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WEAR PREVENTION IN MOLDS USED TO
MOLD BORON-FILLED ELASTOMERS

MASTER

Conference Paper

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Technical Communications

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ABSTRACT

An investigation was conducted to identify surface coatings which would improve the wear characteristics of compression molds used to mold contoured parts from elastomers filled with crystalline boron particles. An analysis was made of the mode of wear present on the surfaces of a production mold, followed by selection and modification of a capillary rheometer as the test device. Test specimens were coated by electroplating, electroless plating, plasma spraying, chemical vapor deposition, sputtering, and a fused salt process. Testing was conducted under conditions simulating those encountered in the production molding operation.

Techniques used in evaluating the results included optical microscopy, scanning electron microscopy, transmission electron microscopy, and surface profilometry. The results are expressed as a ratio of volumetric wear of the tested coating to that of unprotected mold steel.

Results indicate that titanium diboride (TiB_2) applied by chemical vapor deposition provides wear resistance superior to plasma-sprayed aluminum oxide mixed with titanium dioxide, plasma-sprayed chromium oxide, electrodeposited chromium, electroless nickel containing synthetic diamond powder, and chemical-vapor-deposited tungsten carbide (W/W_2C), aluminum oxide, and aluminum oxide over chromium carbide. Sputtered titanium diboride was also superior to these coatings and to sputtered titanium carbide and boron carbide.

INTRODUCTION

The compression molding of contoured parts from a mixture of crystalline boron powder and organic polymers has caused severe wear of mold cavity surfaces. Typical polymers used in this work are neoprene, silicone elastomer, EVA (ethylene vinyl acetate), and VCE (ethylene/vinyl, acetate/vinyl, alcohol terpolymer). Boron particle sizes range from 10 or less, up to 200 or more micrometers. The degree of filler content and the amount of pressure required to mold some of the required configurations have caused a degree of volumetric wear sufficient to render a steel mold useless after molding from a few dozen parts to a few hundred parts. This wear problem exists with some of the equipment used to mix the boron and polymer together. One would expect wear prevention on the mixing equipment generally to be a simpler problem to solve than wear prevention on the compression molds.

Common tool steels, such as AISI H-13 and AISI A-6 hardened to approximately R_c40 , have been used in these molds.

Figure 1 is a Scanning Electron Microscope photomicrograph (SEM), showing the sharp edges and points of a sample of the powdered boron. Figure 2 is a typical example of the wear condition produced on the steel mold surface by this product. The plastic deformation and ploughing typical of two-body abrasive wear are clearly visible in this illustration.

Previous attempts to reduce this mold wear have included experiments with nitrided mold surfaces and electrodeposited chromium-plated mold surfaces. The chrome plating increased the useful life of some molds up to about three times the life of unplated molds; but the cost of reconditioning worn chrome-plated molds compared to reconditioning steel surfaces made this a feasible solution for only a limited number of applications. Mold contours for these applications are normally machined on numerically controlled equipment. Therefore, duplicating mold contours to close tolerances is relatively inexpensive, provided the contour can be recut into the same piece of steel.

One of the negative aspects of using chrome-plated mold surfaces was that wear failures were localized, seeming to concentrate along irregularities in the machined and polished mold substrate surface. This produced local imperfections in the molded parts and subsequent severe erosion of the substrate. The wear of the unplated mold surfaces was generally quite uniform until product wall thicknesses approached maximum limits, resulting in excessive rejected product.

This paper is a report of the investigation into means to extend the useful life of these molds.

PROCEDURE

It was first necessary to determine the basic wear mode present on the mold surfaces. The techniques of optical microscopy, scanning electron microscopy, transmission electron microscopy, and surface profilometry were utilized to confirm the assumption that two-body abrasion was responsible for a majority of the wear. Because of the use of heat in the presence of a chemical reaction in the cure of thermosetting polymers, the possibility of some corrosive wear is present; but this could be only a minor influence compared to the severe scouring and scraping produced by the boron particles. (See Figure 2.)

Deposited by Chemical Vapor Deposition

1. Aluminum oxide (Al_2O_3)
2. Aluminum oxide over chromium carbide ($\text{Al}_2\text{O}_3/\text{Cr}_3\text{C}_2$)
3. Titanium diboride (TiB_2)
4. Tungsten carbide ($\text{W/W}_2\text{C}$)

Deposited by Plasma Spray

5. Aluminum oxide, plus titanium dioxide ($\text{Al}_2\text{O}_3 + \text{TiO}_2$)
6. Chromium oxide (Cr_2O_3)

Deposited by Electroless Plating

7. Synthetic diamonds in a matrix of electroless nickel plate ($\text{C} + \text{Ni}$)

Deposited by Electroplating

8. Chromium (Cr)

Deposited by Sputtering

9. Titanium diboride (TiB_2)
10. Titanium carbide (TiC)
11. Boron carbide (B_4C)

Deposited From Fused Salt Bath

12. Titanium diboride (TiB_2)

Substrate Material

AISI A-6 tool steel heat-treated to R_{c38-40} .

Nominal Composition:

C	0.7
Mn	2.0
Si	0.3
Cr	1.0
Mo	1.3
Fe	Remainder

The chrome plate was included, to provide a basis for comparison of test results of the various coatings with a material for which production experience existed. It was also desirable to compare results of coatings tests with tests on unprotected steel surfaces, so polished steel was included in the test program, at hardnesses of R_{c38-40} and R_{c48-50} .

TEST APPARATUS

A comprehensive examination of wear testing methods and devices described in the literature failed to reveal the existence of a test device which produced test conditions even remotely resembling the conditions encountered in the production operations. The desire to duplicate in the test device the actual molding conditions, as nearly as possible, led to the decision to modify a capillary rheometer, a device marketed by the Instron Corporation as an accessory to their

Figure 1. Sample of Powdered Boron (SEM)

Figure 2. Surface Wear on a Steel Mold, Caused by Boron-Filled Elastomer (SEM)

The hardness of boron, which is variously reported from 2900 to 3300 (Knoop, 100-g load), indicated the most feasible approach was to coat hardened die steel with materials of hardness close to that of boron. In addition to high hardness, coating materials would also have to have thermal expansion properties comparable to steel, and the ability to form a metallurgical bond with the steel substrate. The method of application would provide good adherence without degrading the steel substrate (hardness reduction from overheating and excessive oxidation).

COATING MATERIALS AND METHODS

The following coating materials and methods of application were selected for abrasion resistance evaluation.

Figure 1
BDX-613-1684

Figure 2
BDX-613-1684

Universal Tension - Compression Test Instrument. This device provided the means of accurately controlling the temperature (and therefore the viscosity) of the boron-polymer mixture, and the rate at which it was moved over the test surface. It also measured the force required to produce the relative motion necessary to produce wear. The modification (Figure 3) consisted of mounting a conical test specimen just below the bottom of the bore of the rheometer barrel, surrounded by a conical member of sufficient proximity to confine the extruding boron-polymer mixture, producing pressures approximating those experienced in the molding operations. Experimentation was necessary to arrive at the final geometry and to develop a test procedure which could be used repetitively with a minimum of variation.

The wear test is performed by forcing the boron-filled polymer through the rheometer barrel with a plunger attached to the crosshead of the test machine, between the test specimen and the confining member, and out through openings in the test specimen support. Accurate weighing of the initial boron-polymer placed in the barrel and the material remaining above the test specimen after termination of the crosshead movement determines the amount of abrasive material extruded during the test.

The test procedure was designed to permit consideration of *run-in*, or the more rapid rate of initial wear sometimes encountered in a wear situation. This was accomplished by preliminary testing to establish the point at which a more or less uniform rate of wear was reached.

TEST METHODS

Several methods were selected to measure, evaluate, and express wear. The most important consideration was the application which brought about this study: the volumetric loss of the wear surface. This can be determined by measuring weight loss, and by using the density of the coating, converting this to volume loss. The particular method of failure can also be important. Various microscopic techniques can be used to examine the surface subjectively, and metallographic techniques can be used in conjunction with microscopy to examine the integrity of the bond between the coating and the substrate. There are other sophisticated techniques in use in fundamental studies of the wear process, but the purpose of this investigation was to rank various coatings under simulated molding conditions. Volume loss in combination with microscopic examination seemed most likely to yield a good assessment for this purpose.

The wear tests were performed on groups of test specimens by extruding the boron-polymer mixture from the rheometer over the coated test specimens. These specimens were weighed on a Mettler microbalance before and after testing, following an extensive cleaning procedure which included ultrasonic scrubbing and vapor degreasing. The accuracy of the weighing operations was estimated at plus or minus 20 micrograms. This proved to be adequate for purposes of establishing rankings of coating performance and obtaining relative numerical wear values. A *run-in* period, which had been established by preliminary testing, was followed by weighing the specimens, after which the testing was completed. Reweighing the specimens then permitted a comparison of *run-in* wear with steady-state wear.

Figure 3. Rheometer Wear Test Assembly, to Test Wear Resistance of Various Mold Surface Coatings Against Boron-Filled Elastomer

The original intent had been to limit the duration of the test so that none of the coatings would be worn completely through to the substrate. However, there was enough variation in durability of the various coatings and, in some cases, in durability of the specimens in one coating group, that this intent did not prevail. Some of the coatings wore through very quickly in fairly large areas, while some developed very small areas of severe wear. This appeared to be related to imperfections in the substrate, which may have existed before the coating application, or to incomplete cleaning of the substrate prior to coating. In those instances where local or relatively large-scale penetration of the coating occurred, a portion of the wear value derived represents wear of the substrate. While this does not provide a true picture of the durability of the particular coating, it does represent the durability of the coating system, which includes the durability of the coating, its adherence to the substrate, and the substrate itself. Assessment of this *system wear* would then appear to be valid.

EXPERIMENTAL RESULTS

The results of the *run-in* and steady-state wear were placed in perspective by considering the wear of unprotected steel at the hardness normally used in the molds as the standard. The wear of the various coatings was then expressed as a ratio of the wear of the standard to the wear of the coating, each expressed as a volume of coating loss per unit weight of the abrasive mixture which had been extruded over the coating. The wear factor of the standard thus became

1. PLUNGER
2. RHEOMETER BARREL
3. TEST SPECIMEN
4. TEFLON GASKET
5. HEATERS IN AN INSULATING JACKET
6. SUPPORT
7. CONSTRICTOR
8. CLAMPING NUT

Figure 3
BDX-613-1684

unity, and any coating providing more durability than unprotected steel had a value exceeding unity. This method produced the values shown in Table 1.

The superiority of the CVD TiB₂ coating is readily apparent in these values. There is some question as to the validity of the two significant figures shown for the TiB₂ wear factor, because the total measured weight loss was in the range of the assumed accuracy of the weight determinations. For the other coatings, however, the weight losses ranged from several hundred to several thousand micrograms. (As discussed earlier, some of the weight losses included substrate material which was abraded away when the coating wore through.) A total of approximately 30 grams of boron-filled elastomer was extruded over each test specimen during the run-in portion of the test, and approximately 40 grams during the steady-state portion. This provides an indication of the severity of the wear environment encountered in this molding activity. Even though the test conditions only simulated the molding conditions, they were not judged to be significantly more severe than actual molding conditions.

The examination of magnified images of the worn coatings substantially confirmed the ratings as established by coating volume loss, with the exception that the Al₂O₃ deposited by chemical vapor deposition appeared to have earned a better ranking. The bond between the Al₂O₃ coating and substrate appeared to be generally excellent and, where the coating was intact, it had fairly well resisted penetration and scarring by the boron particles.

Taper sections were made of the worn specimens to permit examination of the surface and subsurface structure together by scanning electron microscopy. Using this method, plasma-sprayed Al₂O₃ + TiO₂, with poor durability, and the TiB₂ CVD coating, with very good durability, were compared. Figure 4 shows the worn surface, the coating in section, and the metal substrate. Since the coating section is a tapered section, it has a greater vertical than horizontal magnification. Therefore, two scales are shown on this illustration, and on all other taper sections, to indicate magnification.

The coating structure shown in section is porous, and the jagged interface between the steel substrate and the coating (exaggerated by the taper section) indicates considerable agitation of the steel surface during the coating process. In fact, evidence of mixing of substrate material into the coating section can be seen. The wear surface is also porous, and a close-up of the same surface in Figure 5 shows the abrasion process proceeding by chipping of the weakened structure. By contrast, the TiB₂ CVD coating structure shown in Figure 6 is very dense. It should also be noted that the polishing process for specimen preparation removed the steel substrate at a faster rate than it did the coating, leaving the coating standing higher above the polished surface of the section. This is further evidence of the high density and hardness of the coating. The wear surface shown in detail in Figure 7 indicates some directionality relating to the flow direction of the abrading medium. It is presumed that the boron particles did produce a very limited amount of plastic deformation in the surface of the TiB₂ coating. Comparing the worn surface with the as-coated surface, however, it can be seen that the abrasion process was just beginning to remove the initial

Table 1. Relative Durability of Various Wear-Resistant Coatings Tested Against Boron-Filled Elastomers (Initial Phase)

Coating (Method)	Thickness (μm)	Run-In	Steady State
TiB ₂ (CVD)	3.8 to 8.6	19	130
Al ₂ O ₃ /Cr ₃ C ₂ (CVD)	---	4.2	5.2
W/W ₂ C (CVD)	6.7 to 38.6	3.0	4.8
Hard Chrome (Electro-plate)	---	3.5	4.0
Al ₂ O ₃ (CVD)	3.8 to 7.5	5.1	3.5
Nickel/ Diamond (Electroless Ni plate)	50	3.9	3.2
A-6 Steel (R ₃₈₋₄₀) (Standard)	0	1.00	1.00
A-6 Steel (R _{C48-50})	0	1.00	0.99
Cr ₂ O ₃ (Plasma Sprayed)	48	0.91	0.99
Al ₂ O ₃ + TiO ₂ (Plasma Sprayed)	66	0.74	---

surface topography. Many of the deeper original pits from the as-coated surface still can be seen in the worn surface.

The behavior of the Al₂O₃ CVD coating was disappointing in that the alumina should be about the same hardness level as the TiB₂. From the standpoint of relative hardness levels, alumina should be as resistant to cutting abrasion as TiB₂. A section of a worn Al₂O₃ CVD-coated specimen is shown in Figure 8. This illustration shows a coating defect in the process of growth. It is a defect in the coating surface resulting from localized poor adhesion. A typical defect in the as-coated sample, about 0.076 mm (0.003 inch) in diameter, is shown in Figure 9. This micrograph was made in the backscatter mode, and the heavier elements in the steel show up as a white patch in a generally gray field. It appears from the steep-sided wall and cracking at the lower border of the pit that localized poor adhesion or bridging over a void occurred during the coating process, and the coating subsequently chipped off during handling. The higher apparent wear of this coating resulted as the pits were undercut at the metal-coating interface, producing chipping of the edges and pit growth. As the metal was exposed, it wore, contributing to

Figure 4. Taper Section; SEM of Worn Plasma-Sprayed $Al_2O_3 + TiO_2$ Coating on Steel, Showing the Worn Surface and Subsurface Structure. Arrow Indicates Flow Direction of Abrading Medium

Figure 6. Taper Section; SEM of Worn CVD-Coated TiB_2 on Steel. Arrow Indicates Flow Direction of Abrading Medium

Figure 5. SEM of Worn Surface of Plasma-Sprayed $Al_2O_3 + TiO_2$ Coating. Arrow Shows Direction of Flow of Abrading Medium

Figure 7. SEM of Worn Surface of CVD TiB_2 Coating

the total weight loss. A close look at Figure 8 shows that the major portion of the coating is well-bonded, and wear of the well-bonded area is minimal.

In spite of the apparent wear resistance superiority of the TiB_2 coating, one aspect of this situation caused concern. This was the effect on hardened die steel of the substrate temperature of approximately 850 deg C (1562 deg F), which was necessary to successfully deposit TiB_2 by chemical vapor deposition methods. AISI A-6 and H-13 steels are

air-hardening steels, but 850 deg C is well above the temperature at which they are drawn to final hardness. The second phase of this investigation was initiated, therefore, with two general objectives:

- o To measure the effect on a typical mold of the TiB_2 CVD process, and to permit further evaluation of TiB_2 under actual production conditions; and
- o To test TiB_2 and additional hard coatings as applied by other processes.

The mold details selected for TiB_2 CVD coating were subjected to measurements of hardness and to precision measurements of flatness, roundness, and certain diameters before being coated and again after

Figure 4
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Figure 5
BDX-613-1684

Figure 6
BDX-613-1684

Figure 7
BDX-613-1684

Figure 8. Taper Section; SEM of Worn CVD Al_2O_3 Coating on Steel. Arrow Indicates Flow Direction of Abrading Medium

Figure 9. SEM of CVD Al_2O_3 Coating on Steel in As-Coated Condition Prior to Wear Testing

being coated. These measurements showed a decrease in hardness from $R_{\text{C}}34$ to $R_{\text{C}}30-31$. Flatness of a 0.355-m (14-inch) diameter flat surface was not affected, but there was an apparent decrease in some large diametral measurements beyond that which could be attributed to coating thickness.

As of the date of submission of this manuscript, the evaluation of this coated mold under production conditions had not been completed.

The additional hard coatings selected for testing were boron carbide (B_4C) and titanium carbide (TiC), applied by sputtering. TiB_2 was also applied to test specimens by sputtering.

The commercial supplier of the sputtered coatings was requested to deposit B_4C at two thicknesses: approximately 2 micrometers, and at 5 micrometers, or as near to this thickness as possible. Several attempts were made to deposit the thicker coating without success, after which the specimens were cleaned and coated to just over 2 micrometers. Apparently, this process disturbed the surface excessively, because this coating failed to survive the run-in portion of the test.

The thinner B_4C coating performed better than all others except TiB_2 during the run-in test and during the steady-state test; but microscopic examination of the coating after testing indicated numerous penetrations of the coating and imminent complete failure.

The sputtered TiC coating was deposited at a thickness of about 5 micrometers, and it barely survived the run-in test. It failed completely during the steady-state test.

The sputtered TiB_2 was also deposited at a thickness of 5 micrometers. Although microscopic examination showed significant differences in wear characteristics than did the CVD TiB_2 , the durability again proved to be outstanding compared to all other coatings tested.

The TiB_2 deposited by fused salt process had not been tested as of the date of submission of this manuscript.

Test data from the sputtered coatings are tabulated in Table 2.

Table 2. Relative Durability of Additional Wear-Resistant Coatings Tested Against Boron-Filled Elastomer [Second Phase (Sputtered Coatings)]

Coating	Thickness (μm)	Run-In	Steady State
TiB_2	5	24	650
B_4C	2	22	13
TiC	5	2.6	---

CONCLUSIONS

The apparent durability of TiB_2 as applied by both chemical vapor deposition and sputtering have indicated that this coating is the best candidate of those evaluated for the mold coating application under study. In the process of selecting the coating method to use, overall economic considerations ruled in favor of the sputtering method; and planning for the construction of a production sputtering facility has begun.

This program has demonstrated the effectiveness of ultra-high hardness coatings in the solution of a specific, severe abrasion problem. Although the initial selection of material for coating was based on the material's hardness, relative to the hardness of the abrading medium, other equally important factors

Figure 8
BDX-613-1684

Figure 9
BDX-613-1684

Figure 9
BDX-613-1684

were essential for the solution of the problem. These factors included matching thermal properties of the coating and substrate, consideration of the methods available for application of the coating, precoating treatment of the substrate, and economics of coating the actual mold parts.

BIOGRAPHICAL SKETCH

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