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THE EFFECT OF ANNEALING ON THE CREEP OF PLASMA SPRAYED CERAMICS

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SUMMARY

The creep of plasma sprayed ZrO_2-$8Y_2O_3$ has been measured at temperatures from 98° to 1250° C (180°to 2200°F), and compared to creep of identical samples after annealing at temperatures from 980° to 1316° C (180° to 2400° F). Loads and temperatures which produced significant creep of as-sprayed ceramics produced no creep after annealing.

INTRODUCTION

Thin section ceramics have a potential application in gas path seals in gas turbine engines and in other high temperature applications that require a refractory ceramic for a thermal/mechanical insulation. Plasma spraying is a conveniently rapid, easily adaptable, and widely available method of forming ceramic thin sections.

However, there is disturbing evidence of ceramic spalling off of metallic substrates when heated to 1000° C (1830°F). Figure 1 shows ceramic buckling when heated to approximately 1040° C (1900° F).

Since the performance at high temperature of thin section ceramics is critical, it is necessary to understand the causes of the spalling of the plasma sprayed ceramics in order to be able to predict its behavior and to have any hope of circumventing the problem. Previous work measured the inelastic flow of plasma sprayed thin sections of ZrO_2-Y_2O_3 heated above 1010° C (1850° F) (ref. 1). This report extends the study of plastic flow of ZrO_2-Y_2O_3 to lower temperature regimes and addresses the effect of pretest annealing.

EXPERIMENTAL PROCEDURE

Materials and Ceramic Deposition

The samples may be divided into two types, bonded and free form. For the bonded type samples, sheet metal stainless or tungsten was plasma sprayed with a NiCrAlY bondcoat and then with a ceramic. The surface was first grit blasted with Al_2O_3 for cleaning and surface roughening. Then it was plasma sprayed in air with 0.013 cm Ni-18Cr-12Al-0.3Y, followed by plasma spraying with 0.038 cm of ZrO_2-Y_2O_3. Free form samples of ZrO_2-Y_2O_3 or Al_2O_3 were plasma sprayed on 10 micro-cm RMS stainless steel, and then removed by acid disolution of the substrate.

Apparatus and test procedure

A 0.15 cm stainless steel strip bonded type sample (plasma sprayed with NiCrAlY and ZrO_2-$8Y_2O_3$), was heated to the desired absolute temperature and when cool, the length was accurately measured on an optical comparitor, (the temperature, rates, and times are recorded in the data tables). Next the metal was dissolved away and the length of the ceramic alone was measured. Samples were heated to temperature in either an argon or a hydrogen filled furnace; in one case a vacuum furnace was used.

RESULTS AND DISCUSSION

It was previously shown that a plasma sprayed ZrO_2-Y_2O_3 on a flat, stainless steel substrate could be plastically deformed to a radius as small as, 30 cm and then separated to form an integral, free standing, curved ceramic sheet (ref. 1). This experiment indicated that the plasma sprayed ceramic was stretching on the tension side of the bend specimen and compressing on the inside of the bend. A series of measurements were made to determine the amount of plastic flow of the ceramic.

In these experiments the difference in length between the ceramic-substrate specimen and the ceramic with the metal substrate dissolved away were measured. The results are presented in table 1 and in figure 2. The amount of plastic extension of the ZrO_2-$8Y_2O_3$ varies linearly with the temperature to which the ZrO_2-Y_2O_3 was heated. The thermal expansion coefficient of the ZrO_2-Y_2O_3 is 10 x 10^{-6} cm/cm-C (ref. 2). The expansion coefficient of 304 stainless is 20 x 10^{-6} cm/cm-C (ref. 3). If the full difference in thermal expansion produced plastic flow, the increase in length at 1205° C would be 0.012 cm/cm[1]. Using the value of 37 GPa (5.4E6 x 10^6 psi) for the compressive modulus at return to ambient (ref. 6), yields a compressive stress on the ceramic of 222.8 MPa (32.3 ksi) for the measured strain and 0.44 GPa (64.8 ksi) based on calculated strain. In order to determine whether the atmosphere in which the ceramic was heated influenced the plastic stretch, samples were heated in both argon and hydrogen; in one case, the vacuum furnace was used. The results are presented in table 2.

There is no evident difference in the plastic stretch of the ceramic whether it is heated in argon or hydrogen. One specimen of 0.038 cm ZrO_2-$8Y_2O_3$ plasma sprayed on stainless was heated for four hours in vacuum at 1357° C. The plastic flow of the ceramic is 0.0042 cm/cm; again, no significant difference is noted.

In order to determine whether the chemistry of the ceramic was influencing the plastic flow of the ceramic, stainless sheet specimens were plasma sprayed with ZrO_2-$8Y_2O_3$, ZrO_2-$12Y_2O_3$, $ZrO_2 8CaO$, and Al_2O_3-$2.5TiO_2$, and then were

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[1] While use of the bondcoat thermal expansion coefficient would result in good agreement between theory and data, we are at this time unsure as to its effect.

furnace heated for 24 hours[2]. The results for the plastic flow of the ceramic specimens are shown in table 3. The compressive stress/shear strength relationship for ZrO_2-8CaO was such that after heating, the ceramic separated from the metal substrate, possibly in shear. When the ceramic separated, the compression was relaxed and the ceramic extended beyond the end of the metal such as shown in figure 3. Figure 4 shows the region of shear along the edge of the specimen. There was no significant difference between the plastic flow of ZrO_2-8Y_2O_3, ZrO_2-12Y_2O_3, ZrO_2-8CaO and Al_2O_3-2.5TiO_2.

The compressive plastic flow of the ZrO_2-8Y_2O_3 was checked by plasma spraying the ceramic onto tungsten substrate and then heating to 1205° C for 24 hours. The results are presented in table 4, and the inelastic behavior of the various ceramics as a function of the treatment temperature is illustrated in figure 5. The samples were run at different times and yet the measurement of plastic flow is equivalent. The thermal expansion of the tungsten is $4.5 \times 10^{-6}/^{\circ}C$ which is less than that of the ZrO_2-8Y_2O_3, so that the ceramic is compressed upon heating. The calculated contraction is 0.0066 cm/cm.

The ceramic/stainless specimen flows in extension on heating whereas the ceramic/tungsten specimen flows in compression. This indicated that if allowed sufficient time, that the ceramic/stainless might flow in compression as the plasma sprayed ceramic substrate combination was cooled. A 0.038 cm ZrO_2-8Y_2O_3 specimen was introduced into an argon filled furnace at 665° C, heated at a linear rate to 1205° C in 5 hours, held at 1205° C for 5 hours and then lowered at a linear rate to 275° C in 60 hours or a rate of 15° C/hr. After separation of the ceramic from the substrate, the ceramic had increased in length by 0.0056 cm/cm. The cooling cycle does not appear to recompress the ceramic.

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[2] The thermal soak time is longer than required to achieve creep at a fixed temperature (ref. 1).

While the plasma sprayed ceramic is readily stretched in plastic flow when the ceramic/substrate combination is raised to above 600° C (and probably even below this temperature) some process is occuring which makes the plasma sprayed ceramic far less susceptible to plastic flow.

The plasma spraying/deposition is a nonequilibrium operation (ref. 5). The particle of ceramic which is heated in the plasma is impacted on a relatively cool substrate and is rapidly quenched. While ZrO_2-Y_2O_3 is not as strong a glass former as SiO_2 or B_2O_3 (ref. 2, p. 99), the two factors of violently rapid quench from a quasi melted state in the plasma arc and also being mixed with a second oxide, undoubtedly lead to the formation of "glassy," or partially "glassy," state in the deposited ceramic boundary, (see Appendix for a discussion). When the ceramic on the metal substrate is raised in temperature, the two processes of plastic stretch due to the larger thermal expansion coefficient of the metal substrate and simultaneous devitrification (structural changes) are occuring. Hence the plasma sprayed ceramic plastically stretches as the temperature is raised but does not flow in compression as the temperature is lowered. The plastic stretch results in compressive stress on the ceramic when the ceramic/metal substrate drops in temperature.

In order to confirm the evident existance of devitrification in the plasma sprayed ceramic, measurements were made of elevated temperature plastic flow of thin sheets of plasma sprayed ceramic which had all been stripped from the metal substrate directly after plasma spraying and before any thermal treatment.

The tests were made of plastic flow by ball indentation of a 0.038 cm thick 2.5 cm diameter plasma sprayed disk. These tests were all run at 1205° C (2200° F), and the apparatus is illustrated in figure 6. In another series of tests, the ball indentation measurements were made on: i) virgin

ZrO_2-$8Y_2O_3$, ii) ZrO_2-$8Y_2O_3$ annealed at 945° C iii) ZrO_2-$8Y_2O_3$ annealed at 1278° C (2330° F), and iv) as plasma sprayed Al_2O_3. The results are presented in table 6. From these results, it is obvious that heating plasma sprayed ZrO_2-$8Y_2O_3$ to 1278° C changes the ZrO_2-$8Y_2O_3$ so that it shows much less plastic flow at 1205° C (test temperature). By comparison with the lesser indentation of the plasma sprayed Al_2O_3, it also is evident that the large indentation of the ZrO_2-$8Y_2O_3$, plasma sprayed ceramic which has not been heated above 945° C indicates that the mixed oxide plasma sprayed ceramic, ZrO_2-$8Y_2O_3$, is much more susceptible to plastic flow even though the melting temperatue of the ZrO_2-$8Y_2O_3$ is 500° C more than the melting temperature of Al_2O_3.

The large plastic flow of the as sprayed ZrO_2-$8Y_2O_3$ and the removal of this ease of plastic flow on heating to 1278° C confirms that the plasma sprayed ZrO_2-Y_2O_3 is probably vitreous, or partially vitreous.

CONCLUSIONS

Plastic flow as large as 0.006 cm/cm has been measured for ceramics plasma sprayed on a metal substrate after the substrate and ceramic are heated to 1205° C (2200° F). It has been shown that the plastic flow of plasma sprayed ceramic sheets can be greatly decreased by annealing the plasma sprayed ceramic for a short time at 1278° C (2330° F).

The results are applicable to the design of ceramic high temperature gas passage seals with sheet, plate, or built-up plasma sprayed materials as required by the design configuration.

APPENDIX

The central issue of this paper is a practical method on how to control creep although the question of why creep occurs is a more fundamental issue. Among several approaches as to why creep occurs, consider the following equilibrium and nonequilibrium approaches.

Microcracking would lead to inelastic behavior as the differential thermal expansion (contraction) acted on the ceramic/substrate specimen with subsequent elastic behavior similar to that noted in reference 5. The effects of microcracking would diminish at elevated temperature due to an increase in "ductility." Also the effects of the porous structure on ceramic longevity are opposed because the microcrack functions as a crack-source while the open structure functions as a crack-sink. Sintering represents a volumetric change which occurs when "point" contacts become "area" contacts thereby providing increased density and changes in other properties such as increased thermal conductivity. Phase changes or changes in structure have not been adequately established at elevated temperatures for the rates involved in plasma spraying; however some effort is being made to investigate the nature of transitions at elevated temperatures under load and perhaps with acoustic emission. Among these several approaches as to why creep occurs, perhaps one could consider two, equilibrium and nonequilibrium.

Equilibrium

Central to the equilibrium appoach is the phase diagram. In the compositional region to 5 wt.-percent monoclinic is dominant, from 7 to 9 wt-percent monoclinic and cubic are present and from 12 to 96 wt-percent single cubic phase is present (ref. 6). For plasma sprayed ZrO_2-X-Y_2O_3, others cite the range of $5 < X < 12$ wt.-percent where the product formed is non-transformable tetragonal phase by a diffusionless reaction (refs. 7,8). Upon heating this single phase decomposes into a two phase system; a high solute (fluorite) phase and a low solute tetragonal phase. In other tests, no computational changes were found with the emergence of monoclinic both before and after test runs in a Mach 0.3 burner flame (ref. 9).

Amorphous ZrO_2 has been formed as hydrated ZrO_2 precipitated from $ZrO_2C\ell_2{*}8H_2O$ by the Henderson-Higbee method, with NH_3 (ref. 10) and was devitrified (to a tetragonal state) by annealing at 410° C.

Sintering of the plasma sprayed materials (ref. 11) and porosity (ref. 2) may have a significant influence on creep behavior.

Nonequilibrium

Central to the nonequilibrium approach is applied gradient. If gradients imposed on a substance, mixture, or process are sufficiently large, metastable states can occur. In such states transitions do not occur at the recognized boundries associated with phase diagrams (refs. 12-14). This implies that any substance has a cooling rate beyond which it can become amorphous (glassy). For plasma spraying the quenching rates are of the order of $10^6 - 10^9$ K/sec (ref. 15) and although we have no substantiating data, a thin "glass-skin" boundary should form upon impact. Furthermore under such conditions the classic heat conduction and diffusion equations which are pararbolic predict infinite rates in the limit of zero time. This is not correct and these equations require modification such that the rates are governed by a critical wave propagation (ref. 16).

For our specimens annealed at 1200° C (2200° F) there is a significant reduction in creep. These results are supported by significant changes in compression creep behavior of YSZ bricks (ref. 17). The compressive stress power law dependence changes from linear to cubic when bricks are annealed above 1900° C (3450° F) or fired in service to 2240° C (4060° F) and was attributed to the appearance of substructure within the grains of deformed samples. While neither of these results substantiate changes from a 'glassy' state, they do imply changes in structure as does devitrification, micro- cracking, sintering and other phase changes.

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TABLE I. - PLASTIC STRETCH OF ZrO_2-Y_2O_3 AT VARIOUS TEMPERATURES

Temperature, °C	As plasma sprayed	595	815	982	1205
$\Delta\ell/\ell$	0.0008	0.0022 .0021	0.0039	.0060	.0062

TABLE II. PLASTIC STRETCH OF ZrO_2-Y_2O_3 AFTER HEATING 24 HOURS AT 1205°C IN DIFFERENT ATMOSPHERES

Atmosphere	Plastic flow, cm/cm
Argon	0.0056
Hydrogen	.0046
Hydrogen	.0044
Vacuum	.0042 (4 hr only)

TABLE III. PLASTIC FLOW OF PLASMA SPRAYED CERAMIC AFTER HEATING 24 HOURS

Ceramic	Temperature °C	Plastic flow, cm/cm
ZrO_2-$8Y_2O_3$	1205	0.0053
ZrO_2-$12Y_2O_3$	1205	.0055
ZrO_2-8CaO	1000	.004
Al_2O_3-2.5TiO_2	1000	.004

TABLE IV. PLASTIC FLOW ON HEATING TO 1205° C ZrO_2-$8Y_2O_3$ PLASMA SPRAYED ON TUNGSTEN

Sample	Plastic flow, cm/cm
1	-0.0034 cm/cm
2	-0.0027

TABLE V. PLASTIC FLOW OF ZrO_2-$8Y_2O_3$ AFTER SLOW COOL

Temperature, °C	Cooling rate,	$\Delta \ell / \ell$ cm/cm
1205	15° C/hr	0.0056

TABLE VI. INDENTATION OF CERAMIC DISKS AT 1205° C

Sample	Indentation, cm
ZrO_2-$8Y_2O_3$ As plasma sprayed	0.102, .094
ZrO_2-$8Y_2O_3$ Annealed at 945° C	.122, .127, .094, .127
ZrO_2-$8Y_2O_3$ Annealed at 1278° C	.0928, .051, .051, .038
Al_2O_3	.076
As plasma sprayed	.076

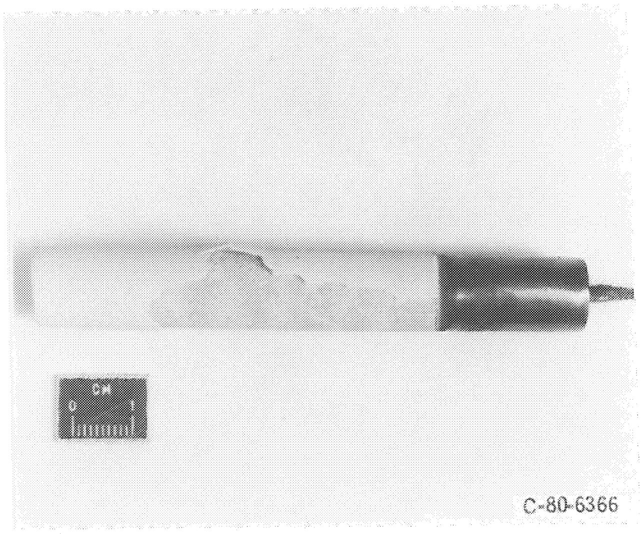

Figure 1. - Explusive sheading of a ceramic from an inconnel rod substrate after several heating and cooling cycles.

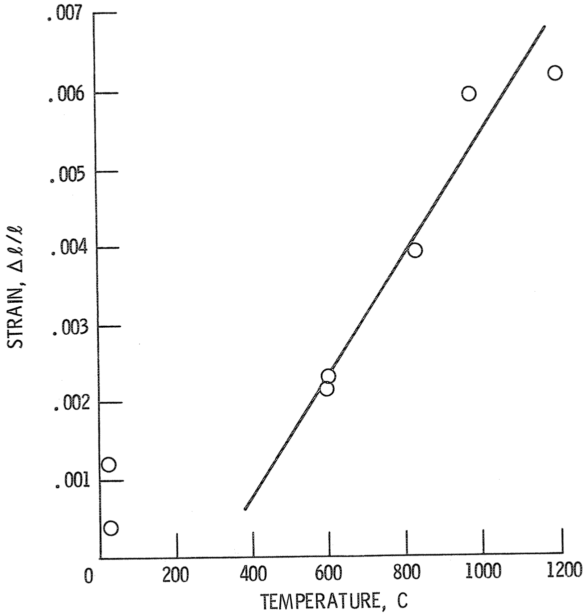

Figure 2. - Inelastic extension of ZrO_2-Y_2O_3 with absolute temperature.

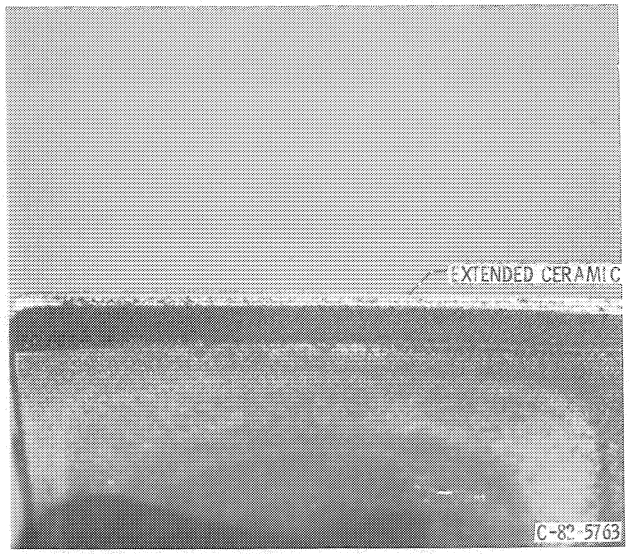

Figure 3. - Photograph illustrating the inelastic extension of ZrO_2-Y_2O_3 beyond the length of the metallic substrate.

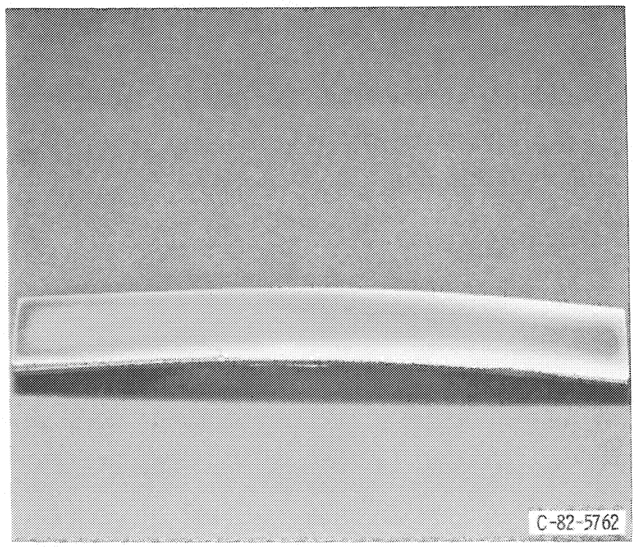

Figure 4. - Photgraph illustrating the delamination along the edges between the ceramic and the substrate.

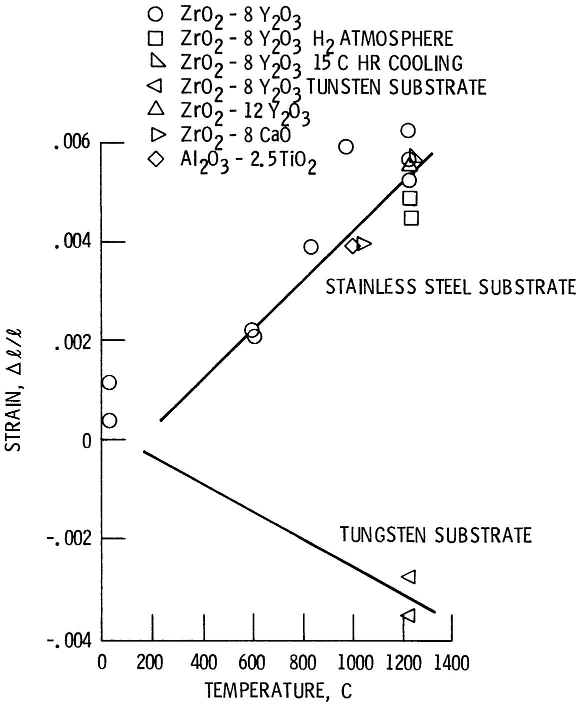

Figure 5. - Plastic flow of plasma sprayed ceramic as a function of temperature at which the specimen was treated.

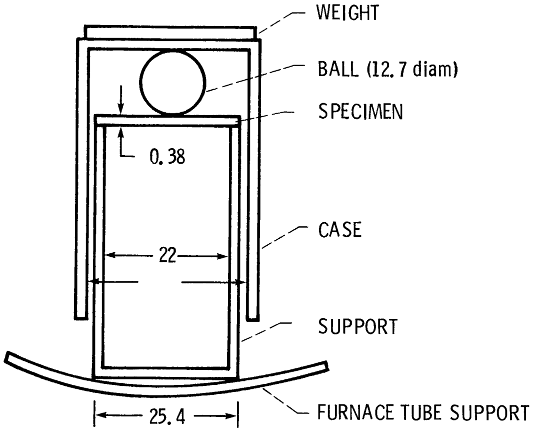

Figure 6. - Schematic of ball indenter. Dimensions in cm.

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16. Abstract

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