Tellurium Core Wash and Its Use in Solving Internal Shrinkage Defects

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ABSTRACT

Tellurium, when used in small concentrations in a core wash, is an effective method of providing localized solidification control. The carbide forming potential of Te can be selectively placed on a mold or core surface creating a rapidly formed skin of iron. This change in solidification rates can be used to prevent shrinkage in localized areas.

There are many variables that affect the Te wash’s ability to produce consistent results. The concentration of the Te in the wash is discussed providing information determining the amount of primary carbide resulting from any given percentage of Te suspended in a core wash. Application thickness is evaluated determining the criticality of the applied coat of Te wash. The difference in the resulting chill depth as a function of the number of applications is also discussed. In addition evaluating concentration and application thickness, the effect of the location of the Te wash is discussed. Comparisons between horizontal and vertical applications are made with explanations of the differences in the resulting reaction. Also included in this evaluation is a discussion of the impact iron chemistry, predominantly the sulfur content, has on the formation of the carbide reaction, and how layering the Te wash with a protective ceramic changes the reaction between the Te and the iron.

INTRODUCTION

It is often necessary to change a part’s original design to accommodate the casting process. However, changing the design is not always an option available to the foundryman. When a casting’s design results in shrinkage scrap and cannot be changed, alternative methods to stop the shrink must be found. Conventional means of solving shrinkage defects (risers, mechanical chills, etc.) should always be tried first. If they fail, an alternative solution is available. This solution uses a special core wash containing small concentrations of Te.

The Te core wash works by promoting primary carbides in the iron where it is applied. Small amounts of Te are transferred from the wash into the iron and promote localized carbides. This reaction starts the solidification process faster, making a large section size react like a smaller section size. The chilling effect, induced by the Te, is dependent on many variables. This report describes variables that change the ability of a Te core wash to control localized solidification and promote the desired carbide. Laboratory experiments were designed to answer several fundamental questions and provide guidelines for the foundryman using a Te core wash: 1) What effect does variable Te concentration have on the formation of chill? 2) How important is the application thickness to the effectiveness of the core wash? 3) What change does the Te wash have on the solidification characteristics of the iron? 4) How do the iron filling characteristics change Te’s reaction? 5) What effect does the application of a protective coat of core wash have on the reactivity of the Te?; and 6) What variables in the iron chemistry change the effectiveness of the Te core wash?

Common Experimental Procedures

Tellurium Core Wash Specifications
The Te wash used in all experiments is a combination of silica, kaolinite, talc, iron oxide and Te combined with a mixture of suspension ingredients. The Te is measured on a Wt% basis. For these experiments, the concentration of Te was varied between 0.0 and 10.0% Te. The core wash was mixed to 50° ± 2° Baume for all applications unless otherwise noted.

Iron and Temperature Control
The iron used was an alloyed gray iron containing various concentrations of Ni, Cu, Cr, and Mo. The C content ranged from 3.20-3.40%. The Si content ranged from 2.15-2.30%, yielding a CE ranging from 3.92-4.17%. The Mn levels average 0.58% and the S content was between 0.06-0.07%.

The iron was taken from an 80-ton induction holding furnace and transferred into a 6000-lb. teapot ladle. During this transfer, the iron was inoculated at 5.0 lb./ton with an Sr bearing FeSi. The iron was then transferred to a two-man pouring ladle or taken with an iron sampling cup for use. The pouring temperature for all tests ranged between 2600-2650°F.

Microstructural Analysis
The Te wash will produce two distinct zones at the iron-core interface. The zone closest to the core wash is primary carbide or chill. The next zone, just past the primary chill, is a degenerate mesh type graphite. These chill depth measurements for all experiments do not include any of the mesh graphite zone. All samples were etched with 5% nitral and measurements were taken at 100X.

Core Process
Unless otherwise specified, the core system used is a cold box phenolic urethane system with 1.25% binder and 0.5% Macor addition.

Experiment 1. Te Concentration

Design and Procedure
A test block measuring 2 x 2 x 6 in. was constructed. The gating and venting can be seen in Figure 1. The Te wash was applied to the drag surface with the coverage rate of ½ cubic centimeter of wash per square inch of core surface. The Te concentration was varied between 0.5 and 10.0%. The molds were dried, assembled,
CHILL DEPTH VS. PERCENT TELLURIUM

Linear Regression Fit = Solid Line
95% confidence limits = Dashed Line

Fig. 2. Chill depth vs. Te concentration in core washes exposed to iron.

and sealed with a general purpose core plate. The castings were
quenched, cooled to room temperature, and sectioned for examina-
tion.

Chill Depth at Variable Te Concentration

The depth of chill increases as the concentration of Te increases.
The graph in Figure 2 illustrates this relationship. A linear regres-
sion curve fit shows the 95% confidence limits along with the
mean value for any given percentage of Te. The equation fits the
following general format:

\[ Y = b_0 + b_1 \cdot X \]

Experiment 2. Application Thickness

Experimental Design and Procedure

A test block identical to Experiment 1 (Fig. 1) was used. The drag
was divided into four equal areas. The Te core wash was applied
to the drag at the same coverage rate (0.2 cm^2/dist.). One fourth
of the drag (nearest the gate), one application was used. On the
second fourth of the drag, two applications were used. On the
third fourth of the drag, three applications were used. On the fourth
area (farthest from the gate), four applications were used.

Applied Coats vs. Chill Depth

Application thickness is a critical factor in the effectiveness of the
wash. As the thickness of the wash increases, the amount of chill
depth increases. Increasing the number of applied coats of wash
increases the chill depth approximately 30% for each additional
layer of Te wash. This relationship can be seen in Figure 3. This
experiment also showed that lower concentrations of chill depth
provide a more consistent layer of chill than did higher concentra-
tions. If a consistent depth is critical, it is advantageous to use
multiple coats of a lower percent Te wash instead of one coat of
a higher percent Te wash.

Experiment 3. Effect on Solidification

Introduction and Scope

The reaction of the Te based core wash goes beyond the layer of
chill that is induced at the core/iron interface. If the simple presence
of the layer of chill prevented the shrinkage in massive areas, then
concentrations as low as 1.0% Te could be used to stop the shrink.
SOLIDIFICATION CURVES
COOLING CUPS WITH TELLURIUM EXPOSED

\[A = \text{Untreated Iron}\]
\[B = 1.0\% \text{ Tellurium Wash}\]
\[C = 3.0\% \text{ Tellurium Wash}\]
\[D = 5.0\% \text{ Tellurium Wash}\]
\[E = 7.0\% \text{ Tellurium Wash}\]
\[F = 9.0\% \text{ Tellurium Wash}\]

![Graph showing solidification curves](image)

Fig. 5: Plot of critical cooling curve temperatures for Te concentrations.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Color Description</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquidus</td>
<td>Transparent, greenish green</td>
<td>Tungsten</td>
</tr>
<tr>
<td>Solidus</td>
<td>Dark green</td>
<td>Tungsten</td>
</tr>
<tr>
<td>Undercool</td>
<td>Light green</td>
<td>Tungsten</td>
</tr>
</tbody>
</table>

Unfortunately, low concentrations of Te does not always stop shrinkage. It is theorized that the reaction between the Te wash and the iron happens as a gas-metal transfer. In washes with large Te concentrations, greater percentages of Te are transferred into the iron and primary carbides are formed. At slightly smaller concentrations, just beyond the primary chill layer, a mesh type graphite is formed. Both of these reactions are seen at the Tc wash/iron interface. This experiment to determine if small levels of Te transferred into the iron change the solidification pattern.

**Design and Procedure**
Standard Type K thermocouple cooling curve cups were used (see Fig. 4 for design details). Varying percentages of the Te wash were applied to the wall of the cooling cup. The samples were poured with the same base iron and the data were gathered with a computerized data acquisition system.

**Solidification vs. Te Percent**
A comparison of the cooling curves reveals a difference in the solidification of the iron dependent on the Te concentration. The solidus and the undercool temperatures were lowered as the percentage of Te increased. The liquidus temperature remained unchanged. Table 1 lists the percent of Te in the wash, the concentration of Te transferred into the metal and the critical cooling curve temperatures. See Figure 5 for the graphic representation of the Te concentration and iron solidification relationship. A comparison of the actual curves (Fig. 6), illustrates that an increase in the Te content increases the undercool of the iron.

**Microstructural Analysis**
The graphitic structure of the samples are indicative of expected microstructures as the undercool and solidus temperatures are suppressed. Examples of the structures are shown for normal iron (Fig. 7a), 3% Te wash (Fig. 7b), and 9% Te wash (Fig. 7c).

It is apparent that small amounts of Te (when transferred evenly into the iron) will change the iron's solidification. This effect will change the way a section size reacts. The amount of Te transferred into the sample's matrix depends on the violence of the reaction, the time the iron remains liquid, and the amount of Te in the wash.

By remaining liquid for an extended time, none of the Te in the wash created a chilled boundary at the core/iron interface. All of the Te available either volatilized as a gas or was transferred evenly into the iron and acted as an alloy. The amount of the change in the solidification ranged from little (tendencies to type D graphite) to total type D and E graphite.

**Experiment 4. Protective Ceramic Wash**

**Design and Procedure**
To reduce the tendency of total Te transfer into the iron matrix (as seen in Experiment 3), a protective coat of core wash was applied over the Te wash. The core wash used was silica based ceramic type wash. Similar Te concentrations and the same metal handling procedures were used as in Experiment 3.
Change in Solidification vs. Te Percent
The cooling curves for this test showed that a protective coat of core wash prevented any change in the solidification pattern at the center of the sample (Fig. 8). In addition, a chemical analysis of the sample did not show an increase in the Te concentration of the metal.

An interesting point should be noted: Although there wasn’t a detectable increase in the Te content in the iron, there was a layer of chill at the core/iron interface. This indicated that the presence of the protective core wash either prevented the erosion of the Te or sufficiently delayed the gas/metal reaction.

For the percentages of Te over 4.0%, a chilled surface was produced. The 2.5% Te mixture showed evidence of Te; however, only slight amounts of chill were present and small quantities of mesh graphite to a depth of 0.4 mm were seen. The structures at the center of the sample were nearly identical for all samples. The general microstructure consisted of 95–100% type A graphite with 0–6% type D graphite. The reduction or loss of chill on the outside boundary of the test mold for percentages under 4.0% indicates the reaction being delayed or redirected to prevent Te from being transferred to the metal at the iron/wash boundary. The fact that the Te was not mixed into the iron sample and was reduced at the iron/wash interface lends validity to the theory that the reaction is dependent on the ability of the gas to be transferred into the iron and the time the iron stays liquid.

Experiment 5. Premature Reaction
Design and Procedure
All previous tests evaluated the effectiveness of the Te wash on a horizontal surface. The horizontal surface was chosen to have the iron cover the Te as fast as possible to reduce the variable of fill rate on the effectiveness of the wash. This test was designed to determine the impact a vertical surface would have on the reactivity of the Te.

A test mold was designed to support a cylindrical core vertically in a test mold (see Fig. 9). The cylinder cores were made with a thermoplastic setting sand (shell sand) and the support mold was
SOLIDIFICATION CURVES
COOLING CUPS WITH TELLURIUM PROTECTED

Fig. 8. Cooling curves when Te wash is protected with a ceramic wash compared to an unprotected wash.

made using the phenolic urethane cold box system. To reduce the variability of the application thickness, the cylindrical center cores were dipped into the appropriate concentration of Te wash. The fill rate of the mold was measured at one vertical centimeter per second.

Loss of Chill on a Vertical Plane
As the mold is filled with iron (7 sec.), the radiant heat of the molten iron preheats the core. As the core is heated prior to iron contact, the Te can begin to evolve (sublimate) into a gas. Te oxide will evolve into a gas near 850°F. If the Te reacts before any iron contact, there will not be a chill reaction. Figure 10 shows the chill depth versus the height on the vertical core for two concentrations of Te in the wash.

The amount of Te remaining to react with the iron is a function of 1) the initial amount of Te present; 2) the fill rate of the mold; and 3) how much of the Te is lost due to sublimation prior to iron contact. Figure 10 illustrates the location of the last chill reaction as the height on the core increases. If the point where the reaction stops is plotted versus the percent of initial Te concentration, a nearly linear relationship is seen.

Protective Washes and Vertical Applications
In an earlier experiment, it was observed that applying a protective wash over the Te wash slows down the Te/iron reaction. Various layering techniques were evaluated to determine the best protective scheme for vertical surface applications. The layering consisted of using 7.5% concentration Te wash and a silica-based ceramic wash. The following layering methods were used: 1) CORE—Te Wash—IRON; 2) CORE—Te Wash/Ceramic Wash/IRON; 3) CORE—Te Wash/Ceramic Wash/Te Wash/Ceramic Wash/IRON; and 4) CORE—Ceramic Wash/Te Wash/Ceramic Wash/Te Wash/IRON.

Fig. 9. Mold design for vertical filling test and protective overcoat of ceramic wash test

CHILL DEPTH COMPARISON VS CORE HEIGHT
1.0%, 5.0%, AND 7.0% TELLURIUM WASH

A = 1.0% Tellurium Wash
B = 5.0% Tellurium Wash
C = 7.0% Tellurium Wash

Fig. 10. Chill depth vs. height on a shell sand core for varying percents of Te.
HEIGHT OF ZERO CHILL VS TELLURIUM MEASURED FROM BASE OF CASTING.

Linear Regression Fit

Fig. 11. Height of zero chill vs. percent of Te for various Te concentrations.

Figure 12 illustrates the chill depth for each layered method used. Note that there is some chill depth loss for all of the applications. The layering technique with the best results for consistent chill depth and minimal Te loss is the third method.

The reactivity of the Te wash can be controlled with the protection of a ceramic wash. Depending on the amount of protection and the layering used, successful depths of chill can be achieved for nearly any vertical application need. It should be noted that as the number of protection coats increases, the depth of chill provided decreases.

Experiment 6. Iron Chemistry

Design and Procedure

All previous tests were performed with an alloyed gray iron with a S content of 0.06-0.07%. When trying the Te wash with compacted flake graphite iron, it was noticed that regardless of the Te concentration used, no chill could be created. Based on some inferences from literature search, a test determining the effect of S content on the reactivity of the Te wash was designed.

Sulfur Content and Chill Depth

A test cylinder, 2.0 in. dia. and 2.5 in. deep, was coated with a 3.0% Te wash. The iron was treated with iron pyrite to obtain levels of S from 0.06-0.14%. The test molds were poured and the structures were analyzed. The actual S contents and chill depth averages can be seen in Table 2.

The chill depth was read six times around the circumference of the test specimen. The actual values were plotted and a linear regression performed. The results can be seen in Figure 13. This data (and the inability to get the Te to work in a low S CG iron) indicates a relationship between the S content and the effectiveness of the Te wash. It is necessary to have the correct chemical balance for the promotion of the carbide at the desired location. It is unknown at this point if the chill is a by-product of a S/Te reaction or the over abundance of Mn. Regardless of the stoichiometric relationship, Te washes do not work with nodular or compacted graphite irons.

EXPERIMENTAL RESULT DISCUSSION

Concentration

Concentration is one of the variables under the control of the user. By using a dilution wash (of the same basic materials as the Te wash), the final percent of Te can be adjusted to any desired value.
Table 2. Sulfur Content of the Iron with the Resulting Chill and Mesh Graphite Depths

<table>
<thead>
<tr>
<th>Coating weight</th>
<th>Properties</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.27-0.43 g/m²</td>
<td>Excellent lacquer</td>
<td></td>
</tr>
<tr>
<td></td>
<td>adhesion</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Minimum in mill. spec.</td>
<td></td>
</tr>
<tr>
<td>0.32-0.41 g/m²</td>
<td>Top corrosion protection.</td>
<td></td>
</tr>
<tr>
<td>0.11-0.35 g/m²</td>
<td>Lacquer undersurface</td>
<td>ASTM B494 P2</td>
</tr>
<tr>
<td>&lt; 0.11 g/m²</td>
<td>Transparent, Class 3</td>
<td></td>
</tr>
</tbody>
</table>

* 1.08 g/m² chromium oxide corresponding to 6000 Å (0.6 micron thick film)

* 1.08 g/m² chromium phosphate corresponding to 4800 Å (0.48 micron thick film)

This is the first point of control in getting the desired chill depth and effect from the Te wash. The increase in the chill depth is 0.06 mm for each additional percentage of Te in the wash. The relationship is near linear between 1.0-10.0% Te. Below the 1.0% Te, the curve will drop dramatically to zero chill. For this reason, this range is not included in the evaluation.

**Application**

In addition to the concentration of the material, the application thickness is also under the control of the user. Depending on the application method and Baume, the final wash thickness can be varied as needed. Doubling the thickness of the Te wash will increase the depth of chill approximately 30%. This increase in chill depth is not dependent on the initial concentration of the Te wash. Multiple layers of a lower concentration Te wash will provide a more consistent depth of chill than a single layer of a higher concentration wash. This is primarily because the thickness of the applied wash is more consistent. It should be noted that multiple washes, unless applied and dried properly, can spall and migrate to unwanted areas. A decision must be made between the simplicity of a single (more potent) application or several less concentrated applications.

**Solidification**

The presence of Te as an alloy to gray iron will change the solidification of the iron. The extent of the change will depend on the concentration of the Te transferred to the metal. An increase of 0.0014% Te transferred to the matrix is sufficient to increase the solidification rate of the iron. However, the amount transferred is dependent on the initial concentration, the application thickness, the presence of a protective wash and the mold fill rate. Without these variables being controlled, the amount transferred will be erratic and the results will be erratic.

At the wash interface, sufficient amounts of Te are transferred to induce primary carbide. This will decrease the time for the formation of the skin of solidified metal. The primary carbide at the wash interface should be expected as should the zone of mesh type graphite. Under tensile strength applications, careful evaluations should be made before using a Te wash. This is because the resulting boundary structure is lower in tensile strength (mesh graphite) and quite brittle (primary carbide).

**Chemistry**

The effectiveness of a Te based core wash is dependent on the chemistry of the iron. Large swings in the CE will change the normal solidification of the iron and will also change the effectiveness of the Te wash. The single most important element that must be monitored is the S content. It is recommended that a minimum of 0.03% S be present in the base iron. Low sulfurs (like those seen in CG and ductile iron) are insufficient for the formation of primary carbide. High sulfurs (like those in cupola operations) require lower Te concentrations to achieve similar results. It is important to reduce large swings in the sulfur due to its effect on the reactivity of the Te.

**Protective Core Wash**

Because of the sublimation characteristics and the erosion properties of the Te wash, it may be necessary to protect the wash with a ceramic wash overcoat. This overcoat will delay the reaction from a time standpoint and will reduce the resulting chill depth slightly. If migration to an unwanted area or a premature reaction persists, it will be necessary to use the protective coat of ceramic core wash. Layering the Te wash with a ceramic wash can also be done to obtain the desired results. This should be performed on a part-by-part basis because the layering procedure is a labor and time intensive procedure.

**SUMMARY**

Te core wash is a sensitive and volatile method of solving shrinkage. Particular attention must be given to minimizing the adverse side effects and still maintain its effectiveness. With the necessary attention given to the application method and concentration, a Te-containing core wash is an effective way of preventing shrinkage.

When using a Te-containing core wash, it is necessary to evaluate the concentration of Te needed. Too much Te could result in migration to an unwanted area or too little Te could be ineffective in stopping the shrinkage. The coating thickness must also be
carefully monitored and controlled. Doubling or halving the application thickness results in a 30% change in chill depth. Protecting the Te core wash from erosion or premature reaction is also important. Without protection, the Te core wash can reheat prematurely or migrate to undesired areas. The pouring rate can also change the effectiveness of the chill depth. The faster the Te wash is covered, the lower the risk for erosion and the more consistent the chill depths will be.

The use of a Te-containing core wash should be evaluated on a casting-by-casting basis. Mold fill rates and solidification patterns are different for every casting and will affect the way the Te reacts. Subsequently, the application method and concentration may need to be different for individual castings.

**DISCUSSIONS**

**Question:** The author has shown how Te can be used to change chill depth but it only relocates the shrinkage. (R. C. Schnay, Pres., Robert Schnay & Assoc., Westmount, Quebec, Canada)

**Answer:** Being able to move or "relocate" a shrinkage defect from an area that cannot be properly fed with liquid iron to an area that can be fed with iron does in fact solve the shrinkage problem. All a riser does is move the shrinkage from the casting into the riser. Mechanical chills provide the same function. Moving the shrinkage from an area where it cannot be fixed to an area where it can be fixed is, in effect, "solving" the problem.

**Question:** What analytical techniques were used to determine the concentration of elemental Te in the experimental washes? (G. Rudd, Tech. Dir., Motor Casting Co., Milwaukee, WI)

**Answer:** A gravimetric method is used where the Te oxide is precipitated from the solution and weighted back against the original weight.

**Question:** Does the treatment by Te change the graphite (chilling) sufficiently to provide machinability problems? (W. Ball, III, Cons., Hill & Griffith Co., Cincinnati, OH)

**Answer:** There are three zones of structure produced by a Te core wash: 1) primary carbide or chill; 2) mesh graphite (free of carbides); and 3) normal type A graphite. The primary carbide zone is not a desirable structure to machine. The carbide is brittle and hard, resulting in poor tool life. Concentrations insufficient to promote this carbide reaction change the graphite morphology only. As a result, there is not any appreciable change in the machining characteristics. It should be noted, however, that there is a fine line between the carbide reaction and changing the graphite morphology and care should be exercised where determining the proper addition.