecura, : "Two-Layer Thermal Barrier Coating for Turbine Airfoils - Furnace and Burner Rig Test Results." NASA TM X-3425, 1976.: "Two-Layer Thermal Barrier Coating for High Temperature Components," Am. Ceram. Soc. Bul., 56 (12) 1082-1085 (1977).
2. S. Stecura, and C.H. Liebert: "Thermal Barrier Coating System." U.S. Patent No. 4,055,704, Oct. 1977.
3. P.E. Hodge, S. Stecura, M.A. Gedwill, I. Zaplatynsky, and S.R. Levine, "Thermal Barrier Coatings: Burner Rig Hot Corrosion Test Results," NASA TM-79005; DOE/NASA/2593-78/3, 1978.
4. C.A. Andersson, S.K. Lau, R.J. Bratton, S.Y. Lee, K.L. Rieke, J. Allen, and K.E. Munson, "Advanced Ceramic Coating Development for Industrial/Utility Gas Turbine Applications," NASA CR-165619, DOE/NASA/0110-1, 1982.
5. R.A. Miller, "Analysis of the Response of a Thermal Barrier Coating to Sodium- and Vanadium-Doped Combustion Gases," NASA TM-79205, DOE/NASA/-2593-79/7, 1979.
6. I. Zaplatynsky, "Reactions of Yttria-Stabilized Zirconia with Oxides and Sulfates of Various Elements," NASA TM-78942, DOE/NASA/2593-78/1, 1978.
7. S. Stecura, "Effects of Compositional Changes on the Performance of a Thermal Barrier Coating System," NASA TM-78976, 1979.
8. S. Stecura, "Effects of Yttrium, Aluminum, and Chromium Concentrations in Bond Coatings on the Performance of Zirconia-Yttria Thermal Barriers," NASA TM-79206, 1979.
9. S. Stecura, "Performance of Two-Layer Thermal Barrier Systems on Directionally Solidified Ni-Al-Mo and Comparative Effects of Alloy Thermal Expansion on System Life," NASA TM-81604, 1980.
10. S. Stecura, "Effects of Plasma Spray Parameters on Two-Layer Thermal Barrier Coating System Life," NASA TM-81724, 1981.

11. I. Zapiatynsky, "Performance of Laser-Glazed Zirconia Thermal Barrier Coatings in Cyclic Oxidation and Corrosion Burner Rig Tests," Thin Solid Films, 95 275-284 (1982).
12. R.A. Miller, J.L. Smialek, and R.G. Garlick; pp. 241-253 in Science and Technology of Zirconia, Vol. 3. Edited by N. Claussen, M. Ruhle, and A.H. Heuer. American Ceramic Society, Columbus, OH, 1981.
13. R.A. Miller, and C.E. Lowell, "Failure Mechanisms of Thermal Barrier Coatings Exposed to Elevated Temperatures." Thin Solid Films, 95 265-273 (1982).
14. R.A. Miller, "An Oxidation Based Model for Thermal Barrier Coating Life," J. Am. Ceram. Soc., 67 [8] 517-521 (1984).
15. N.R. Shankar, C.C. Berndt, and H. Herman, "Phase Analysis of Plasma-Sprayed Zirconia-Yttria Coatings," Ceram. Eng. Sci. Proc. 4 [9-10] 784-791 (1980).
16. C.A. Andersson, J. Gregg, and T.K. Gupta, "Stabilization and Transformation of Tetragonal Zirconia," Westinghouse R&D Center 83-106-CERAM-PI, Feb. 10, 1983.
17. M.A. Gedwill, "Improved Bond Coatings for use with Thermal Barrier Coatings," NASA TM-81567, DOE/NASA/2593-18, 1980.
18. M.A. Gedwill, "Burner Rig Evaluation of Thermal Barrier Coating systems for Nickel-Base Alloys," NASA TM-81684, DOE/NASA/2593-26, 1981.

TABLE I. - COMPOSITIONS OF SPRAY POWDERS AND SUPERALLOY SUBSTRATE

Element	Bond coating, NiCrAlY	Composition, wt %				Substrate MAR-M-200+Hf
		Thermal barrier coating				
		ZrO ₂ -6.1Y ₂ O ₃ ^a	ZrO ₂ -8.0Y ₂ O ₃ ^a	ZrO ₂ -8.4Y ₂ O ₃ ^b	ZrO ₂ -8.4Y ₂ O ₃ ^b	
Al	C5-19	0.014	0.010	0.010	0.010	5.17
B	0.005	<.005	<.005	<.001	<.001	.020
Ba	<.001	<.001	<.001	<.001	<.001	<.001
C	.007	(d)	(d)	(d)	(d)	.140
Ca	<.001	.063	.077	.035	.018	<.001
Co	.045	<.005	<.005	<.005	<.005	10.16
Cr	C16-37	<.001	<.005	.005	<.001	8.45
Cu	.019	.002	.005	.005	.005	<.100
Fe	.027	.032	.043	.010	.008	.410
Hf	.067	1.68	1.72	.050	.6	2.02
K	<.001	<.001	<.001	<.001	<.001	<.001
Li	<.001	<.001	<.001	<.001	<.001	<.001
Mg	<.001	.021	.031	.025	.025	<.001
Mn	.010	<.001	<.001	<.001	<.001	<.001
Mo	<.010	<.005	<.005	<.005	<.005	.005
N ₂	.032	(d)	(d)	(d)	(d)	(d)
Na	<.001	<.001	<.001	<.001	<.001	<.001
Nb	.045	<.005	<.005	<.005	<.005	1.13
Ni	Major	.021	.029	<.001	<.001	Major
O ₂	.025	Major	Major	Major	Major	(d)
P	.002	(d)	(d)	(d)	(d)	(d)
S	.004	(d)	(d)	(d)	(d)	(d)
Si	.074	.061	.059	.026	.010	<.200
Sr	.010	<.010	<.010	<.010	<.001	(d)
Ta	<.050	<.020	<.020	<.020	<.020	(d)
Ti	.026	.042	.046	<.010	<.010	2.20
V	.025	<.001	<.001	<.001	<.001	<.001
W	.010	<.05	<.05	<.05	<.05	11.68
Y	C0.70-1.60	Major	Major	Major	Major	(d)
Zn	<.050	<.005	<.005	<.005	<.005	<.050
Zr	.012	Major	Major	Major	Major	.080

^aStandard purity.

^bNuclear grade.

^cAluminum, chromium, and yttrium concentrations in NiCrAlY bond coatings are specified in the experimental data.

^dNot determined.

TABLE II. - PLASMA SPRAY COATING DEPOSITION PARAMETERS^a

Operating parameters	NiCrAlY	ZrO ₂ -Y ₂ O ₃
Arc gas	Argon	Argon
Arc gas flow, l/min	26.0±0.5	28.3±0.5
Powder gas	Argon	Argon
Powder gas flow, l/min	5.2±0.2	5.6±0.2
Current, A	400±5	600±5
Voltage, V	28±1	31±1
Powder feed rate, gm/min	12.1	15.6
Stand-off-distance, cm	12±2	12±2
Bond coating thickness, cm	0.020±0.002	-----
Thermal barrier coating thickness, cm	-----	0.039±0.003

^aStandard conditions used unless others are specified.

TABLE III. - CALCULATED AND EXPERIMENTALLY DETERMINED OPTIMUM YTTRIUM CONCENTRATIONS AND OPTIMUM DENSITIES OF THE THREE BEST THERMAL BARRIER SYSTEMS EVALUATED IN THIS STUDY

Thermal barrier system	Bond coating				Thermal barrier coating	
	Yttrium concentration, wt %		Density, gm/cm ³		Density, gm/cm ³	
	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental
Ni-35.0Cr-5.9Al-0.95Y/ZrO ₂ -6.1Y ₂ O ₃	0.710	0.95	7.050	6.997	5.199	5.206
Ni-35.0Cr-5.9Al-0.95Y/ZrO ₂ -8.0Y ₂ O ₃	.797	.95	7.051	6.997	5.185	5.171
Ni-25.5Cr-6.2Al-0.75Y/ZrO ₂ -6.1Y ₂ O ₃	.833	.75	7.052	7.138	-----	-----
Ni-24.0Cr-6.2Al-0.75Y/ZrO ₂ -8.1Y ₂ O ₃	.885	.75	7.053	7.138	-----	-----
Ni-35.9Cr-5.6Al-0.85Y/ZrO ₂ -6.1Y ₂ O ₃	.792	.85	7.034	6.997	-----	-----
Ni-35.9Cr-5.6Al-0.85Y/ZrO ₂ -8.0Y ₂ O ₃	.886	.85	7.012	6.997	-----	-----

ORIGINAL PAGE IS
OF POOR QUALITY

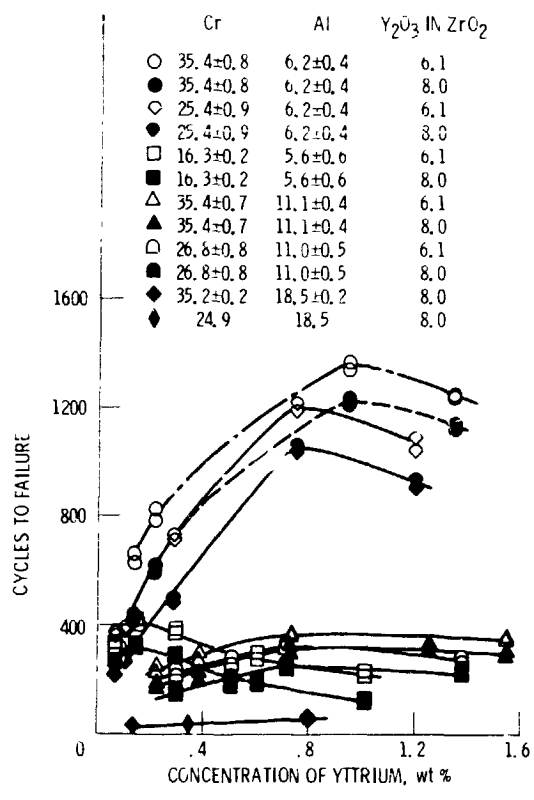


Figure 1. - The effects of yttrium, chromium, and aluminum concentrations in the bond coatings on thermal barrier system lives as determined in a cyclic furnace at 1110 °C. (Cycle = 9 min heat-up, 60 min at temperature, and 60 min of cooling to about 300 °C.)

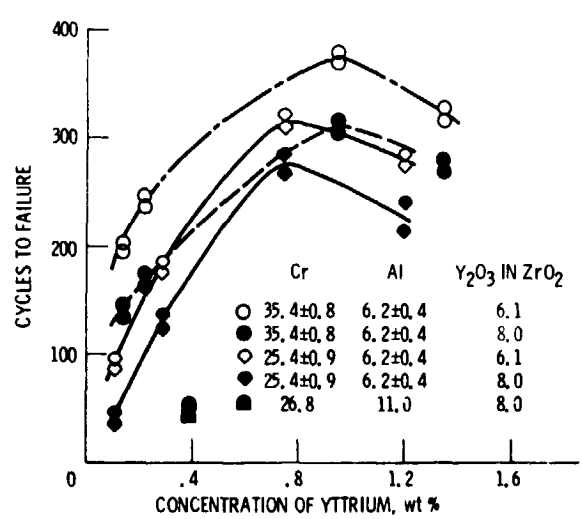


Figure 2. - The effects of yttrium, chromium, and aluminum concentrations in the bond coatings on the thermal barrier system lives as determined in a cyclic furnace at 1160 °C. (Cycle = 9 min heat-up, 60 min at temperature, and 60 min of cooling to about 300 °C.)

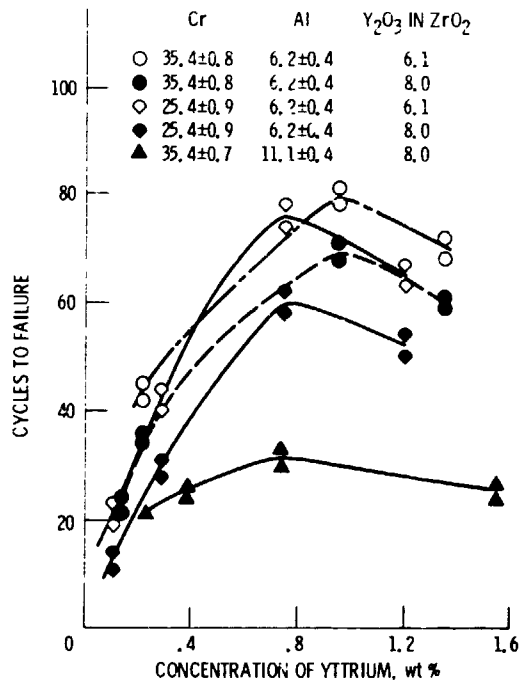


Figure 3. - The effects of yttrium chromium, and aluminum concentrations in the bond coatings on thermal barrier system lives as determined in a cyclic furnace at 1220 °C. (Cycle - 9 min heat-up, 60 min at temperature, and 60 min of cooling to about 300 °C.)

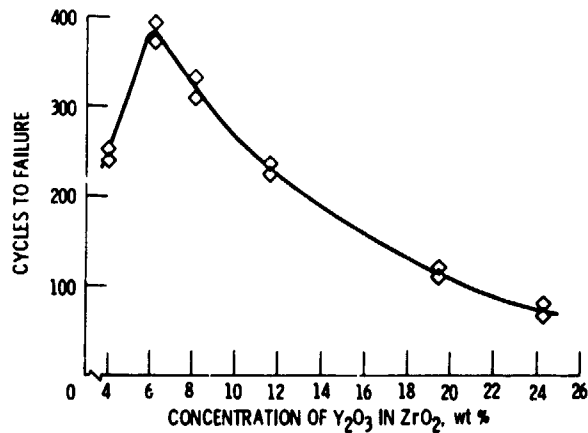


Figure 4. - The effect of yttria concentration in zirconia on the life of a thermal barrier system consisting of about 0.020 cm thick Ni-16.5Cr-5.9Al-0.17Y bond coating and about 0.038 cm thick ZrO₂-Y₂O₃ thermal barrier coating as determined in a cyclic furnace at 1110 °C. (Cycle - 9 min heat-up, 60 min at temperature, and 60 min of cooling to about 300 °C.)

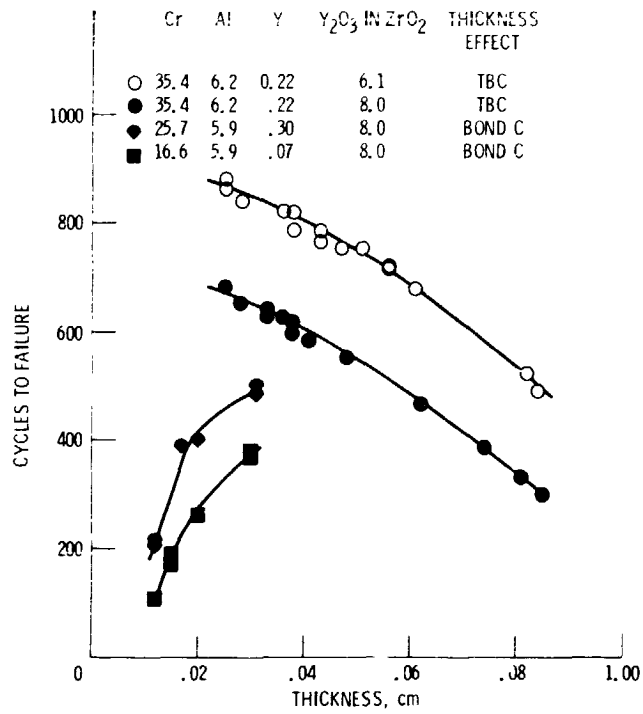


Figure 5. - The effects of bond and thermal barrier coating thicknesses on thermal barrier system lives as determined in a cyclic furnace at 1110 °C. (Cycle - 9 min heat-up, 60 min at temperature, and 60 min of cooling to about 300 °C.)

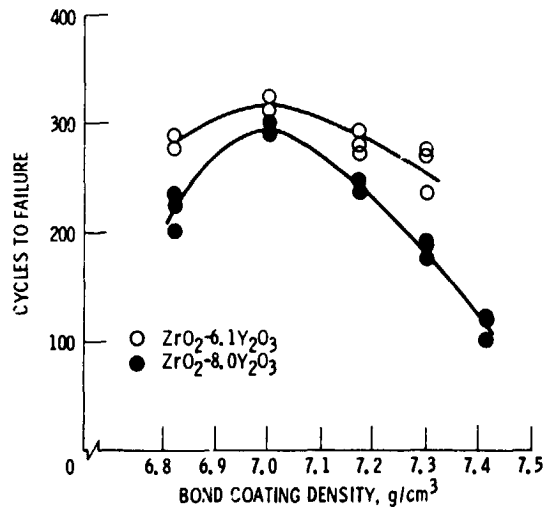


Figure 6. - The effect of bond coating density on the lives of the Ni-35, 9Cr-5, 6Al-0, 85Y/ZrO₂-Y₂O₃ systems as determined in a cyclic furnace at 1170 °C. (Cycle - 9 min heat-up, 60 min at temperature, and 60 min of cooling to about 300 °C.)

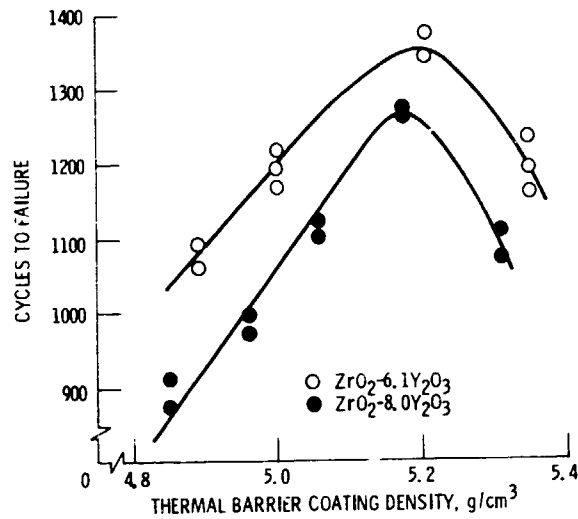


Figure 7. - The effect of thermal barrier coating density on the lives of the Ni-35, 0Cr-5, 9Al-0, 95Y/ZrO₂-Y₂O₃ systems as determined in a cyclic furnace at 1110 °C. (Cycle = 9 min heat-up, 60 min at temperature and 60 min of cooling to about 300 °C.)

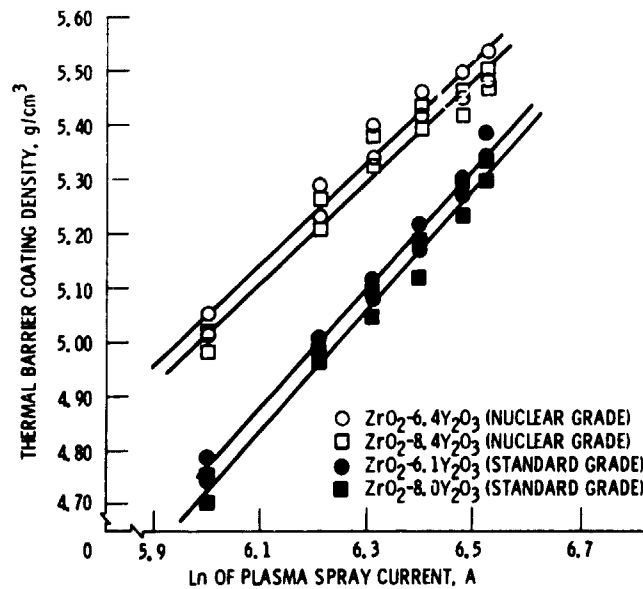


Figure 8. - The effect of power used during plasma spray deposition of standard and nuclear grade thermal barrier coatings on coating densities.

CHARACTERIZATION
OF POWDER QUALITY



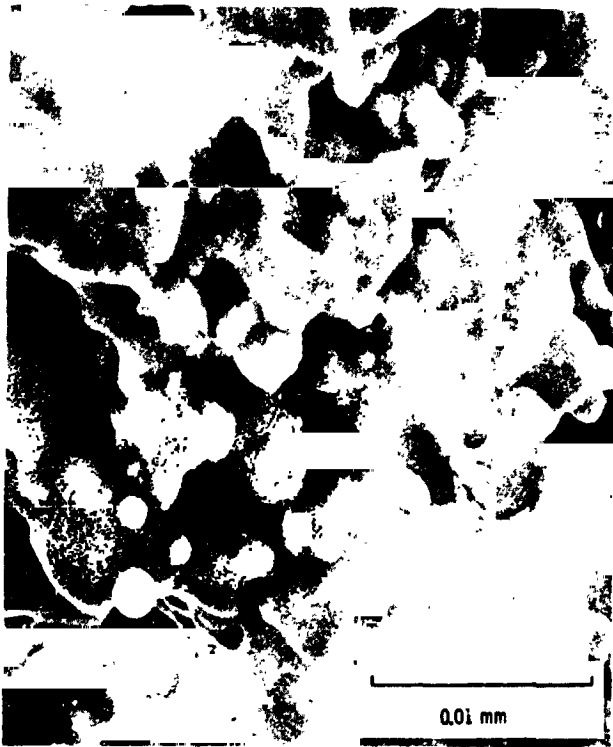
(a) Standard purity $ZrO_2-6.1Y_2O_3$.



(b) Nuclear grade $ZrO_2-6.4Y_2O_3$.

Figure 9. - Scanning electron microscopy photomicrographs of as-received powders taken at 40 kV and 0° angle.

ORIGIN...
OF F... ..



(a) Standard purity $ZrO_2-8.0Y_2O_3$.



(b) Nuclear grade $ZrO_2-8.4Y_2O_3$.

Figure 10. - Scanning electron microscopy photomicrographs of thermal barrier coating deposited under conditions specified in Table II and taken at 40 kV and 35° angle.

CRITICAL EFFECTS
OF POWER USED

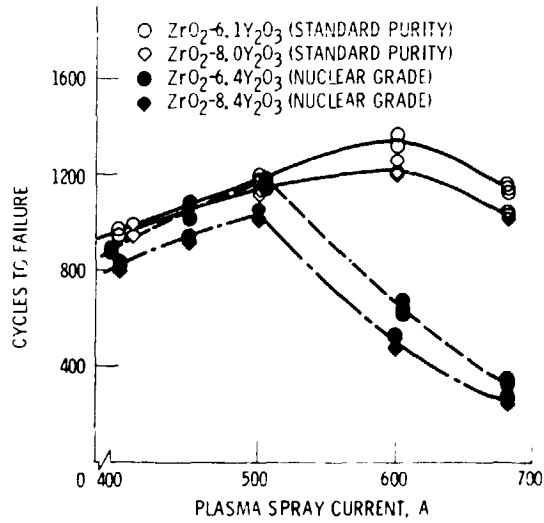


Figure 11. - The effect of power used during deposition of standard and nuclear grade $ZrO_2-Y_2O_3$ on Ni-35, 0Cr-5, 9Al-0, 95Y bond coating on the thermal barrier system lives as determined in a cyclic furnace at 1110 °C. (Cycle = 9 min heat-up, 60 min at temperature, and 60 min of cooling to about 300 °C.)

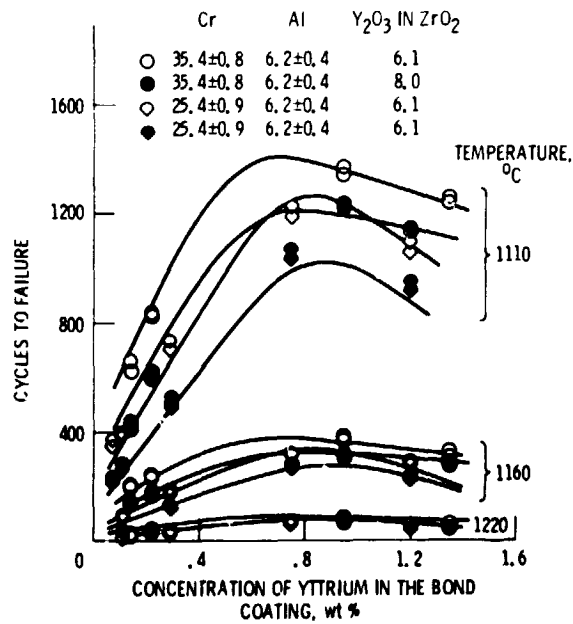


Figure 12. - Comparison between the calculated (solid lines) and the experimentally determined yttrium concentration effects (symbols) on the thermal barrier system lives at three temperatures.

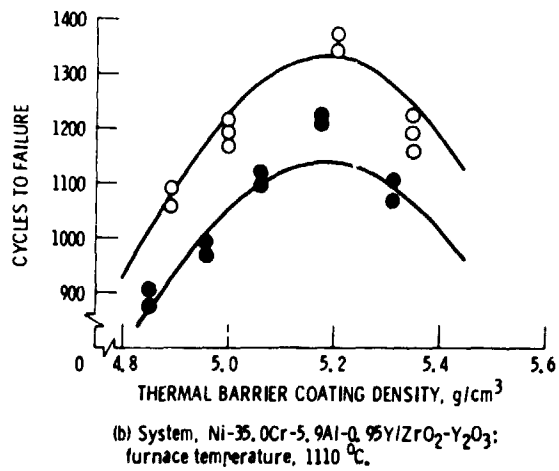
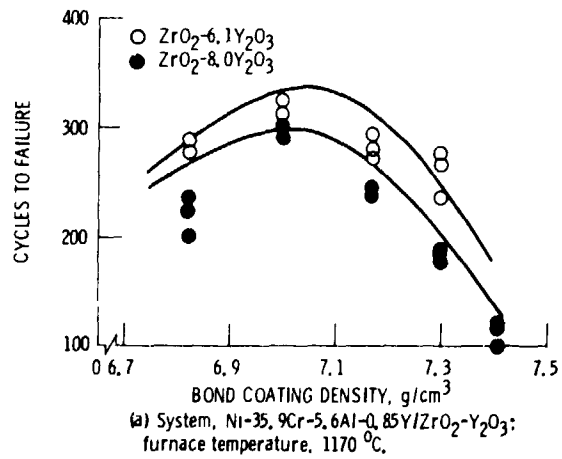


Figure 13 - Comparison between the calculated (solid lines) and experimentally determined coating density effects (symbols) on system lives as determined in a cyclic furnace.

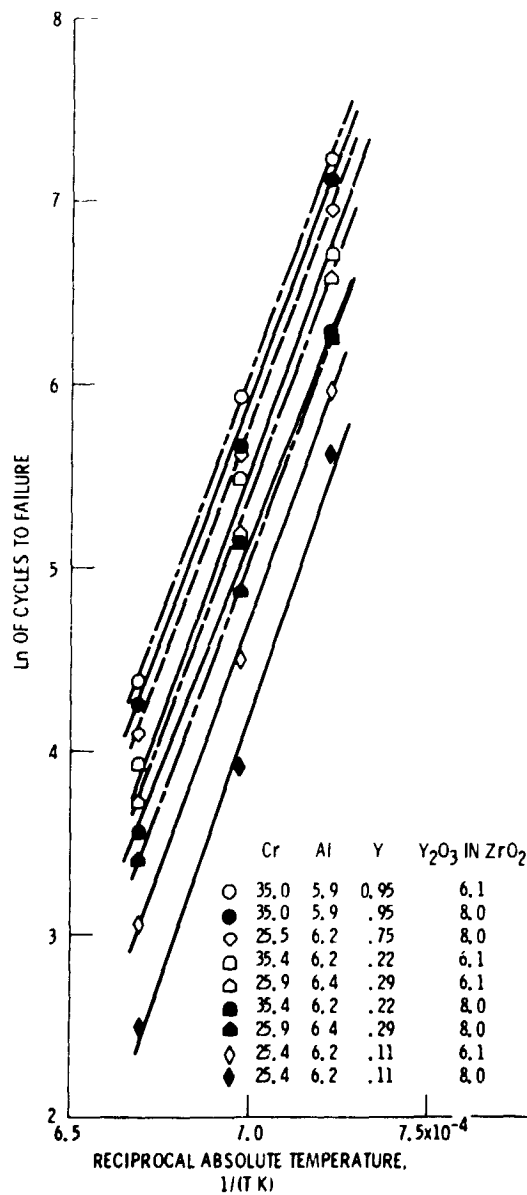


Figure 14. - The relationship between NiCrAlY/
ZrO₂-Y₂O₃ thermal barrier system life and
temperature. (Test cycle = 9 min heat-up,
60 min at temperature, and 60 min of cooling
to about 300 °C.)