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**Erosion-Resistant TiB₂ Coatings
Formed by Chemical Vapor Deposition**

A. J. Caputo
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***Research sponsored by the Pittsburgh Energy
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METALS AND CERAMICS DIVISION

EROSION-RESISTANT TiB_2 COATINGS FORMED BY CHEMICAL VAPOR DEPOSITION

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NOTICE

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EROSION-RESISTANT TiB₂ COATINGS FORMED BY CHEMICAL VAPOR DEPOSITION*

A. J. Caputo, D. P. Stinton, and J. C. McLaughlin

ABSTRACT

Erosion-and wear-resistant coatings are needed for numerous applications for coal liquefaction and gasification plants. Titanium diboride is unusually hard and stable and, in earlier work, had shown promise for use in highly erosive and corrosive environments. Our objective was to continue to study the deposition of TiB₂ with emphasis on obtaining erosion-resistant coatings on various substrate materials.

Coatings of TiB₂ were deposited at temperatures from 800 to 1000°C by using TiCl₄ and BCl₃. Substrates used included commercial and experimental cemented carbides, nickel-bonded and hot-pressed TiB₂, and abrasion-resistant grades of cast iron. The erosion resistance of the deposited coatings was determined by a hot coal-oil or silica-oil slurry impingement test.

Some coatings deposited at 900 and 1000°C were found to be erosion resistant, although coatings could not be reproducibly deposited. Erosion-resistant coatings were deposited on the various substrates tested. Coatings deposited at 800°C were not erosion resistant, and their microhardness was lower than that of coatings deposited at 900 or 1000°C.

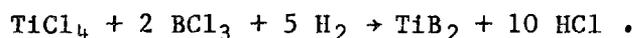
INTRODUCTION

Interest in the use of TiB₂, in the form of chemically vapor-deposited coatings,¹⁻⁵ and monolithic ceramics⁶ is the result of favorable material properties such as high hardness, moderate strength and toughness, and excellent resistance to erosion, wear, and corrosion. These desirable properties are retained by TiB₂ even at high temperature. Such properties make the application of TiB₂ coatings desirable in coal conversion systems, particularly in coal liquefaction plants, where erosion can limit the service lives of letdown valves to a few weeks. In those valves, a large volume of coal-oil slurry must pass through a small orifice to produce the required pressure drop of 10.3 to 13.8 MPa (1500-2000 psi).

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Previous studies^{1,2} of the chemical vapor deposition (CVD) of TiB₂ demonstrated that erosion-resistant coatings could be produced at 900°C. Unfortunately, the results were not predictable^{1,7} because apparently identical processing conditions produced coatings with varying deposition rates, varying grain sizes, and (most important) varying erosion rates. The objective of this research was to further develop the TiB₂ deposition process and equipment so that erosion-resistant coatings could be reproducibly deposited.

The TiB₂ coatings were deposited according to the following reaction:



This reaction has been used by previous researchers,¹⁻⁵ and the thermodynamics and kinetics have been studied extensively.⁸⁻¹⁰

MATERIALS, EXPERIMENTAL APPARATUS, AND PROCEDURE

The initial coating runs were made with the equipment shown schematically in Fig. 1. The equipment, which is described in more detail elsewhere,¹ consisted essentially of a substrate held by a support rod in the center of a coating furnace. The flow of TiCl₄ out of a heated reservoir was controlled by the flow rate of hydrogen carrier gas and by the temperature of a reflux condenser on the exit line from the reservoir. Hydrogen in excess of that needed for the TiCl₄ flow was added separately. The BCl₃ flow was controlled by a volumetric flowmeter. The inlet lines to the coating chamber were heated to prevent condensation of the gases before they reached the coating chamber. Calibration curves were established for the flow rates of TiCl₄ and BCl₃ at various temperatures and carrier gas flow rates. However, observed periodic variations in the deposition rate, coating roughness, coating color, etc. indicated that closer control of the gas flow rate was needed.

The gas flow systems were modified as shown in Fig. 2. The TiCl₄ was stored in a large reservoir and transferred as needed to a pipette amenable to measuring the low flow rates. The standard TiCl₄ flow rate of 0.2 cm³/min of liquid TiCl₄ (40 cm³/min of gas) could be measured visually by using the pipette. The liquid TiCl₄ flowed through flexible capillary

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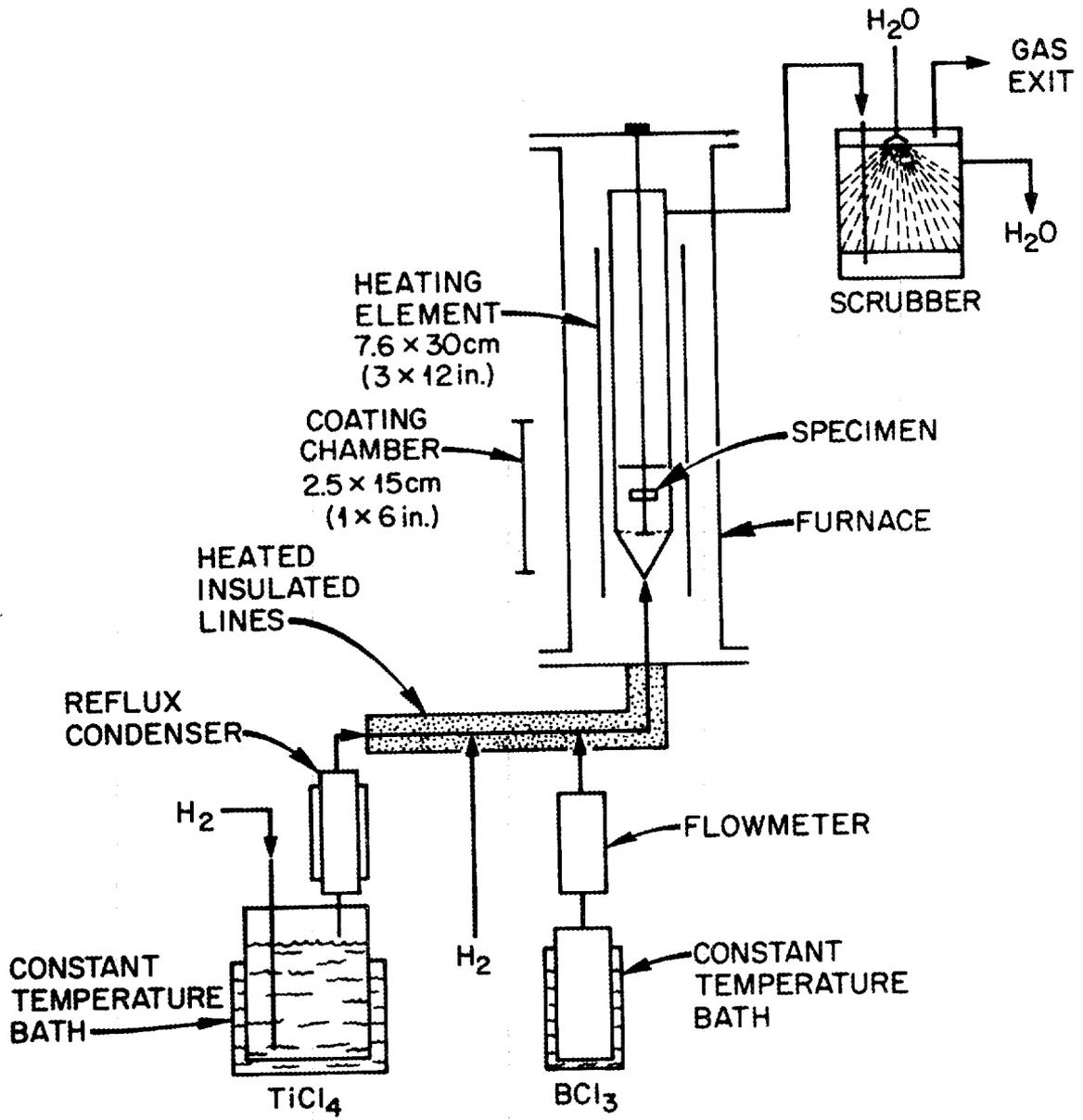


Fig. 1. Original equipment for deposition of TiB_2 on a substrate.

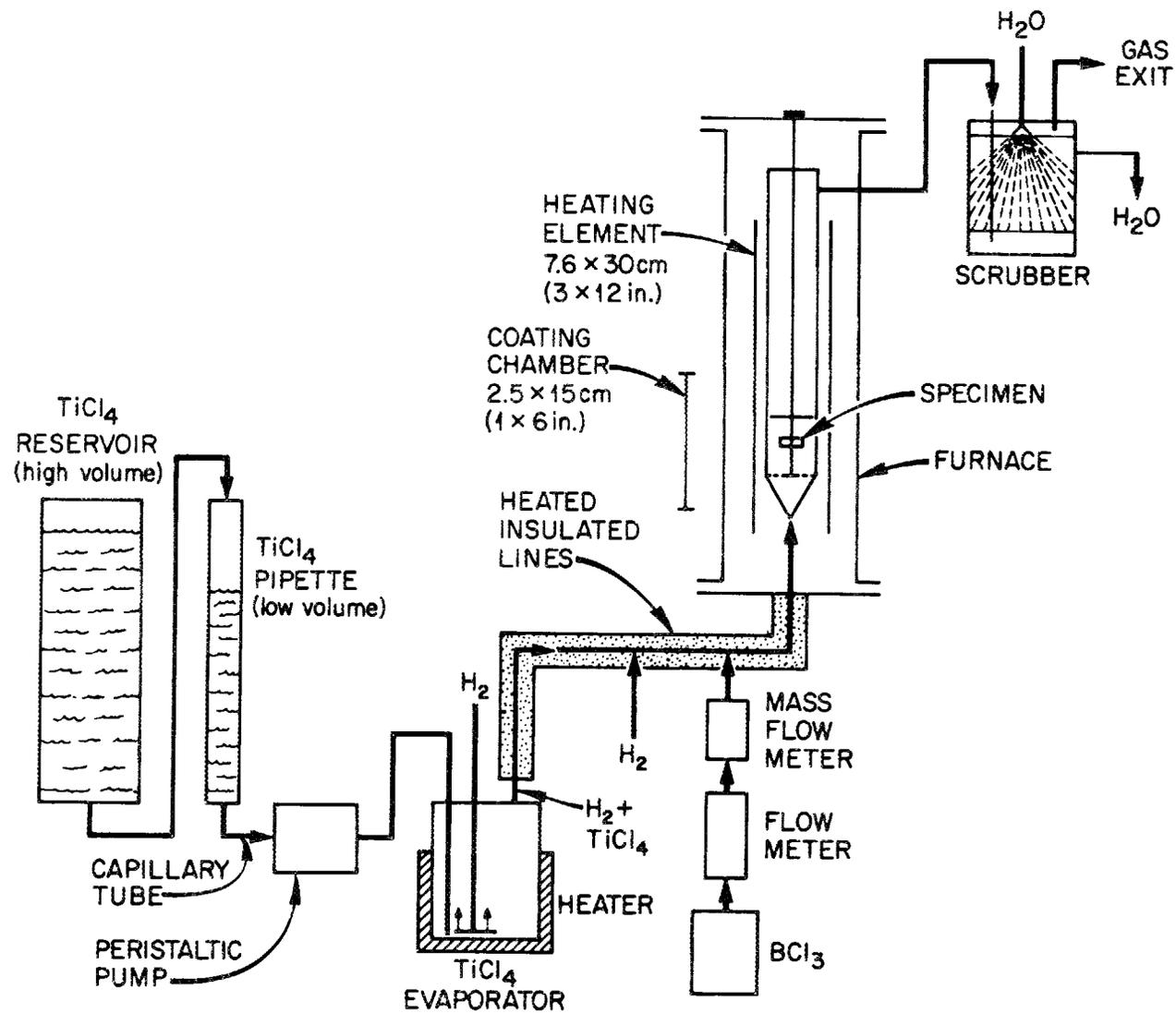


Fig. 2. Deposition equipment for TiB_2 with modified $TiCl_4$ and BCl_3 flow system.

tubing (1 mm I.D.) to a peristaltic pump that maintained a constant flow rate throughout the deposition period. The liquid TiCl_4 was pumped to the heated evaporator, where it vaporized and was swept into the CVD furnace by hydrogen carrier gas. A mass flow rate meter was added to the BCl_3 flow system to provide continuous indication of the BCl_3 gas flow.

Another modification to the process utilized a fluidized bed of particles in an attempt to produce coatings with smooth surfaces. Coatings were deposited with the substrate suspended in the fluidized bed of particles (500 to 1000 μm diam).

The standard deposition conditions for the coating runs were established from the prior work¹ ($\text{TiCl}_4 = 40 \text{ cm}^3/\text{min}$, $\text{BCl}_3 = 240 \text{ cm}^3/\text{min}$, $\text{H}_2 = 2200 \text{ cm}^3/\text{min}$ at 900°C and 100 kPa). Deposition for 20 min produced coatings with a thickness of about $20 \pm 5 \mu\text{m}$. The terms "high" and "low" gas flow rates used later in the report will refer to flows 50% higher and 50% lower than the standard flow rates. Most of the coating runs were made at 900°C , with the remaining runs made at 800 or 1000°C . The run times ranged from 10 min to 2 h to obtain the desired coating thickness.

This study was divided into two main sets of coating runs. The first set of 69 runs used the gas flow-control system shown in Fig. 1. While selected samples of this set were being erosion tested, the modifications to the gas flow-control system were designed, fabricated, and installed. The second set of 16 runs used the modified gas flow system shown in Fig. 2.

The coating experiments of the first set were conducted to investigate the effect of various process parameters (gas flow rates, deposition temperature, substrate type, etc.) on coating properties and subsequent erosion performance. Of the 69 coating runs, 12 were deposited at 800°C , 54 at 900°C , and 3 at 1000°C . The runs at 800°C and 900°C investigated various deposition conditions, various coating thicknesses, and the effect of a post-coating anneal at 1000°C in hydrogen for 1 h. The runs at 900°C also examined the effect of various substrates on the properties of the coating. In addition to the standard cemented tungsten carbide substrate (GE-370), we studied sintered TiB_2 (PPG), two grades of

abrasion-resistant cast iron (Abex HC-250 and Amax 1503), two grades of impact resistant WC (Kennametal 3833 and 3109), and several other grades of WC (Kennametal K-701, Kengard A, and Kengard B). (See Table 1.)

Table 1. Substrates for TiB₂ deposition

| Vendor | Description | Grade | Composition (wt %) | Coefficient of thermal expansion ^a ($\times 10^{-6} \text{ K}^{-1}$) |
|---------------------------|--------------------------------------|-----------|--------------------------|---|
| General Electric | Cemented tungsten carbide | GE-370 | WC-11 TaC- 8 TiC-9 Co | 5.8 |
| Pittsburgh Plate Glass | Sintered TiB ₂ | | TiB ₂ | 8.8 |
| Abex Corp. | Abrasion-resistant cast iron | HC-250 | Fe-28 Cr-3C | 16.0 |
| Amax Inc. | Abrasion-resistant cast iron | 1503 | Fe-15 Cr-3 Mo | N/A ^b |
| Kennametal | Wear-resistant tungsten carbide | K-3833 | N/A | 5.4 |
| Kennametal | Impact-resistant tungsten carbide | K-3109 | N/A | 6.1 |
| Kennametal | Wear-resistant tungsten carbide | Kengard A | N/A | N/A |
| Kennametal | Wear-resistant tungsten carbide | Kengard B | N/A | N/A |
| Kennametal | Wear-resistant tungsten carbide | K-701 | WC-10 Co-4 Cr | 6.5 |

^aFor comparison the coefficient of thermal expansion of chemically vapor-deposited TiB₂ is $8.0 \times 10^{-6} \text{ K}^{-1}$.

^bNot available.

The second set consisted of nine runs to test and calibrate the new gas flow system and to coat the standard cemented tungsten carbide substrates. Then, seven runs were made to coat pressure letdown valve

trim pieces similar to those used in the Wilsonville, Alabama, Advanced Coal Liquefaction Research and Development Facility. The trim pieces were coated while suspended in a fluidized bed of particles to obtain a more uniform and smooth coating.

After coating, selected samples were evaluated for erosion resistance at Battelle Columbus Laboratories (BCL). The erosion test procedure and equipment are more fully described elsewhere.¹¹ In summary, during earlier erosion work at BCL samples were impacted at an angle of 20° and 100 m/s with a coal-oil slurry (8% solids in anthracene oil) at 315°C for 1 h (Fig. 3). However, when the initial coatings discussed in this report were tested (mid FY 1984), a slurry of fused silica and oil was being used. Thus, tests on our initial samples could not be directly compared with the tests on samples exposed to the coal-oil slurry. To obtain this direct comparison, some samples were tested with the coal-oil slurry. The amount of erosion resistance was determined from profilometer traces of the crater produced on the coating surface by the abrasive slurry. For coatings that exhibited very little erosion, distinguishing the crater depth from the normal surface fluctuations of the as-deposited surface was difficult. Some samples were polished before erosion testing to reduce the roughness (a few μm) of the as-deposited surface and thereby aid in the determination of very small crater depths.

Characterization of coatings deposited in this study emphasized hardness, erosion resistance, and chlorine content. More extensive coating characterization was done in the earlier work.¹

RESULTS AND DISCUSSION

PROCESS CONTROL

Shortly after the initiation of coating depositions for this study (FY 1984) it became apparent that more control of the process was needed. Variations were seen in the deposition rate, coating color, surface smoothness, and coating thickness uniformity across the specimen. Modifications were made to the temperature and pressure controls of the

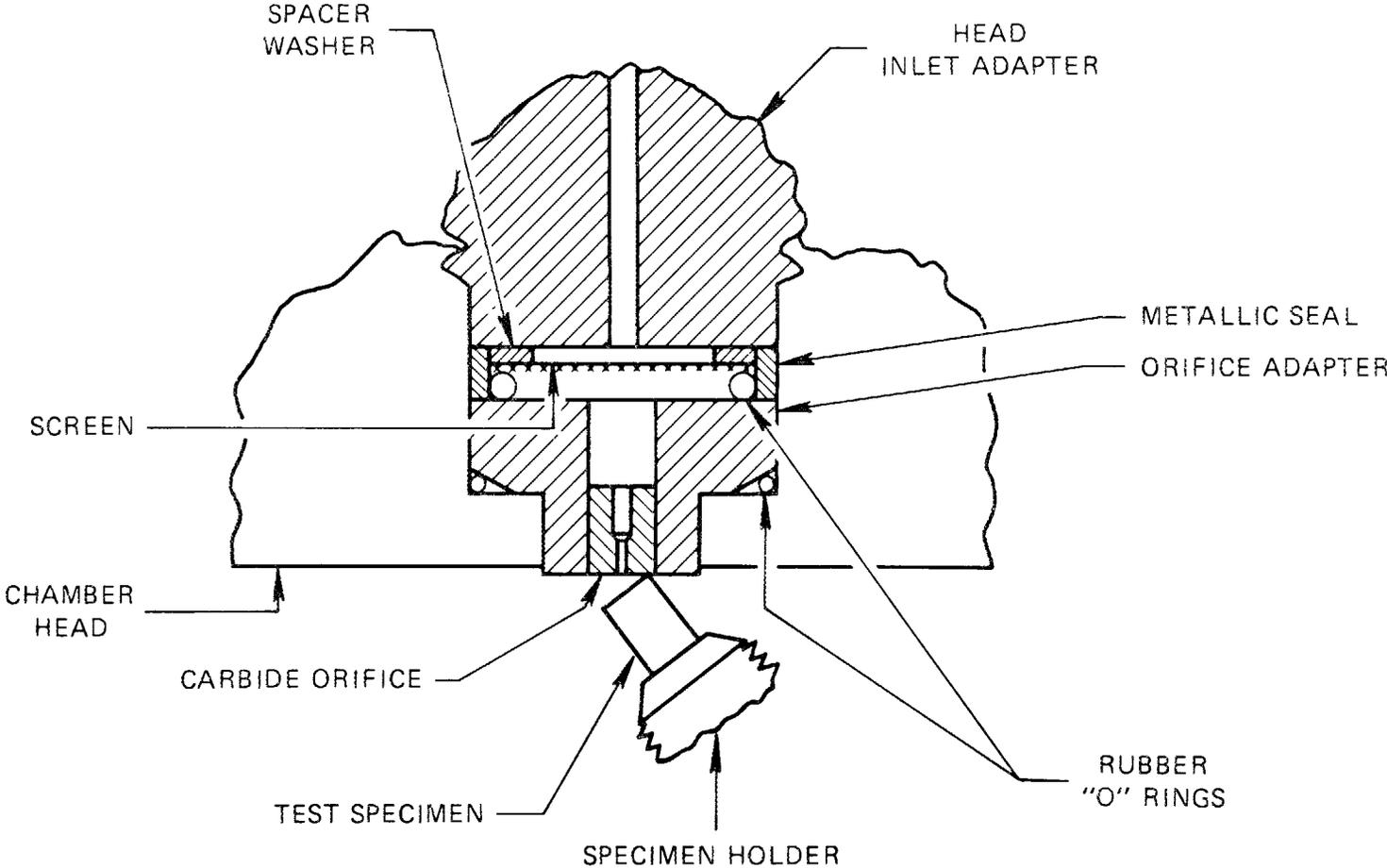


Fig. 3. Schematic of the specimen fixturing for the slurry erosion test.

gas flow system shown in Fig. 1. Additionally, internal furnace parts were heated to ensure that the $TiCl_4$ did not condense before it entered the coating chamber. After the installation of the flow system shown in Fig. 2, only a limited number of coating depositions were made and erosion tested because of the limited availability of the erosion testing equipment. The repeatability of the coatings produced by the new flow control system was certainly much better than that of the previous system; however, some variations remained.

Several depositions were made to coat actual valve trim pieces. These runs were made with the fluidized bed arrangement, and surrogate pieces made of carbon were coated first to conserve the limited supply of actual valve trim pieces. Depositions on the K-701 material were done at $900^\circ C$ for 2 h, resulting in 50- μm -thick coatings. These coatings appeared to be acceptable and relatively smooth, and they were subsequently erosion tested.

COMPOSITION AND IMPURITY CONTENT

The coatings were analyzed for chlorine, and the content was found to decrease with increasing deposition temperature (as in the earlier work).¹ Coatings deposited at 800, 900, and $1000^\circ C$ had chlorine concentrations of 5.72, 0.33, and less than 0.05 (limit of detection) wt %, respectively, as shown in Table 2.

In an attempt to increase the hardness of the coatings by reducing the chlorine content, several coatings deposited at 800 or $900^\circ C$ were heat treated in hydrogen at $1000^\circ C$ immediately after coating. Unfortunately, as discussed below, the annealed coatings showed no improvements in hardness (see Table 2 for chlorine contents). The data (Table 2) also show that the TiB_2 coating deposited at $1000^\circ C$ has a boron-to-titanium atomic ratio of 2.002, which is essentially stoichiometric. However, coatings deposited at 900 and $800^\circ C$ have a slight excess of boron, the ratios being 2.006 and 2.066, respectively. Note that large amounts of excess chlorine in the coatings result in high boron-to-titanium ratios. Also note that the heat treatment may have altered the boron-to-titanium ratio of the $800^\circ C$ coating to nearer the stoichiometric value.

Table 2. Properties of TiB₂ coatings at various deposition temperatures

| Run | Deposition temperature (°C) | Heat treat ^a temperature (°C) | Chlorine (wt %) | Atomic ratio B-Ti |
|-----|-----------------------------|--|--------------------|-------------------|
| 480 | 800 | None | 5.72 | 2.066 |
| 479 | 900 | None | 0.33 | 2.006 |
| 520 | 1000 | None | <0.05 ^b | 2.002 |
| 512 | 800 | 1000 | 0.74 | 2.012 |
| 518 | 800 | 1000 | 2.55 | 2.029 |
| 511 | 900 | 1000 | 1.16 | 2.013 |

^aHeat treated in hydrogen for 1 h immediately after coating.

^bLimit of detection.

MICROHARDNESS

Microhardness data for the TiB₂ coatings were determined and are consistent with previous results.¹ The main objective of this effort was to determine if the 1000°C anneal increased the hardness of the coatings. Coatings deposited at 800°C were significantly softer than coatings deposited at 900 or 1000°C (Table 3). The 1000°C heat treatment of coatings deposited at 800 or 900°C appears to have had no effect on the coating hardness.

SURFACE MORPHOLOGY

Profilometer traces were performed on about 50 of the TiB₂ coated specimens. The specimens had coatings prepared at various deposition temperatures (800 to 1000°C), various coating thicknesses (7 to 175 μm), and various substrates. The measurements showed that, generally, somewhat smoother coatings are produced at lower temperatures and lower coating thicknesses. Coatings deposited at 900°C by using the

Table 3. Microhardness of chemically vapor-deposited TiB₂ at various conditions

| Deposition temperature (°C) | Flow rates ^a | Knoop microhardness (GPa) at indenter loads (g) of | | |
|-----------------------------|-------------------------|--|----|----|
| | | 100 | 50 | 25 |
| 1000 | Standard | 35 | 43 | 57 |
| 900 | Standard | 29 | | |
| 900 | High-high | | | 13 |
| 900 | Low-low | | 54 | 57 |
| 900 | Standard ^b | | | 56 |
| 800 | Standard | | 14 | 18 |
| 800 | Standard ^b | | | 12 |

^aStandard: TiCl₄ = 40, BCl₃ = 240 cm³/min;
 high-high: TiCl₄ = 60, BCl₃ = 360 cm³/min; low-low:
 TiCl₄ = 20, BCl₃ = 120 cm³/min.

^bHeat treated at 1000°C in hydrogen for 1 h immediately after coating.

fluidized-bed reactor were smoother than those deposited in the standard reactor at the same temperature. Diamond grinding and polishing was performed on some coatings in order to produce smoother surfaces before erosion testing. Typical profilometer traces of as-deposited coatings (Fig. 4) show that the 800°C coating is somewhat smoother than the 900°C coating, but, in both cases, the nodular growth features result in peaks and valleys that span several microns. Profilometer traces of a 900°C coating as deposited and as diamond ground are shown in Fig. 5. Even at the expanded scale the smoothness of the ground specimen is apparent. Profilometer traces of 14- and 55- μ m-thick coatings deposited at 900°C in a fluidized bed are shown in Fig. 6. The coatings are somewhat smoother and the number of maxima and minima somewhat less. Profilometer traces of even thicker coatings (90 and 175 μ m) deposited at 900°C in the standard reactor are shown in Fig. 7. These traces show reasonable smoothness even for the relatively thick coatings.

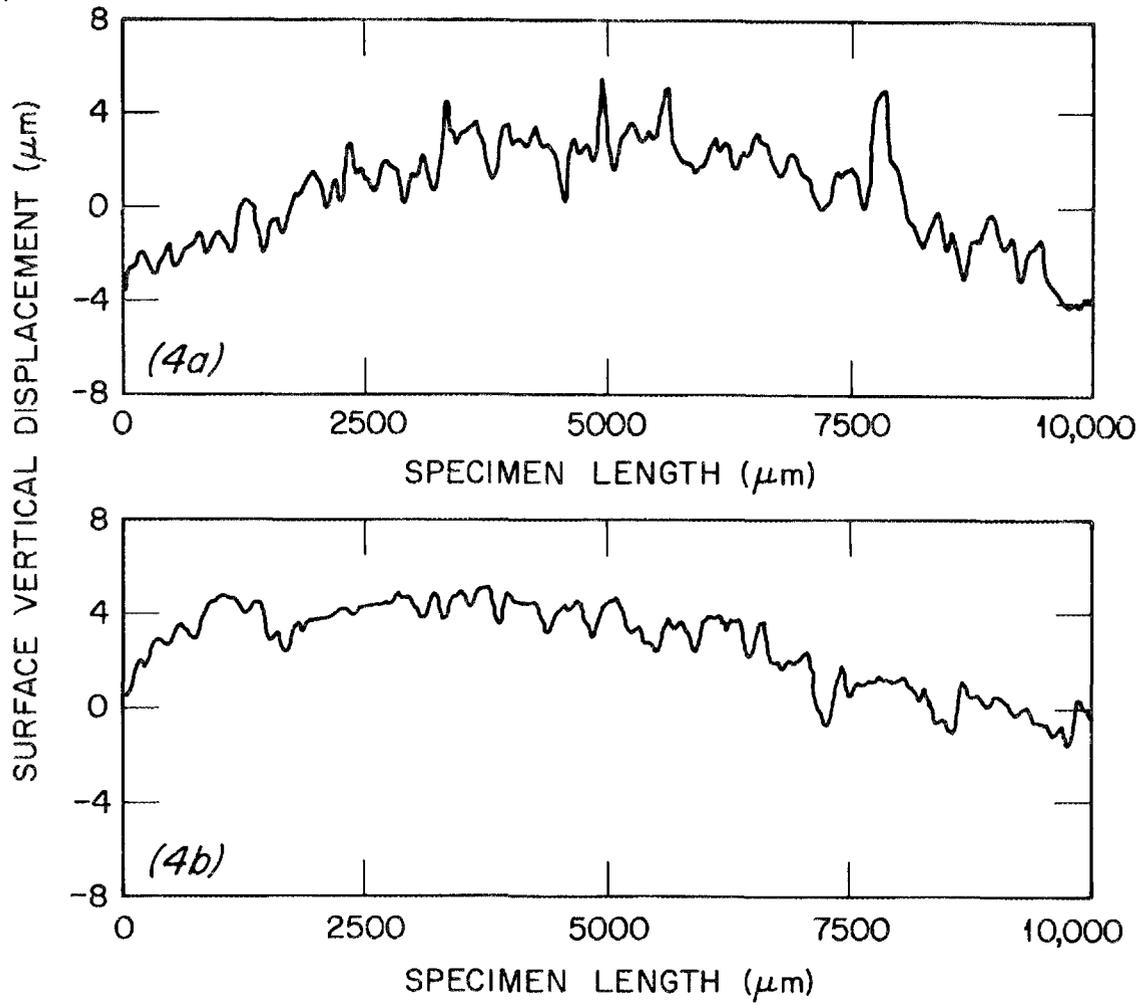


Fig. 4. Profilometer traces of TiB_2 coatings deposited at (a) 800°C and (b) 900°C .

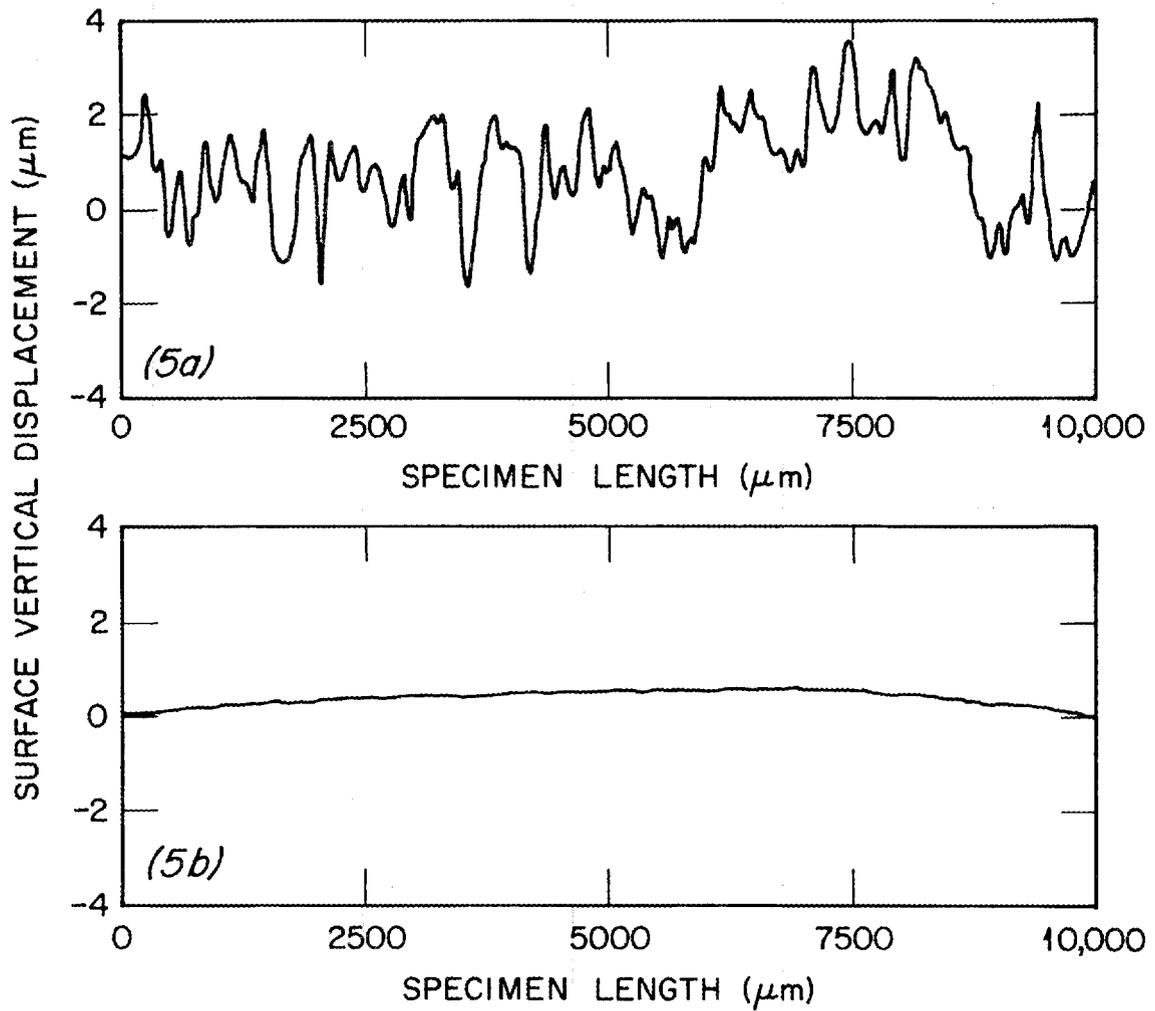


Fig. 5. Profilometer traces of a TiB_2 coating deposited at 900°C . (a) As deposited. (b) As diamond ground.

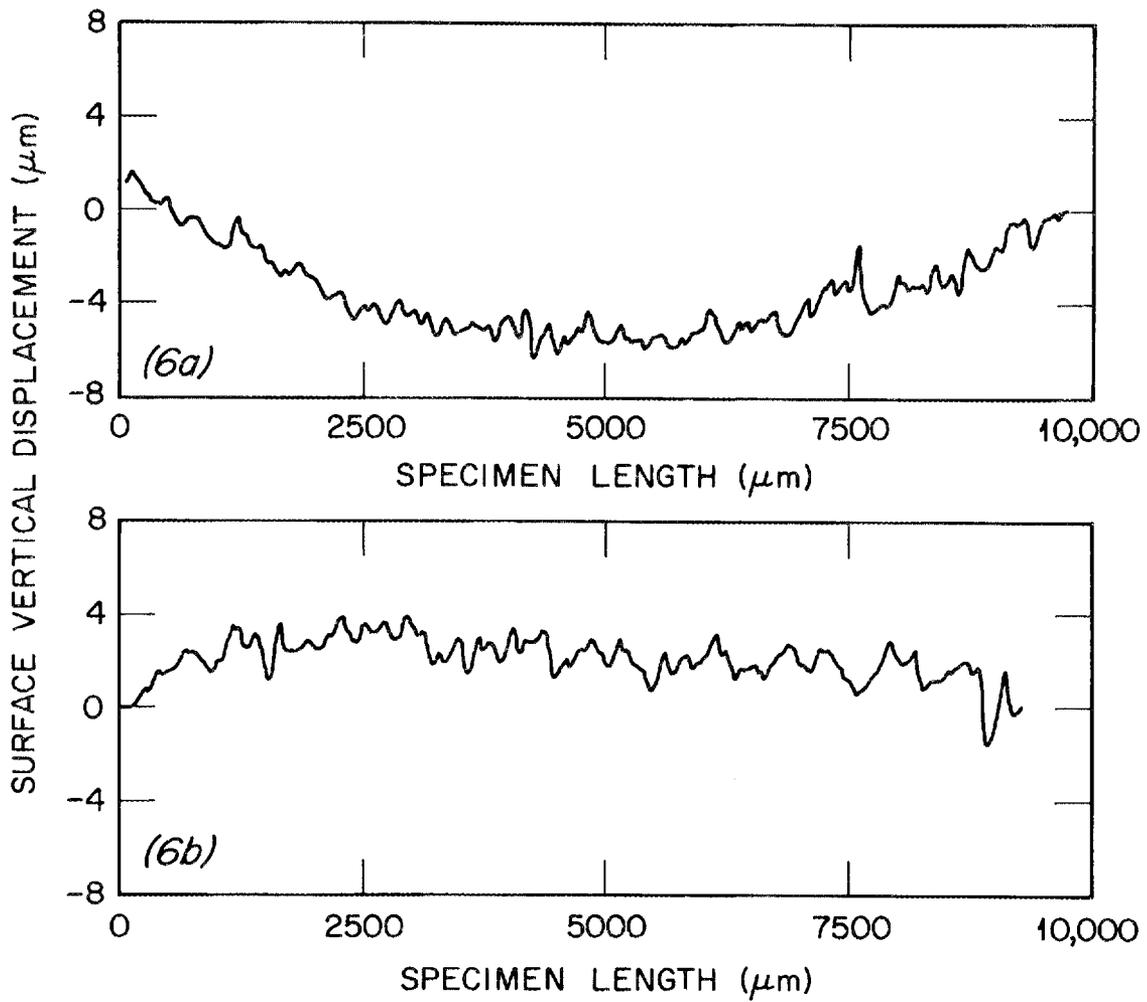


Fig. 6. Profilometer traces of TiB_2 coating deposited at 900°C in a fluidized bed. (a) Thin coating (14 μm). (b) Thicker coating (55 μm).

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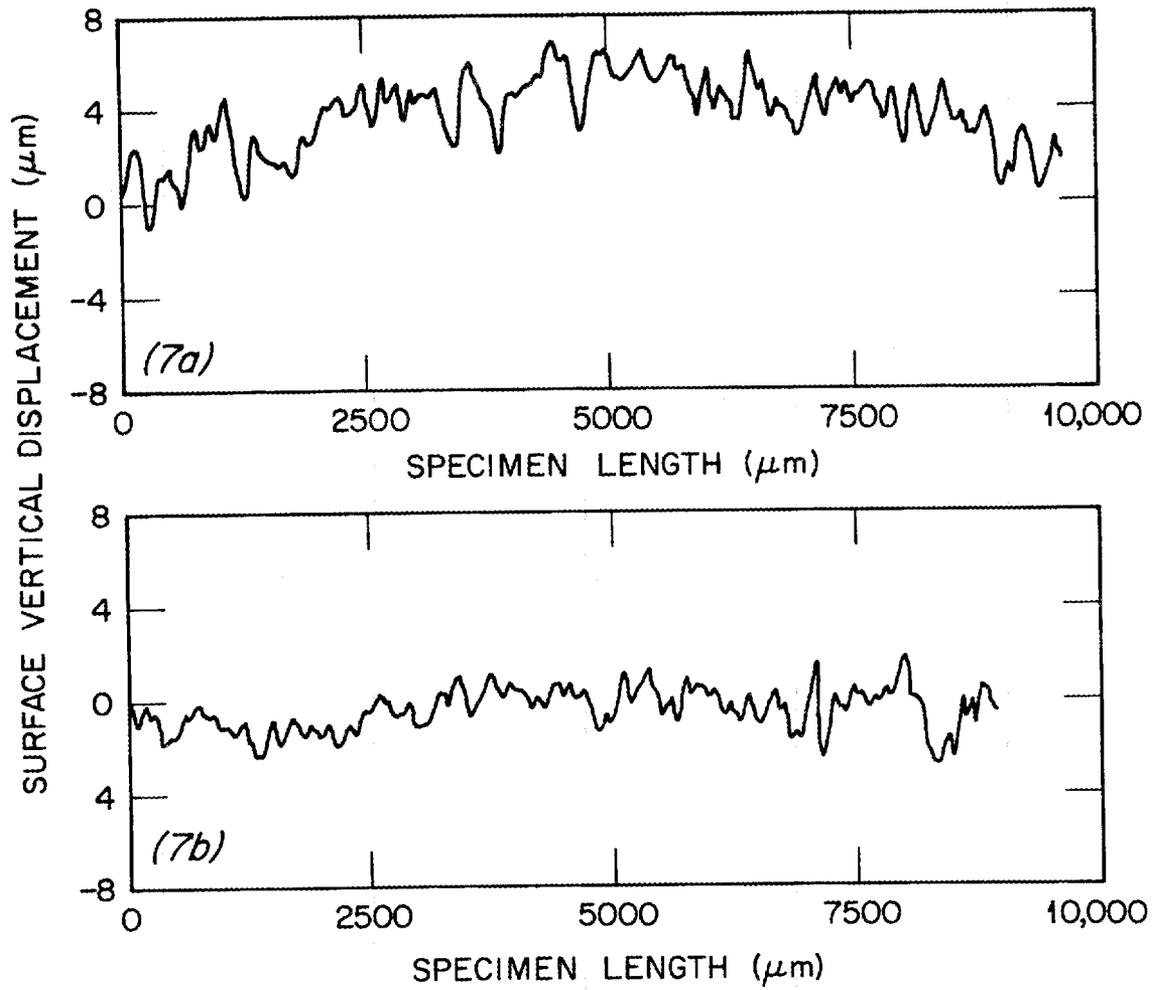


Fig. 7. Profilometer traces of TiB_2 coatings deposited at 900°C in standard reactor. (a) $90 \mu\text{m}$ thick. (b) $175 \mu\text{m}$ thick.

Scanning electron microscopy performed on various coatings revealed that the coatings consist of nodular TiB_2 crystallites, with the nodules becoming somewhat larger at the higher deposition temperatures. Coatings that were optically dull or somewhat discolored tended to have many more and smaller nodules than the optically brighter coatings had.

SUBSTRATES

One of the objectives of this study was to expand the investigation of the different types of substrates that could be coated and provided with improved erosion resistance. In addition to the standard cemented carbide (WC-TaC-TiC-Co), other substrates successfully coated by using our standard conditions included hot-pressed and sintered TiB_2 , two grades of impact-resistant WC (Kennametal 3833 and 3109), and several other experimental grades of WC (Kennametal K-701, Kengard A, and Kengard B). These substrates showed no unusual behavior and were coated in the normal manner. However, the two grades of abrasion-resistant cast iron (Abex HC-250 and Amax 1503) behaved differently. No coating was deposited on either substrate at $900^\circ C$; at $1000^\circ C$, only the HC-250 substrate was coated. The free-energy curves of the iron chloride reaction and the titanium diboride reaction are similar in magnitude but have different slopes. The crossover point is in the range of the deposition temperatures being investigated, with the iron chloride reaction favored below $1000^\circ C$ (and probably disrupting the coating deposition) and the TiB_2 reaction favored above $1000^\circ C$. The HC-250 that was coated contains about 70% iron, and the 1503 that did not coat contains about 82% iron, which suggests that the different iron activities in those two alloys may explain the observed difference in deposition at $1000^\circ C$.

EROSION TESTING

Erosion testing of the coatings in this study involved three distinct groups of tests. When the first coatings were available for testing, the erosion equipment at Battelle Columbus Laboratories employed a slurry of fused silica and oil instead of the previously used coal-oil slurry. This change was made to obtain a more consistent erosive material for testing

purposes. The second group of tests was done after BCL converted back to the coal-oil slurry because it is more representative of actual service and also allows a direct comparison with coatings that had been previously tested with the coal-oil slurry. The bulk of the testing and the most meaningful results were obtained from this group of tests. After the major objectives had been reached, silica-oil testing was resumed for other programs. Therefore, the third series of tests on coatings for this work was performed with the silica-oil slurry.

Initial testing of TiB₂-coated substrates with the silica-oil slurry at a 90° impingement angle indicated that the coated substrates eroded faster than the reference K-701 substrate. It was recognized that (1) the 90° impingement angle is more severe than lower incidence angles on hard materials such as TiB₂, and (2) lower angles (such as 20°) are probably more typical of actual service. Thus, additional testing was done using a 20° impingement angle. The results are shown in Table 4. The erosion performance is given as the ratio of the wear rate of the coating to the

Table 4. Erosion testing of chemically vapor-deposited TiB₂ coatings with silica-oil slurry at 20° impingement angle at 315°C

| Sample number | Substrate type | Coating | | Erosion performance ratio | |
|------------------|----------------|-----------------------------|----------------|---------------------------|------------------|
| | | Deposition temperature (°C) | Thickness (μm) | As-deposited coating | Polished coating |
| 476 | WC-TaC-TiC-Co | 900 | 20 | 0 | 0.8 |
| 476 | WC-TaC-TiC-Co | 900 | 20 | 1.2 | |
| 476 | WC-TaC-TiC-Co | 900 | 20 | 3.6 | |
| 476 | WC-TaC-TiC-Co | 900 | 20 | 1.8 | 1.3 |
| 473 | WC-TaC-TiC-Co | 900 | 20 | | 1.1 |
| 463 | WC-TaC-TiC-Co | 900 | 20 | | 1.6 |
| 520 | WC-TaC-TiC-Co | 1000 | 42 | | 1.4 |
| 404 ^a | WC-TaC-TiC-Co | 900 | 20 | | 3.5 |
| 411 ^a | WC-TaC-TiC-Co | 900 | 20 | | 0.9 |

^aCoatings previously tested (FY 1983) that showed no measurable wear when tested with a coal-oil slurry.

wear rate of uncoated K-701. As shown in Table 4, the erosion performance for four samples (463, 473, 476, and 520) indicated that the coatings did wear and that the rates varied considerably. This was true for both as-deposited and polished coatings. Also, two samples (404 and 411) that showed no measurable wear when tested in FY 1983 with a coal-oil slurry showed wear in the silica-oil slurry. Therefore, we conclude that the erosion rate of the coatings as measured with silica-oil slurry was typically greater than that of the uncoated reference material; however, some results occasionally indicated no wear or wear slightly less than that of the uncoated reference material.

Testing continued after converting back to the use of a coal-oil slurry (second group of tests). These results are summarized in Table 5. More detailed information on the results presented in Tables 4 and 5 is shown in the Appendix. The confirmatory tests on a group of samples that had been previously tested in FY 1983 showed results ranging from no wear to wear greater than that for K-701. The substrate type, coating thickness, or whether the coating was as deposited or polished had no obvious effect on the results.

The remaining samples listed in Table 5 are specimens that were coated during this work. The most significant result for this group was that a 2-hour test on a recent TiB_2 sample (463) coated at $900^\circ C$ showed no measurable wear (ratio is 0). This result was observed for a polished sample so there is no question about its validity. To verify this result, the sample was retested. Again, there was no measurable wear after the 2-hour test. These results clearly indicate that chemically vapor-deposited TiB_2 coatings can have very low erosion rates under very hostile conditions and be superior to the reference carbide. Another sample (520) coated at $1000^\circ C$ eroded slightly less than did K-701, with a ratio of 0.9. However, two other samples (472 and 497) also coated at $900^\circ C$ showed erosion greater than that of K-701. Thus, specimens coated under apparently identical conditions gave different results. Further modifications and testing of the deposition apparatus and understanding of the factors affecting deposit characteristics will be required before wear-resistant TiB_2 coatings can be deposited consistently.

Table 5. Erosion testing of chemically vapor deposited TiB_2 coatings with coal-oil slurry at 20° impingement angle at $315^\circ C$

| Sample number | Substrate type | Coating | | Erosion performance ratio | |
|---------------------|--------------------------|---------------------------------------|-----------------------|---|------------------|
| | | Deposition temperature ($^\circ C$) | Thickness (μm) | Wear rate of coating / Wear rate of K-701 | |
| | | | | As-deposited coating | Polished coating |
| 411 ^a | WC-TaC-TiC-Co | 900 | 20 | 0 | 1.8 |
| 411 ^a | WC-TaC-TiC-Co | 900 | 20 | 3.3 | |
| 391 ^a | WC-TaC-TiC-Co | 900 | 20 | 0 | 2.6 |
| 391 ^a | WC-TaC-TiC-Co | 900 | 20 | 1.3 | |
| 404 ^a | WC-TaC-TiC-Co | 900 | 20 | 0 | 2.4 |
| NT90AD ^a | Hot-pressed TiB_2 -Ni | 900 | 50-100 ^b | 1.3 | 1.2 |
| 454B ^a | Hot-pressed TiB_2 -Ni | 900 | 20 | | 1.0 |
| 463 | WC-TaC-TiC-Co | 900 | 20 | | 0 |
| 463 | WC-TaC-TiC-Co | 900 | 20 | | 0 |
| 472 | WC-TaC-TiC-Co | 900 | 20 | | 2.5 |
| 497 | Sintered TiB_2 | 900 | 20 | | 3.4 |
| 520 | WC-TaC-TiC-Co | 1000 | 42 | | 0.9 |
| 483 | WC-TaC-TiC-Co | 900 | 90 | | 8.0 |
| 484 | WC-TaC-TiC-Co | 900 | 175 | | 4.0 |
| 488 | Sintered TiB_2 | 900 | 85 | | 2.6 |
| 526 | WC-TaC-TiC-Co | 900 | 55 ^c | 2.0 | 2.8 |
| 532 | Valve trim made of K-701 | 900 | 49 ^c | 1.3 | |

^aThese samples were coated and tested with the coal-oil slurry in FY 1983.

^bCoated at Sandia Laboratories.

^cCoated in fluidized bed.

Testing also was done on samples coated at $900^\circ C$ that had coating thicknesses considerably greater than the normal $20 \mu m$. Samples with a thickness of $85 \mu m$ (TiB_2 substrate) and of 90 and $175 \mu m$ (WC-TaC-TiC-Co substrate) all had wear rates greater than that of the K-701 reference. Although the performance was less than desirable, it was noteworthy that the thicker coatings did not debond from the substrate.

Additional testing was done on samples coated while suspended in a fluidized bed. A sample (526) with a moderately thick coating (55 μm) on a WC-TaC-TiC-Co substrate had an erosion rate greater than that of K-701. In addition an actual K-701 valve trim (typical of those used in the Wilsonville plant) also was coated at 900°C in a fluidized bed (532). The 49- μm -thick coating had an erosion rate somewhat higher than that of K-701.

The third group of specimen tests was done on coatings that had been deposited on various substrates (Table 6). These coatings were deposited at 900°C by using the standard flow conditions except as noted. The testing was done with the silica-oil slurry at a 20° impingement angle. The type of substrate material had no measureable effect on the wear rate of the TiB₂ coating. However, one very significant finding resulted from this series of tests. An abrasion-resistant cast-iron substrate (HC-250) can be coated with TiB₂ at 1000°C (sample 510) and exhibit a wear rate nearly equal to that of tungsten carbide.

Table 6. Erosion testing of chemically vapor-deposited TiB₂ coatings deposited on various substrates

(Twenty-min test with silica-oil slurry at 20° impingement angle; all coatings approximately 20 μm thick except as noted.)

| Sample number | Substrate material | | Deposition temperature (°C) | Erosion performance ratio |
|------------------|---------------------------|-----------|-----------------------------|---|
| | Type | Grade | | $\frac{\text{Wear rate of coating}^a}{\text{Wear rate of K-701}}$ |
| 462 | WC-TaC-TiC-Co | GE-370 | 900 | 1.4 |
| 463 | WC-TaC-TiC-Co | GE-370 | 900 | 1.0 |
| 520 ^b | WC-TaC-TiC-Co | GE-370 | 1000 | 1.2 |
| 508 | Sintered TiB ₂ | | 900 | 0.5 |
| 510 ^c | Cast iron | | 1000 | 1.4 |
| 498 | Tungsten carbide | Kengard A | 900 | 2.3 |
| 499 | Tungsten carbide | Kengard B | 900 | 1.2 |
| 505 | Tungsten carbide | K-3109 | 900 | 3.5 |
| 505 | Tungsten carbide | K-3833 | 900 | 1.4 |
| 505 | WC-TaC-TiC-Co | GE-370 | 900 | 2.3 |

^aCoatings tested in as-deposited state.

^bCoating thickness 42 μm .

^cCoating thickness 29 μm .

Two new experimental grades of wear-resistant WC (Kennametal Kengard A and B) were coated and tested. Coated Kengard B gave results essentially equal to that of K-701, but coated Kengard A had a somewhat greater erosion rate. Two grades of impact-resistant WC (Kennametal 3833 and 3109) were also coated and tested. Grade 3833 gave results about the same as that for K-701, but 3109 had an erosion rate greater than that of K-701.

In addition to these coatings that were deposited at 900°C, several erosion tests were done on coatings deposited at 800°C. Previous testing had shown that coatings deposited at 800°C were not erosion resistant, so process variables were altered in an attempt to improve the erosion resistance. Three specimens (480, 481, and 482) coated with different $TiCl_4$ and BCl_3 flow rates did not show any improvement in erosion resistance, nor did specimens that were heat treated after deposition.

CONCLUSIONS

This work demonstrated that erosion-resistant TiB_2 coatings can be produced by chemical vapor deposition. A TiB_2 coating deposited at 900°C was erosion tested for 2 hours with a coal-oil slurry and showed *no* measurable wear. This was a polished sample, so there is little uncertainty in the measured erosion depths. This result was confirmed when the sample was retested for another 2 h and again there was no measurable wear. This is verification that CVD TiB_2 can have very low erosion wear rates and be superior to the uncoated K-701 reference material. However, other samples coated under identical conditions had wear rates greater than that of the uncoated K-701 reference material. Furthermore, most of the testing showed wear rates greater than that of the reference material. Therefore, further work will be required before wear-resistant TiB_2 coatings can be reproducibly deposited.

Testing of coatings deposited on various substrates yielded one very significant result. A coating deposited at 1000°C onto an abrasion-resistant cast-iron substrate exhibited a wear rate essentially equal

to that of the K-701 reference material. This is very significant because it demonstrates that ferrous materials (not just cemented carbides or other hard materials) can be coated and used in severely erosive environments.

This work re-emphasized the difficulties of measuring shallow erosion craters by profilometry when the deposited coating has inherent surface roughness. Deposition in a fluidized bed aided but did not eliminate this problem. Grinding and polishing of the surfaces also reduced this problem, but it presents a danger of inducing microstructural damage that could affect the erosion resistance and adherence of the coating. The coatings deposited at 800°C were not erosion resistant and had lower microhardness than coatings deposited at 900 or 1000°C. The heat treatment at 1000°C of coatings deposited at 800°C failed to increase the microhardness or improve the erosion resistance.

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Appendix

EROSION TESTING OF CHEMICALLY VAPOR-DEPOSITED TiB₂ COATINGSTable A.1. Erosion testing of chemically vapor-deposited TiB₂ coatings with silica-oil slurry at 20° impingement angle

| Specimen | Surface | Preparation | Crater depth (μm) | | |
|----------------------|---------|----------------|--------------------|--------|--------|
| | | | 10 min | 20 min | 60 min |
| CR-476 | 1 | Diamond ground | | 2.3 | |
| | 2 | As deposited | No measurable wear | 3.5 | |
| | 3 | As deposited | 4.3 | 5.1 | |
| | 4 | Diamond ground | | 3.7 | |
| Reference | | K-701 uncoated | 1.2 | 3.1 | |
| Reference | | K-701 uncoated | | 2.6 | |
| CR-473 | | | | | 12.7 |
| Reference | | K-701 uncoated | | | 11.1 |
| Reference | | K-701 uncoated | | 3.1 | |
| AJC-404 ^a | | Diamond ground | | 10.1 | |
| AJC-411 ^a | | Diamond ground | | 2.8 | |
| CR-463 | | Diamond ground | | 4.6 | |
| CR-520 ^b | | Diamond ground | | 4.0 | |
| Reference | | K-701 uncoated | | 2.6 | |

^aPortion of a sample previously tested in 1983 with coal-oil slurry for 1 h at 20°, which showed no measurable wear but was tested in as-deposited state.

^bTiB₂ deposited at 1000°C; all other coatings deposited at 900°C.

Table A.2. Erosion testing of chemically vapor-deposited TiB₂ with coal-oil slurry at 20° impingement angle

| Group | Substrate | Sample | Erosion wear rate (μm/h) | | | | | | | | |
|-------|-----------|--------------------------|--------------------------|--------------|---------------|--------------|-------------------|--------------|---------------|--------------|-----|
| | | | As-deposited coatings | | | | Polished coatings | | | | |
| | | | Sample 1 h | K-701 1 h | Sample 2 h | K-701 1 h | Sample 3 h | K-701 1 h | Sample 2 h | K-701 1 h | |
| a | b | CR-411 | No measurable wear | 2.0 | 2.0 | 0.6 | | | | 1.1 | 0.6 |
| a | b | CR-391 | No measurable wear | 2.0 | | | | 1.2 | 0.7-1.1 | 1.8 | 0.7 |
| a | b | CR-404 | No measurable wear | 1.1 | | | | | | 1.7 | 0.7 |
| | | Reference K-701 uncoated | | | | | | 0.5 | 0.7-1.0 | | |
| a | c | NT90AD ^d | | | 0.9 | 0.7 | | | | 0.6 | 0.5 |
| a | c | CR-454B (NT80K) | | | 0.8 | 0.6 | | | | 0.5 | 0.5 |
| e | b | CR-463 | | | | | | | | None | 0.5 |
| e | b | CR-463 | | | | | | | | None | 0.5 |
| e | b | CR-472 | | | | | | | | 1.5 | 0.6 |
| e | f | CR-497 | | | | | | | | 1.7 | 0.5 |
| e | b | CR-520 ^g | | | | | | | | 0.7 | 0.8 |
| h | b | CR-483 | | | | | | | | 3.2 | 0.4 |
| h | b | CR-484 | | | | | | | | 2.0 | 0.5 |
| h | f | CR-488 | | | | | | | | 1.3 | 0.5 |
| h | b | CR-526 ⁱ | | | 1.0 | 0.5 | | | | 1.4 | 0.5 |
| h | j | CR-532 ⁱ | | | 0.5-1.1 | 0.6 | | | | | |

^aSamples coated at 900°C that showed no measurable wear when tested in FY 1983 (for 1 h in as-deposited state) when tested 1 h last year with the coal-oil slurry.

^bWC-TaC-TiC-Co.

^cHot-pressed TiB₂-Ni.

^dCoated at Sandia; TiB₂ thickness was 50 to 100 μm.

^eSamples coated at 900°C (unless otherwise noted) in this work with TiB₂ about 20 μm thick.

^fSintered TiB₂.

^gCoated at 1000°C; TiB₂ thickness was 42 μm.

^hSamples coated at 900°C for times up to 3 h to give thicker coatings (CR-483 was 90 μm; CR-484 was 175 μm; CR-488 was 84 μm; CR-526 was 55 μm; and CR-532 was 49 μm).

ⁱCoated in fluidized bed.

^jAn actual valve trim of K-701.

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