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ABSTRACT

The thermal shock resistance of zirconia with 15 mole titanium prepared either by cold-pressing and vacuum-sintering or by vacuum hot-pressing was determined by radially quenching disks with thermally insulated faces under various heat-transfer conditions. The thermal shock resistance of calcia-stabilized-zirconia disks was also determined for comparison purposes. For quenches from below the transformation temperature range of zirconia, the thermal shock resistance of zirconia with 15 mole percent titanium was much better than that of calcia-stabilized zirconia, but for quenches from above the transformation range it was slightly inferior. The thermal shock resistance of zirconia with 15 mole percent titanium is fairly insensitive to the various methods of manufacture used in this investigation.

SUMMARY

The experimental thermal shock resistance of zirconia with 15 mole percent titanium was determined by radially quenching disks with thermally insulated faces. The thermal shock resistance of calcia-stabilized zirconia was determined concurrently for comparison purposes. The effect of processing variables on the thermal shock resistance of zirconia with 15 mole percent titanium was also investigated and showed little effect on thermal shock resistance.

For quenches from below the transformation temperature of zirconia, the thermal shock resistance of zirconia with 15 mole percent titanium was definitely better than that of calcia-stabilized zirconia. For quenches from above the transformation temperature that of stabilized zirconia was slightly better.

I. INTRODUCTION

The relatively high melting point of zirconia, its resistance to chemical attack, its stability in oxidizing atmospheres, and its relative abundance are characteristics that would make zirconia a useful material for many high-temperature applications. Unfortunately, large volume changes due to the allotropic transformation at about 1000° C cause bodies of pure zirconia to disintegrate during their manufacture or when in use. This difficulty can be circumvented by adding oxides that eliminate the transformation,[1-3] although this procedure introduces some undesirable features such as a lowering of the melting point, an increase in the coefficient of thermal expansion, and - for some types of stabilized zirconia (as this type of material is termed) - a tendency to disintegrate on prolonged thermal cycling.[4,5] Recent research, however, indicates that bodies of zirconia can be manufactured without the benefit of stabilization.

Weber et al.[2,3] reported being able to make sound bodies of zirconia with titanium additions. One of the most intriguing characteristics of these zirconia-titium compositions is their reportedly good thermal shock resistance despite the fact that the thermal expansion - temperature curve for these compositions[2] is similar to that of pure zirconia,[4] that is, the material still undergoes the allotropic transformation. Unfortunately, no quantitative data on the thermal shock resistance of zirconia-titanium compositions are available.

In an effort to determine quantitatively the thermal shock resistance of zirconia with 15 mole percent titanium compositions pioneered by Weber et al., an experimental study of this property was carried out not only on this type of material prepared by different methods but also on calcia-stabilized zirconia for comparison purposes.

The method used for determining the thermal shock resistance of the preceding compositions was that developed by Manson and Smith[7] but with a modified apparatus of the author's design to be subsequently described.

In the method of Manson and Smith[7] for determining thermal shock resistance, disks with thermally insulated faces are quenched from successively higher temperatures in a medium of fixed quench severity until the disk cracks. The maximum temperature difference ΔT that the disk is capable of withstanding without cracking under a specified quench severity - defined as the product of the maximum radius of the disk r_m, and its surface heat-transfer coefficient h - is usually taken as a measure of the thermal shock resistance of the material.[8,9] By these means, the thermal shock resistances of different materials under any given quench severity can be compared.

The surface heat-transfer coefficient h used in this investigation was determined with the same apparatus used for the determination of thermal shock resistance.

The present investigation deals only with the "experimental thermal shock resistance" of zirconia with 15 mole percent titanium as distinguished from the "calculated thermal shock resistance", which is obtained by substitution of the values of the physical properties of the material in the thermal shock equation.[7-9] The evaluation of these properties and the determination of those accounting for the improvement in the thermal shock resistance of zirconia by titanium additions will be the subject of two reports to follow.

II. MATERIALS AND SPECIMEN PREPARATION

RAW MATERIALS

The raw materials used in this investigation were pure zirconia (CP Zirox, TAM Div., National Lead Co.), titanium metal powder (-325 mesh, Metal Hydrides, Inc.), and calcia-stabilized zirconia (Zircoa B, Zirconium Corp. of America).

EQUIPMENT AND PROCEDURES

Sample Preparation

Standard powder-metallurgy techniques were used for the preparation of the disks used as thermal shock specimens. The specimens designated as ZT-15 were prepared by mixing pure zirconia with 15 mole percent titanium metal powder in cone blenders, adding 5 weight percent water as a temporary binder, cold-pressing into disks at 20,000 psi in steel dies, hydrostatically pressing the disks at 46,000 to 50,000 psi, drying in a vacuum desiccator, and vacuum-sintering at 1870° C for 1 hour under pressures less than 0.5 micron of mercury.

Specimens designated as ZT-15-M were prepared by milling pure zirconia with 15 mole percent titanium in tungsten carbide mills with tungsten carbide balls and acetone as grinding media. The powders were milled for 72 hours at 80 rpm. The powders were then dried in a stream of warm air and disk specimens prepared as outlined for ZT-15.

Specimens designated as ZT-15-HP were prepared by mixing pure zirconia with 15 mole percent titanium metal powder in cone blenders followed by vacuum hot-pressing into disks in graphite dies at 1600° C and 2000 psi for 1 hour. Vacuum was at 20 microns or less.

Specimens designated as BM were made from-calcia stabilized zirconia (Zircoa B) by the same methods used for ZT-15-M except that sintering was done in air at 1800° C for 3 hours.

All the disks were ground all over with diamond grinding wheels to the final dimensions of 1.375±0.002 inches outside diameter and 0.312±0.002 inch thick. The surface finish was 50 microinches or better. The edges of the disks were given a radius of about 0.005 inch. All disks were tested for cracks and pinholes by means of die penetrant.

Equipment

Vacuum-sintering was carried out in tungsten sintering boats in an induction-heated vacuum furnace. Hot-pressing was done in double acting graphite dies in an induction-heated vacuum hot-pressing furnace. The equipment used for sintering and hot-pressing was designed to minimize the danger of thermally shocking the specimens during manufacture, and it has been described in detail in reference 10.

III. EXPERIMENTAL PROCEDURES

EXPERIMENTAL THERMAL SHOCK RESISTANCE

Apparatus and Procedure

The apparatus used for the determination of thermal shock resistance is shown in Fig. 1. This apparatus is a modified version of that described by Manson and Smith[7] and consists of a sample carrier, a heating chamber, and a quenching chamber.

The Inconel sample carrier holds the disk between insulating rings of ceramic fiber. The disk is kept aligned and slightly compressed by means of tungsten wires that are kept under tension at all times by means of a high-temperature spring. The hollow stem of the sample carrier allows passage of thermocouples for temperature readings at any point in the disk. The initial and final temperatures of the disks were determined by means of Chromel-Alumel thermocouples touching the upper surface of the disks.

The sample carrier was positioned in the Inconel heating chamber or tube until the sample reached the desired temperature. Heating was always carried out in an argon atmosphere in order to prevent oxidation of the titanium-containing disks and of the tungsten tension wires. In order to quench the disks, the sample carrier was dropped into the quenching tank where the impact of the sample carrier actuated a microswitch, which, in turn, opened the solenoid valve in the quenching gas line. The cooling gas was distributed uniformly around the disk by a radial nozzle provided with deflectors and diffusing screens. The pressure of the cooling gas was adjusted before making the drop.

To determine ΔT (the maximum temperature difference that the specimen can withstand without cracking) a series of quenching experiments with constant cooling gas pressure was carried out from successively higher initial temperatures until the specimens cracked. The value of ΔT was determined by means of the equation

$$\Delta T = \frac{T_1 + T_2}{2} - T_f$$

where

T_1 maximum temperature specimen withstood without cracking

T_2 lowest temperature at which cracking was observed

T_f uniform, final temperature of specimen (temperature of quenching medium)

The temperature increments used in quenching runs were about 10 percent of T_1 in preceding equation (usually 20° to 100° C).

By removing the quenching tank, it was possible to quench the disks in boiling water. In these cases the disks were insulated with either silicone rubber or rubber-impregnated asbestos rings.

To quench through the transformation range of zirconia, the disks were first heated above the transformation temperature range (above 1120° C) then cooled from the same constant temperature of 900° C (which is just above the transformation temperature of this type of material) into successively cooler portions of the heating tube in the apparatus shown in Fig. 1 until the disk cracked. For this type of quench, ΔT was taken as 900° C - T_f.

Heat-Transfer Coefficient

The surface heat-transfer coefficient h as a function of gas pressure was determined in the same apparatus described for the determination of ΔT. The specimens used for the determination of h were disks of ZT-15-M of the same dimensions as the disks used for the determination of ΔT but with thermocouple holes 0.032 inch in diameter located at relative radii r/r_m of 0, 0.5, and 0.8. The temperatures at these points were determined with Inconel sheathed Chromel-Alumel thermocouples. Cooling curves were obtained by means of automatic temperature recorders at a chart speed of 2 inches per minute.

The heat-transfer coefficient h was determined from two of the cooling curves with the aid of a plot of Russell's tables[11] by the procedure described in references 7 and 10.

IV. RESULTS

HEAT-TRANSFER COEFFICIENT FOR ZT-15-M

The plots of surface heat-transfer coefficient h as a function of helium and air pressures are shown in Figs. 2 and 3, respectively.

The value of hr_m on cooling through the transformation range was between 0.009 and 0.01 calorie per centimeter per second per ^{o}C. This severity of quench varied slightly with the flow of argon gas used as an atmosphere, but this flow was kept constant during the experiments.

The heat-transfer coefficient in boiling water was taken from the literature[7]. The value of hr_m to be used in this investigation for boiling water quenches will be 1.0 calorie per centimeter per second per ^{o}C corresponding to a value of h of 0.57 calorie per square centimeter per second per ^{o}C and r_m = 1.745 centimeters. Although this value of h is somewhat arbitrary, there is little error in ΔT because the curves for ΔT against hr_m flatten out at high hr_m values (see Fig. 4 and Ref. 7).

All the values of hr_m given previously will be used for all the compositions to be plotted in the present investigation. Slight variations in grain size and compositions are not expected to alter h significantly.

EXPERIMENTAL THERMAL SHOCK RESISTANCE

The experimentally determined values of ΔT for the various types of zirconia with 15 mole percent titanium compositons (ZT-15, ZT-15-M, and ZT-15-HP) are shown plotted against hr_m in Fig. 4 for quenches both from below and through the transformation range. The experimentally determined curve for ΔT against hr_m for calcia-stabilized zirconia is also shown in Fig. 4 for comparison purposes.

From the results shown in Fig. 4 it is seen that the thermal shock resistance of the zirconia-titanium compositions is not appreciably affected by the different methods of preparation used in this investigation. It should be pointed out that the composition designated as ZT-15 was prepared from the same type of materials and by practically the same procedures used in the investigation of reference 6.

Comparison of the curve for stabilized zirconia with that for the zirconia-titanium compositions shows the latter to be definitely superior for quenches from below their transformation ranges but slightly inferior for quenches through their transformation ranges.

V. CONCLUDING REMARKS

From the results of the present investigation the following conclusions can be drawn:

1. The thermal shock resistance of zirconia with titanium additions is fairly insensitive to the method of manufacture.

2. The thermal shock resistance of zirconia with 15 mole percent titanium is superior to that of calcia-stabilized zirconia for quenches from below the transformation range but slightly inferior for quenches through the transformation range.

3. Considering the large volume changes associated with the allotropic transformation in zirconia, the thermal shock resistance of the zirconia-titanium compositions is greater than anticipated.

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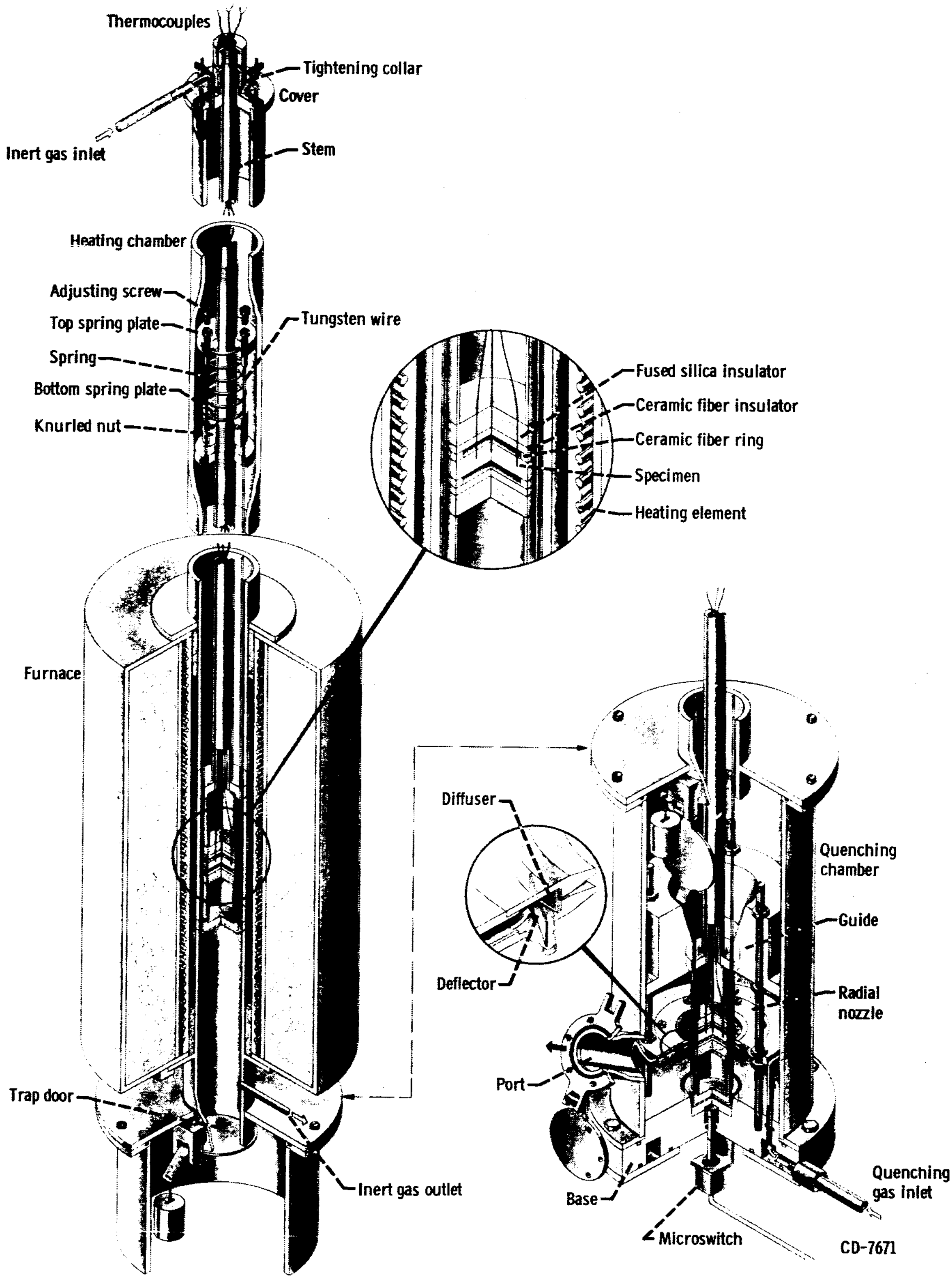

Figure 1. - Thermal shock apparatus.

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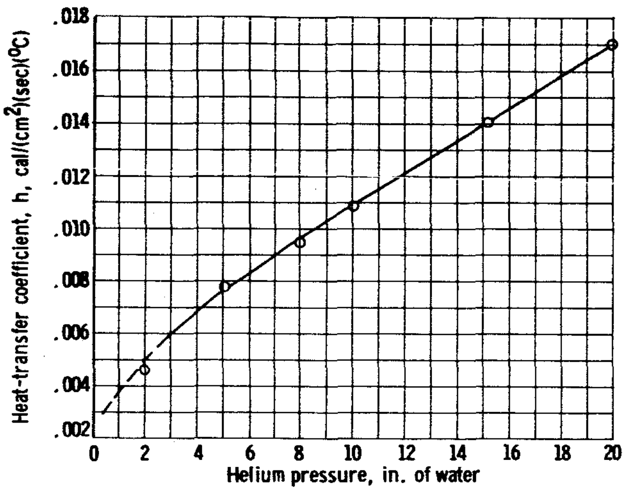

Figure 2. - Heat-transfer coefficient as function of helium pressure for disk of zirconium oxide with 15 mole percent titanium (ZT-15-M).

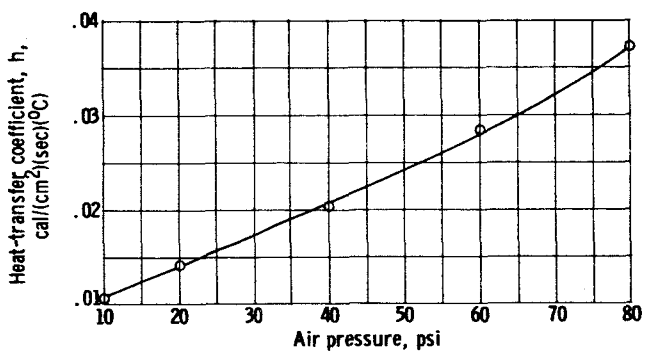

Figure 3. - Heat-transfer coefficient as function of air pressure for disk of zirconium oxide with 15 mole percent titanium (ZT-15-M).

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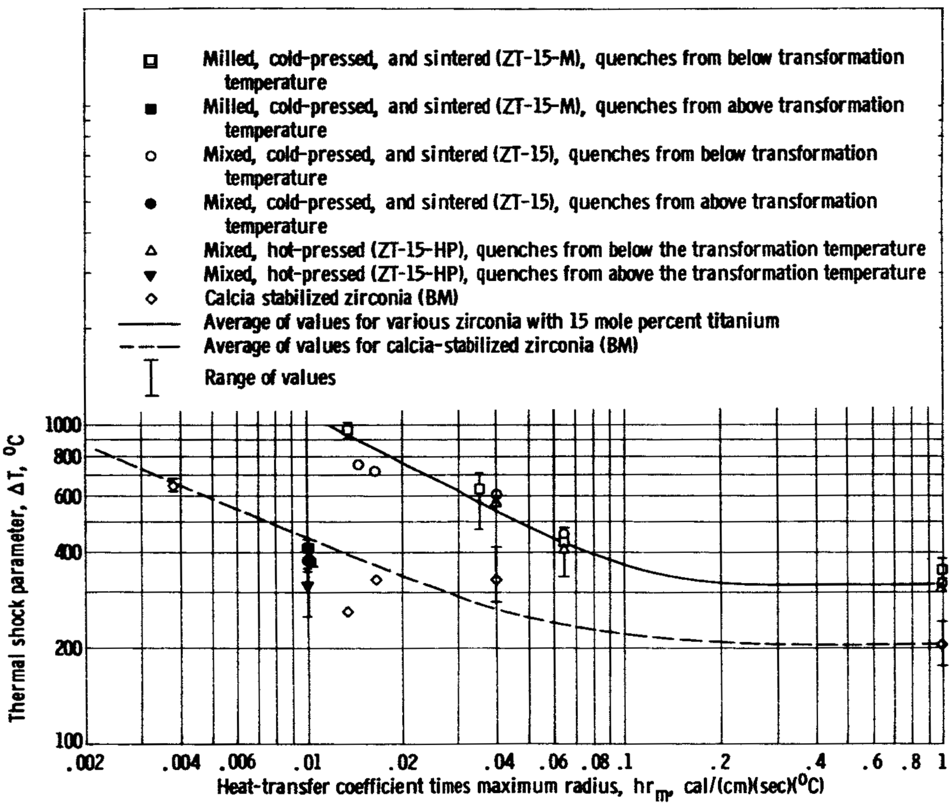

Figure 4. - Effect of processing conditions on thermal shock resistance of zirconia with 15 mole percent titanium and comparison with thermal shock resistance of calcia-stabilized zirconia.