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A NEW METHOD FOR COATING MICROSPHERES WITH ZIRCONIUM CARBIDE
AND ZIRCONIUM CARBIDE-CARBON GRADED COATS

by

C. M. Hollabaugh, R. D. Reiswig, P. Wagner, L. A. Wahman, and R. W. White

ABSTRACT

A new method for the chemical vapor deposition of ZrC and C-ZrC alloys has been developed. This process has been applied to the fabrication of coated particle nuclear fuels of the type used in the large High-Temperature Gas-Cooled Reactor. A powder feeder is used to supply $ZrCl_4$ to the fluidized bed coating furnace where it undergoes reaction with a hydrocarbon to form ZrC. Quantitative metering of the $ZrCl_4$ makes it possible to control the deposition of the ZrC and the codeposition of the C-ZrC alloys on the fuel particles. Examples of both types of coats made using the described technique are discussed and illustrated.

I. INTRODUCTION

During the past few years several papers on the chemical vapor deposition of zirconium carbide, and ZrC-carbon alloys¹⁻¹¹ have appeared in the literature. Techniques for ZrC coating of surfaces of massive bodies,⁴⁻⁶ for preparing low thermal expansion substrates of macrodimensions,¹¹ and for coating microspheres which are hundreds of micrometers (μm) in diameter^{1-3,7-10} have been described in varying degrees of detail. This report describes a method whose description has not appeared in the literature and whose capabilities span many of the likely applications of chemically vapor deposited ZrC and ZrC-C alloys.

The area of particular interest is that concerned with the fissile fuel particles used in the large High-Temperature Gas-Cooled Reactor. These particles are of the TRISO design.¹² In the TRISO fissile fuel particles, a UC_2 or UO_2 kernel ($\sim 200\text{-}\mu m$ -diam) is coated with low-density pyrolytic carbon of nominal $85\text{-}\mu m$ thickness using a fluidized bed chemical vapor deposition process. This, in turn, is covered by a $25\text{-}\mu m$ layer of an isotropic pyrolytic carbon (referred to as LTI because of the relatively low temperature of deposition). The LTI coat has deposited upon it a $25\text{-}\mu m$ layer of SiC and upon

this another LTI coat which is $35\text{-}\mu m$ in thickness. The method described in this report is used in making particles which are nominally of the TRISO design but that have a ZrC coat in place of the SiC layer. This method is also used to fabricate particles where the LTI-SiC-LTI layers can be replaced by a C-ZrC graded coat, a layer of ZrC and a ZrC-C graded coat, or some other combination.

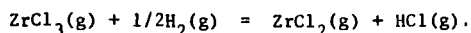
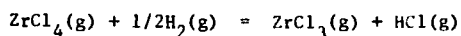
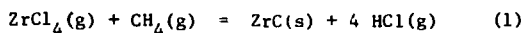
The interest in codepositing ZrC and LTI coats has been stimulated by the possibility of making fuel particles with improved thermal and irradiation performance using a simpler coating process than that now used in the TRISO particle manufacture. With a controllable codeposition process, a continuously graded coat can be made that starts out as pure LTI and has ZrC added in ever increasing amounts (by reaction of $ZrCl_4$ with a hydrocarbon) until pure ZrC is deposited. The process can then be reversed and the ZrC decreased to get back to the LTI. The stress, which is generated by a mismatch of the thermal expansion coefficients of the components in the TRISO design, would be minimized in such a coat. Such a process could be a single step in the fabrication and could be used as a substitute for the three separate steps now used in fabricating the outermost layers of the TRISO-type coated

particles. Other advantages to a graded coat could be a reduction of the irradiation-induced creep in the LTI with a subsequent decrease in the creep-induced stresses in the three outermost coats (one of the causes of coat failure at high fluence). Another favorable factor would be to reduce the magnitude of the physical properties mismatch achieved by the graded coat. A recent article⁹ reported that the ZrC-C composite (sometimes called zirconium carballoy or C-ZrC alloy) is expected to have a higher mechanical strength,¹³ to have better thermal shock resistance than pure pyrolytic carbon,¹⁴ and to be better than stoichiometric ZrC from viewpoints of neutron economy and radiation damage.¹⁵ In addition to these advantages in the use of ZrC, temperature limits on fuel element fabrication, attributable to the SiC in coated particles, are removed when the ZrC is used.¹⁶

These ideas are neither new nor original, but they have not been implemented in the past because of the lack of quantitative control of the feed of the zirconium salt. This has been the chief impediment in the ZrC coating process and the major obstacle to developing a successful and controllable process for codepositing the zirconium carballoy. The Los Alamos Scientific Laboratory (LASL) has solved this problem by using an auger-type $ZrCl_4$ powder feeder. The solid $ZrCl_4$ feed rate is controlled by a dc motor-driven auger and the powder blown by an inert gas stream directly into the hot fluidized-bed coating furnace where it is volatilized. This method has proved to be predictable, controllable, and reproducible for fabricating the ZrC and ZrC-C graded coats on the fluidized bed microspheres.

II. DISCUSSION

ZrC and ZrC-C composites are made by reaction of a zirconium halide with a hydrocarbon gas. The general system may be considered in terms of the following overall reactions.



Wallace⁴ proposed that the rate of ZrC formation may be written as

$$\frac{d(ZrC)}{dt} = (P_{salt} P_{CH_4}^{1/2(n-2)} / P_{HCl}^n)^{Ae^{-B/T}} \quad (2)$$

where

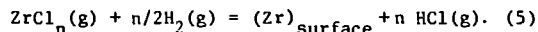
$$P_{salt} = P_{ZrCl_4} + P_{ZrCl_3} + P_{ZrCl_2} \quad (3)$$

$$n = (4P_{ZrCl_4} + 3P_{ZrCl_3} + 2P_{ZrCl_2}) / P_{salt} \quad (4)$$

and

A, B are constants.

Wallace further suggested that the rate-determining step is the reduction of the halide at the surface



If the problem to be solved in the ZrC deposition is really identifiable with the control of the pressure of the chemically sensitive components, then Wallace's analysis makes sense in terms of the past difficulties encountered by investigators in trying to deposit ZrC in a reproducible and controllable manner. $ZrCl_4$ is a solid at room temperature, it has a sublimation temperature of 331°C, and the problem of accurate metering of the $ZrCl_4$ as a gas near this temperature is formidable.

The problem of delivering $ZrCl_4$ gas to a reaction vessel has been approached in a variety of ways. One method that has been used is the reactor technique. This is shown in Fig. 1, schematically, for the formation of the $ZrCl_4$ (other halides have also been used). A gas such as Cl_2 or CH_2Cl_2 is passed over a bed of zirconium sponge kept at a temperature near the sublimation temperature of the $ZrCl_4$. The gaseous reaction product is then swept into the reaction vessel and mixed with the other reactant gases. Reynolds¹⁰ and Ikawa¹ have used this method for the deposition of ZrC coats on microspheres. Ikawa has published several articles^{2,3,7-9} on the application of the reactor technique for preparation of codeposited carbon-zirconium carbide composites (zirconium carballoys).

Another method that has been used is shown schematically in Fig. 2. In this technique, the $ZrCl_4$

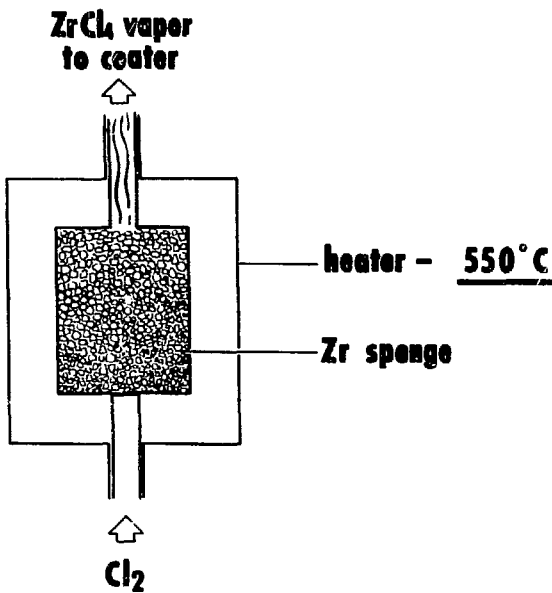


Fig. 1. $ZrCl_4$ reactor.

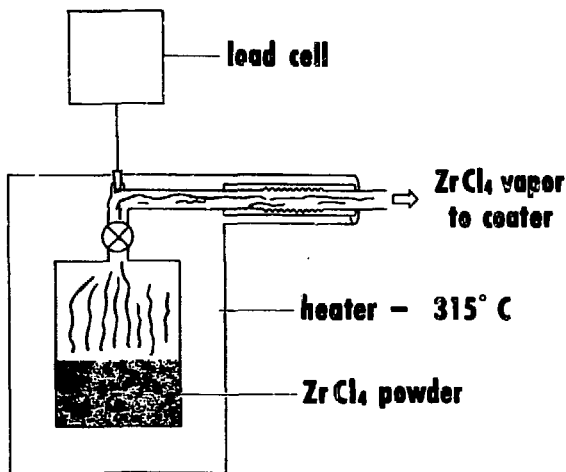


Fig. 2. $ZrCl_4$ vaporizer.

is kept near its sublimation temperature and the evolved gas swept by an inert gas stream into the reaction chamber. Wallace has used this method for production of ZrC-coated coolant channels in nuclear fuel elements⁴ and for fabrication of low-density ZrC fiber insulators.^{5,6} This is also the method used in the fabrication of low coefficient of thermal-expansion (CTE) carbon-zirconium carbide

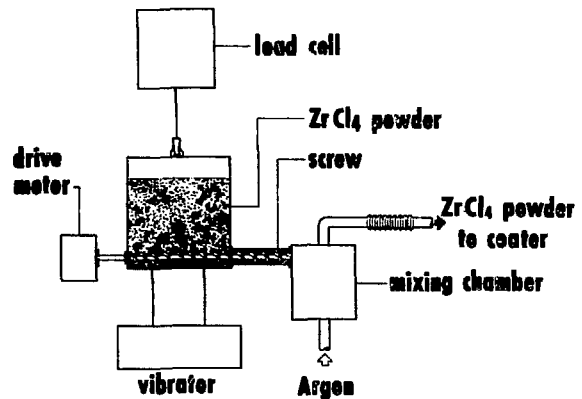


Fig. 3. $ZrCl_4$ powder feeder.

composites which were used as substrates for materials in which the mismatch in the CTE's of adjacent graphite layers were to be minimized.¹¹ In this method, the flow rate of the $ZrCl_4$ is affected by the condition of the $ZrCl_4$ solid (i.e., exposed surface area), the relation of the sweep gas velocity to the surface accessibility of the salt, the cooling effects of the sweep gases, the effect of the sublimation rate of the $ZrCl_4$ on the temperature of the solid, and the temperature of the solid $ZrCl_4$ itself. This method has been used at LASL in the past for fluidized bed coating of microspheres. It was, however, the awkwardness of this system that supplied the impetus for the development of the $ZrCl_4$ powder feeder method that is described in this report.

The design of the $ZrCl_4$ powder feeder is shown in Fig. 3. The entire unit is maintained at ambient temperature. The hopper is purged of air, loaded with $ZrCl_4$ powder in argon, and attached to the coating furnace with a flexible tube. The vibrator shakes the $ZrCl_4$ powder onto the auger, and the load cell output record yields the powder feed rate in terms of weight per unit time. As the powder is fed into the mixing chamber, it is entrained by the argon into the fluidized bed coating furnace. Just before the $ZrCl_4$ powder enters the coating furnace, the other gaseous components (Ar, H_2 , CH_4 , or C_3H_6) are added. The $ZrCl_4$ vaporizes in the coating furnace, the mass of the $ZrCl_4$ is small compared to the mass of the heated furnace materials, and the energy uptake during the sublimation process is

relatively insignificant and does not cause temperature fluctuations in the fluidized bed.

Conditions under which the coatings are applied are derived from two basic factors. First, the overall gas dynamics and furnace charge (materials to be coated) must be matched to the furnace dimensions so that proper agitation and fluidization of the bed is achieved. Second, the gas composition and temperature must be selected to yield the desired coating rate and coat composition. The simplest zirconium-containing coat to consider is the pure ZrC. Once the coating batch weight, gas velocity, and composition have been established, the auger speed to the $ZrCl_4$ powder feeder is set to yield a $ZrCl_4$ flow to allow the reaction [see Eq. (1)] to proceed. Pure ZrC is normally deposited from a gas stream that is substoichiometric in hydrocarbon⁴ to prevent codeposition of carbon in the ZrC. The auger speed is set to optimize the C/Zr ratio in the gas stream, in order to avoid the codeposition problem and to yield the most desirable ZrC deposit.

Production of a graded C-ZrC coat is a far more complex situation. Here, where one wants to start with one pure constituent and to change the composition of the coat gradually until the second component is deposited in the pure state, effective control of the hydrocarbon gas and the $ZrCl_4$ gas is an absolute requirement. Establishment of the batch weight, gas velocity, and composition to produce a particular coat composition must be done for all compositions in a graded coat - from the pure carbon through the C-ZrC alloy and into the pure ZrC, or in whatever order is required. Propylene (C_3H_6) is used to produce pure carbon coats and to provide the carbon for the graded portion of the codeposited carbon and ZrC. Methane is used with $ZrCl_4$ for depositing pure ZrC. A typical composition starts with an argon and C_3H_6 mixture that will deposit an isotropic pyrolytic carbon coat. This is then changed to an argon, H_2 , C_3H_6 , and $ZrCl_4$ mixture in proportions to yield a codeposit containing very little ZrC. To increase the ZrC concentration, the C_3H_6 flow is reduced gradually until pure ZrC is deposited. At this point, CH_4 is substituted for the C_3H_6 . When the desired thickness of ZrC has been deposited, the process is reversed. The CH_4 flow is stopped and the C_3H_6 flow

is started and gradually increased to reduce the ZrC content of the codeposited coat. Finally, the coating process is completed by shutting off the $ZrCl_4$ and H_2 , and a pure isotropic carbon coat is deposited from the Ar- C_3H_6 mixture.

The composition gradient in the graded portion of the coat is controlled by time and coating rate for each composition. Since the coating is done on a sphere that grows with the coating, coating rates are defined as volumetric rates rather than by the conventional time-rate of change of thickness. The volumetric coating rate is assumed to be independent of thickness. It has been established that the coating rate changes almost linearly with propylene gas flow in the C-ZrC composition range investigated. As the volume of the microsphere changes and the C_3H_6 gas flow is changed to change the C/ZrC ratio, these changes must be factored into the coating rate calculations to ensure gradient uniformity.

III. RESULTS

Figures 4 through 7 are photomicrographs of particles made by using the equipment and the techniques described in this report. Figure 4 is a bright field photomicrograph of a TRISO-design¹² coated particle where the ceramic coat is ZrC rather than the SiC which is used in the commercial reactor fuels. The kernel has been coated with a low-density pyrolytic carbon made by using acetylene, and this is overcoated with a low-temperature isotropic pyrolytic carbon (LTI) made by using propylene. The ZrC coat was made by the reaction of Eq. (1), and the outermost coat is an LTI made as before. The ZrC appears fully dense and shows no inclusions, cracks, or laminations.

Figures 5, 6, and 7 show C-ZrC alloys of various types. Figure 5 is a photomicrograph of a H^+ etched coated particle in which the LTI coat is blended into the ZrC coat in a series of steps where the ZrC content is increased (moving outward from the particle kernel) until the coat is pure ZrC (this appears white in the photomicrographs). The propylene flow was then increased in a series of steps to make layers with decreasing concentrations of ZrC in a C-ZrC alloy. The H^+ etching brings out details of the different alloys (these etch at different rates and the resultant surfaces reflect

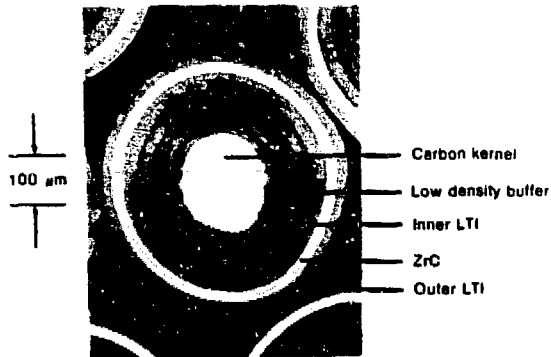


Fig. 4. TRISO-type coated particle with ZrC.

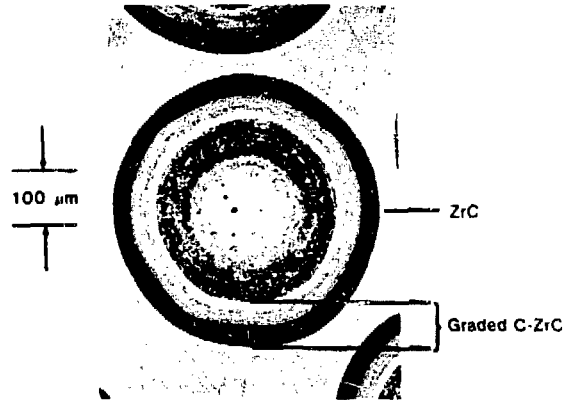


Fig. 6. Coated particle with graded C-ZrC alloy coat. The graded coat has different compositions although it appears to be nearly continuous.



Fig. 5. Coated particle with graded C-ZrC-C alloy coat. Layers in the coat are due to compositional differences.



Fig. 7. Coated particle with graded C-ZrC-C alloy coat. The graded coats contain more than one hundred alloy compositions and appear continuous.

differently), and are seen as discrete coats in Fig. 5. It is to be noted that the degree of blackening on the photomicrographs and the ZrC content are not directly correlated. In Fig. 5, the ZrC content in the graded coat is symmetric about the pure ZrC coat.

Figure 6 shows an example of a C-ZrC alloy coat in which the graded coat starts at the outer surface of the low-density pyrolytic carbon and the ZrC concentration increases with radius until the pure ZrC coat has been deposited. In this example, the steps are finer than those seen in Fig. 5, that is, the differences between alloy compositions in adjoining

coats and the thickness of the individual layers is small enough that they blend into one another.

Figure 7 is a photomicrograph of a coated particle which has the low-density buffer, then a graded C-ZrC coat that starts out as a low-temperature isotropic coat and has a gradually increasing ZrC content, a pure ZrC layer, a gradually decreasing ZrC content, and finally, an outermost thin layer

of the LTI. In this example, more than a hundred different gas stream combinations of C_3H_6 and $ZrCl_4$ were used to deposit the graded coat.

IV. SUMMARY

A technique for making ZrC coats has been described in which the $ZrCl_4$ is supplied at ambient temperature to a hot fluidized bed by an auger-driven powder feeder. The control of the $ZrCl_4$ flow is achieved by the auger speed. The $ZrCl_4$ is vaporized in the coating furnace and reacts with a hydrocarbon species to form the carbide. By altering the ratio of the C/Zr atoms in the coating chamber, it is possible to make coats of different C-ZrC compositions. This has been demonstrated by fabricating C-ZrC alloys in which the C/Zr ratios are altered with a resultant alteration in the character of the deposit as seen in the H^+ etched photomicrographs.

Development of the powder feeder has been the key to making predictable and reproducible coatings of ZrC and C-ZrC alloys. Coats made using this apparatus deposit readily in the furnace, uniformity of the product is good, and metallographic examination of the pure ZrC indicates that it is free of inclusions, cracks, pores, or other flaws. Examination of the C-ZrC graded alloys using the electron microprobe has indicated that systematic changes in the gas stream composition results in corresponding changes in the concentration of ZrC. As deposited, the ZrC has a diffuse x-ray diffraction pattern. Upon heat treatment to 1800°C, this changes to a sharper pattern with a lattice parameter of $4.6983 \pm 3\text{\AA}$. It is thought that the diffuse pattern is caused by residual stresses and nonuniform stoichiometry in the coat. Results after heat treatment suggest an improvement of the crystallinity and uniformity of the ZrC. The high value of the lattice parameter also implies a low impurity content and a high C/Zr value.

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