

NRL Report 6295

An Investigation of Barrier Coatings on Graphite Molds for Casting Titanium

W. A. REAVES AND E. J. CHAPIN

Metallurgy Division

October 13, 1965



U.S. NAVAL RESEARCH LABORATORY
Washington, D.C.

CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
SELECTION OF BARRIER COATINGS FOR GRAPHITE	2
PREPARATION OF EXPERIMENTAL MOLDS	6
METHODS OF APPLICATION OF BARRIER COATINGS	10
MELTING AND CASTING PROCEDURE	13
ANALYTICAL PROCEDURE	17
RESULTS AND DISCUSSION	17
MgO · ZrO ₂ Coatings	17
Calcium Zirconate (CaZrO ₃) Coatings	19
50-50 Mixture of MgO · ZrO ₂ and CaZrO ₃	24
Gadolinium Sesquioxide (Gd ₂ O ₃) Coatings	25
Yttrium Sesquioxide (Y ₂ O ₃) Coatings	31
CONCLUSIONS	35
REFERENCES	38

ABSTRACT

The feasibility of employing barrier coatings on graphite molds for inhibiting carbon pickup in titanium and for possible control of solidification shrinkage during casting was investigated. Oxide coating materials whose known thermal properties appeared to be potentially useful were selected. These oxides included: a solid solution of MgO and ZrO₂; a true oxide compound, CaZrO₃; and two single oxides, Gd₂O₃ and Y₂O₃. The compound oxides were applied to specially cleaned ATJ grade graphite-mold hollow-cylinder inserts by an oxy-acetylene flame spray method, and the single oxides were applied in similar inserts by a plasma spray technique. Coatings composed of the solid solution of MgO and ZrO₂ were attacked by molten titanium during casting with some reduction of the MgO phase to metal and contamination of the cast metal with oxygen. These coatings were considered to be insufficiently stable against molten titanium. Coatings composed of the zirconate CaZrO₃ were found to be fairly resistant to molten titanium, however, sufficient reaction occurred between metal and coating to introduce undesirable contaminants into the cast metal. These coatings were also considered to be insufficiently resistant under casting conditions to qualify as satisfactory barrier coatings. The rare earth oxide Gd₂O₃ was found to be resistant to molten titanium during casting and to provide a good barrier between the graphite mold substrate and the cast metal, with no significant increases in either oxygen or carbon content. The oxide Y₂O₃ was found to have the best characteristics as a barrier coating. This oxide did not appear to be wetted by the molten metal cast against it nor to introduce any significant amounts of contaminants into the case metal.

The barrier coatings were not effective in altering the high heat extraction capability of the graphite substrate and thus did not provide any improvement in solidification center line shrinkage.

PROBLEM STATUS

This is a final report on the problem. This problem is closed.

AUTHORIZATION

NRL Problem M01-17
Project Numbers RR007-01-46-5419; RR011-03-41-6068

This phase was supported in part by long range development and research for sea-based deterrent systems.

Manuscript submitted May 5, 1965.

AN INVESTIGATION OF BARRIER COATINGS ON GRAPHITE MOLDS FOR CASTING TITANIUM

INTRODUCTION

The reactivity of molten titanium with all known refractory materials is a well known problem in the melting and casting of titanium and its alloys. Prolonged contact of molten titanium with a refractory mold material generally results in significant reaction and contamination of the metal which drastically affects metal quality. The effects of impurities derived from such reaction produce loss of ductility and toughness in the casting.

To employ refractory mold materials with any degree of success in casting titanium, the molten metal must freeze and cool rapidly to minimize harmful surface contamination. The solidification time for a given section of a casting must not exceed a certain critical value if contamination or mold material breakdown is to be avoided. This critical value depends solely upon the chemical stability of the refractory material and the length of time the material-metal interface is at high temperature.

Of the refractory materials that have been examined for use in molds for casting titanium, graphite appears to be the least reactive under casting conditions. This circumstance is related to the high thermal conductivity of the graphite and its ability to exert a strong chilling effect upon molten titanium cast against it. This causes a rapid solidification of the molten metal at the mold interface, forming a strong skin almost immediately upon contact. This skin shrinks away from the mold surface due to the contraction of the metal as it solidifies, thereby reducing physical contact between mold surface and the surface of the casting. Since graphite is not wetted by molten titanium under casting conditions, there is no tendency for the metal to adhere to the graphite surface. However, surface contamination of the casting by carbon cannot be avoided. This contamination consists of a hard carbon rich layer, whose depth depends upon the metal section thickness and the type of graphitic mold material used. Castings produced in machined graphite molds tend to exhibit a smaller depth of surface contamination than castings produced in expendable rammed graphite molds. Carbon contamination of casting surfaces is considered to impair metal ductility and to increase its tendency toward notch sensitivity, creating an undesirable situation in applications requiring good mechanical stability.

Apart from the problem of surface contamination, the strong chilling characteristic of graphite introduces the problem of controlling shrinkage during solidification. The combination of a high melting point and low thermal conductivity in titanium leads to steep thermal gradients during solidification which in some respects is an advantage. There is consequently little tendency toward "mushy" or dendritic solidification or the formation of finely dispersed microporosity. Rapid solidification of titanium, however, tends to interfere with adequate feeding of the castings during solidification, with the result that gross porosity and centerline shrinkage are frequently encountered in the heavier sections of titanium castings.

To avoid carbon contamination of metal surfaces during casting and possibly to obtain some measure of control over solidification of metal poured in graphite molds, it was considered important to investigate the possibilities of inhibiting carbon contamination and of reducing the sharp thermal gradient at the mold-metal interface. It was considered feasible to study both of these objectives by coating graphite mold surfaces with

a reaction barrier composed of selected oxides and of oxide compounds and analyzing the effects on titanium cast in such molds.

SELECTION OF BARRIER COATINGS FOR GRAPHITE

A prime requisite for a barrier coating to be effective on graphite for casting of titanium was that it be thermochemically and physically compatible with both the graphite substrate and the exceptionally hostile nature of molten titanium. Therefore, the barrier coating needed to be stable with regard to carbon on one side and to molten and solid titanium on the other. Physically, it is essential for a barrier coating to be continuous and nonporous, similar to the substrate in thermal expansion characteristics, and sufficiently tough to resist erosion action of the molten metal. The barrier coating needs to be refractory and nonvolatile throughout the temperature range of the casting process. In addition, it needs to exhibit good thermal shock resistance and chemical inertness especially toward hydration, and have selective heat transfer properties.

Potential materials for meeting the above requirements are drastically limited in number. At high temperatures there does not seem to be any single material that is thermodynamically stable with respect to graphite above 2000°C. At the melting temperature of titanium (about 1700°C) there is no known refractory material that does not react with molten metal. This dilemma appears insurmountable. However, since both the graphite and the barrier coating would be initially at room temperature when molten metal is cast into a coated mold; the temperature rise of the barrier coating would be expected to be influenced by the chilling characteristic of the graphite, keeping both the interface between graphite and barrier coating and the interface between barrier coating and metal below a temperature where significant reaction would occur.

In considering the problem of the difference of thermal expansion of a barrier coating and of the graphite substrate, it was assumed that mismatches in thermal expansion could be tolerated if relatively thin coatings were employed. A single layer coating was considered preferable over a more complex system since the problems of application, bonding, and compatibility appeared to be less involved in a single layer system.

The materials considered for barrier coatings included three oxide compounds—calcium zirconate (CaZrO_3), strontium zirconate (SrZrO_3), and magnesium zirconate ($\text{MgO} \cdot \text{ZrO}_2$), and three oxides—thoria (ThO_2), gadolinia (Gd_2O_3), and yttria (Y_2O_3). These materials appeared to exhibit suitable thermodynamic behavior with graphite, low thermal conductivity, high refractoriness, chemical stability and low volatility, high melting points, and possible high resistance to attack by molten titanium. Preliminary screening of the zirconates against molten titanium indicated that strontium zirconate (SrZrO_3) was insufficiently resistant to molten titanium and was discarded. Among the oxides, thoria (ThO_2) had to be discarded because of the inability to obtain a satisfactory coating on a cylindrical graphite-mold insert surface.

The zirconates were especially interesting in view of their melting points, refractoriness, and stability. In general, the melting point of a compound oxide is lower than that of the highest melting constituent (strontium zirconate seems to be an exception); the selection of a compound oxide over its most refractory constituent oxide is justified only when it may show some marked improvement in properties. Such improvement may be a drastic reduction in hydration tendency and/or the elimination of an undesirable phase change in a constituent oxide as occurs in the case of calcium zirconate (CaZrO_3). The constituent oxides CaO (melting point, 2600°C) and ZrO_2 (melting point, 2687°C) have undesirable characteristics in simple oxide form but when these oxides are incorporated into a compound oxide (CaZrO_3) the undesirable characteristics of each of the constituents vanish. CaO exhibits a strong hydration tendency which renders it useless as a refractory material. ZrO_2 has a low affinity for water vapor but undergoes a

drastic volume change because of a phase change at about 1200°C. Furthermore, ZrO_2 is stable with respect to carbon only to about 1730°C and gives up part of its oxygen when in contact with molten titanium. Nevertheless, the undesirable hydration and phase change in CaO and ZrO_2 respectively appear to be missing in the zirconate $CaZrO_3$. There is, however, some sacrifice in refractoriness since $CaZrO_3$ melts about 350°C below that of ZrO_2 .

In the case of magnesium zirconate, which incidentally is not a compound but a solid solution of MgO and ZrO_2 , the constituent oxide MgO (melting point, 2800°C) also hydrates, but to a lesser degree than CaO, and is reduced by carbon above about 1850°C to magnesium and carbon monoxide. The melting point of the solid solution $MgO \cdot ZrO_2$ is 2120°C, which is considerably below that of either constituent oxide and indicates lower refractoriness. It was considered desirable, however, to determine if this solid solution would be useful as a barrier coating for graphite mold surfaces.

Simple oxides which contain only one cation are generally more refractory than compound oxides. From a number of oxides that could be classed as reasonably stable with respect to graphite at temperatures prevailing in the casting of titanium, very few would have satisfactory stability with respect to molten titanium.

The stability of rare earth oxides, based on their heats of formation and their high melting points, indicated their potential as barrier coatings. The heats of formation are among the highest known for all of the stable oxides; no metals have a higher affinity for oxygen. This property was considered to be especially important with respect to the chemical stability of an oxide involving containment of molten titanium in molds during casting. In general, the cubic rare earth oxides are stable to water, and thus do not react with water vapor in the atmosphere to form hydrate oxides. Rare earth oxides do not react with the metals platinum and tungsten up to 1400°C and 2400°C respectively and they may be melted in rhenium without any reaction or pickup of rhenium by the oxide. These oxides would therefore be expected to be stable to a number of other metals and their compounds because of their high heats of formation.

All of the rare earth oxides form the sesquioxide (R_2O_3) although some such as cerium, praseodymium, and terbium can form stable oxides with higher valencies while samarium, europium, thulium, and ytterbium can form oxides of lower valency.

Examination of the physical properties of the rare earth oxides showed that most of them crystallize in a cubic modification. Several, however, irreversibly transform to a monoclinic form with a volume decrease of about 9.5% when heated to temperatures from 1000°C to 1500°C. These include Sm_2O_3 , Eu_2O_3 , and Gd_2O_3 .

In general, cubic rare earth oxides are less dense than corresponding rare earth metals by about 5%, but the hexagonal oxides (La_2O_3 , Ce_2O_3 , Pr_2O_3 , and Nd_2O_3) and the monoclinic modifications (Sm_2O_3 , Eu_2O_3 , and Gd_2O_3) have higher densities than the metals.

The rare earth oxides have very high melting points, low coefficients of thermal expansion, and very high electrical resistivities. Their melting points are much more nearly the same although the melting points of the constituent metals vary by nearly 1000°C.

Thermal expansion coefficients for the rare earth oxides are, in general, less than those for the corresponding metals. Exceptions are La_2O_3 , CeO_2 , Pr_2O_3 , and Nd_2O_3 in that their coefficients of thermal expansion are larger than those of the respective metals. Electrical resistivities at about 725°C are of the order of a megohm-centimeter. At room temperature resistivities are above the measurement range.

The boiling points of rare earth oxides are of the order of 4000°C to 4500°C. Despite this fact, all of the oxides seem to dissociate to the monoxide and oxygen and in some cases to metal, at temperatures above 2000°C. Most of the heavy rare earth oxides from Gd_2O_3 through Lu_2O_3 lose a small amount of oxygen when heated to high temperatures in vacuum. These oxygen deficient compounds are characteristically of intense black color compared to the light pastel or white color of the normal oxides.

Generally, oxides which have high melting points become less stable at temperatures above the boiling point of the constituent metal and thermodynamic stability decreases. This was considered to be another important criterion in considering which of the rare earth oxides would be the best representative oxide of the rare earth group for application as a barrier coating on graphite molds for casting titanium.

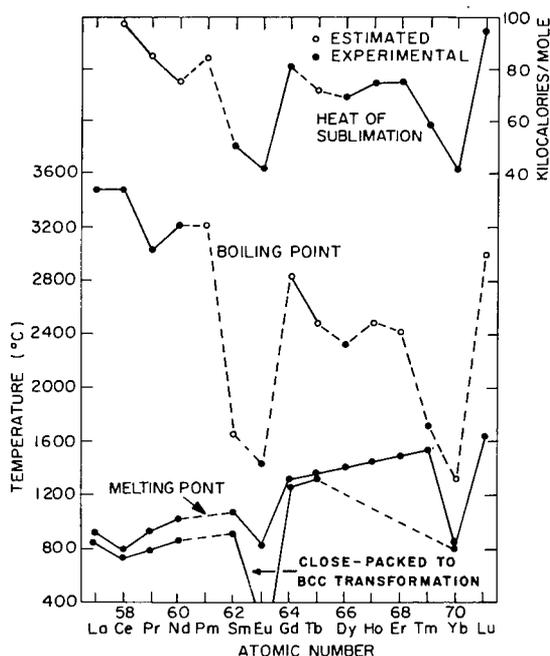


Fig. 1 - Variation of the close-packed to body-centered cubic transformation temperature, melting point, boiling point and heat of sublimation at 25°C (298°K) of the rare earth metals

According to the data of Fig. 1, elemental gadolinium exhibits an optimum combination of melting point, boiling point, and heat of sublimation among the rare earth elements. The sesquioxide, Gd_2O_3 , is characterized by the following properties: heat of formation at 25°C of -433.94 kcal/mole; melting point of 2350°C ± 50°C; specific heat of 0.0842 cal/gm in the temperature range of 0°C to 1000°C; irreversible crystal structure change from cubic to monoclinic upon heating to temperatures above 1300°C; theoretical density of 7.63 g/cm³; coefficient of thermal expansion of 10.5×10^{-6} in./in.-°C in the temperature range 25°C to 1000°C. In view of these properties, the thermodynamic stability was considered to be attractive for the application considered. From experimental evidence there was additional indication that an oxide of gadolinium would be potentially useful against molten titanium in that gadolinium had a higher affinity for oxygen than titanium and was capable of deoxidizing it (1). The oxide did not react readily with molten titanium in attempts to alloy the oxide Gd_2O_3 with molten titanium (2). These factors indicated that the oxide Gd_2O_3 would be relatively stable in contact with molten titanium during casting.

The chemical stability of the oxide Gd_2O_3 in contact with graphite at casting temperatures was somewhat uncertain in view of the lack of pertinent thermodynamic data concerning the reaction of rare earth oxides and carbon at elevated temperatures. These oxides probably react with carbon at an elevated temperature to form a series of carbides. Several carbide compounds are known to exist in the gadolinium-carbon system. These include: the tri-rare earth carbide Gd_3C , in which gadolinium is trivalent and the structure is cubic; the sesquicarbide Gd_2C_3 , whose structure is also cubic; and the dicarbide GdC_2 , whose structure is tetragonal and whose melting point is above 2200°C. From the similarity of properties of yttrium oxide Y_2O_3 and of gadolinium oxide Gd_2O_3 it was assumed that Gd_2O_3 would show similar stability with respect to carbon, to that of

Y_2O_3 at elevated temperatures. In the case of the oxide Y_2O_3 , carbide formation begins at about $1900^\circ C$.

The rare earth carbides appear to be unstable in the presence of water vapor and react with it, liberating gases as a result of hydrolysis. In the case of the tri-rare-earth carbides (R_3C) the carbon atoms are approximately 3.5\AA apart if the carbon atoms are considered to occupy adjacent octahedral holes. These carbides would therefore be expected to form methane (CH_4) and hydrogen (H_2) on hydrolysis such as occurs with methanides. The sesquicarbide (R_2C_3) and dicarbide (RC_2) are very similar to the acetylides, although they do not liberate pure acetylene (C_2H_2) upon hydrolysis but a mixture of acetylene, hydrogen, and other hydrocarbons.

The factor of the hydrolytic behavior of rare earth carbides was considered to be a useful guide in the experimental work since the presence of an acetylide carbide could probably be detected from the characteristic odor of acetylene upon exposure to the experimental molds to the atmosphere after casting.

Since the oxide coating in contact with the graphite substrate would be at a high temperature for only a very short period of time during the casting cycle no significant reaction was expected to occur between the oxide and the graphite.

Yttrium, although quite distinct from the rare earths proper (in the sense of the periodic system), in chemical properties and natural occurrence it is always allied to them. Preceding the rare earths in periodic group IIIA, yttrium presents many analogies to the chemical properties of this group. The lanthanide contraction places dysprosium or holmium close to yttrium in ionic size so that, in many chemical characteristics dependent upon ionic radius, yttrium closely resembles these heavier rare earths.

The stable oxide of yttrium is the sesquioxide Y_2O_3 although a monoxide YO seems to exist as was the case with the rare earth oxides. Yttrium oxide (Y_2O_3) is tan in color and the suboxide is probably dark colored as was the case with rare-earth monoxide.

Salient properties of Y_2O_3 include the following: heat of formation at $25^\circ C$ of -455.45 kcal/mole (somewhat higher than that for Gd_2O_3); melting point of $2410^\circ C$; boiling point of $4300^\circ C$; specific heat of 0.13 cal/g. The calculated dissociation pressure at $1730^\circ C$ is about 1.6×10^{-11} atmosphere which indicates an excellent high temperature stability. The coefficient of thermal expansion is 9.3×10^{-6} in./in.- $^\circ C$ in the temperature range 200 to $1000^\circ C$. These properties indicated that yttrium sesquioxide (Y_2O_3) should be relatively stable against molten titanium under casting conditions.

Yttrium oxide (Y_2O_3) appears to be stable in contact with graphite up to about $1900^\circ C$. Like gadolinium and other rare earths, yttrium forms several carbides which include the following: a tri-yttrium carbide whose composition may vary from $YC_{0.25}$ (Y_4C) to $YC_{0.40}$ (Y_5C_2) and whose structure is face centered cubic with 4 Y and 1.6 C atoms per unit cell; the sesquicarbide, Y_2C_3 , appears to be body centered cubic and isostructural with holmium, erbium, thulium, and lutecium; the dicarbide, YC_2 , has a body centered tetragonal CaC_2 type structure.

The hydrolytic character of the various yttrium carbides would probably be similar to that of the rare-earth carbides with the Y_3C carbide being a methanide and Y_2C_3 and YC_2 being acetylides.

The characteristics of Gd_2O_3 and Y_2O_3 mentioned above strongly indicated that both oxides in the form of coatings would probably be very stable against both molten titanium on one side and against graphite on the other side and thus provide an effective barrier coating on graphite mold surfaces for casting titanium.

National Carbon Company Grade ATJ graphite was selected for use in experimental molds. This grade of graphite was characterized by its extremely fine grain (0.006 inch maximum), its freedom from flaws, its high strength, its premium quality, and its machinability to very close tolerances, sharp detail, and fine surface finish. The average total ash content was 0.158%. The low ash content was considered to be an important characteristic since the presence and nature of certain impurities are known to have a significant effect on the gas content of graphite. Very small amounts of certain metallic carbide impurities trapped inside the graphite structure may cause evolution of gas for a long time under reduced pressure. Calcium is an especially critical impurity since it occurs as a carbide with hydrolyzes in presence of moisture to $\text{Ca}(\text{OH})_2$. With even a fraction of one percent of calcium present, graphite heated under vacuum evolves water vapor, CO_2 , and CO for a long time, making the removal of gas content somewhat difficult. The calcium content of Grade ATJ graphite was reported to be 0.0111% by the manufacturer.

ATJ grade graphite has a coefficient of thermal expansion of 2.36×10^{-6} in./in.- $^{\circ}\text{C}$ with the grain and 3.46×10^{-6} in./in.- $^{\circ}\text{C}$ across the grain. In comparison, the coefficients of thermal expansion for CaZrO_3 , the solid solution of MgO and ZrO_2 , Gd_2O_3 , and Y_2O_3 are each about three times greater than ATJ grade graphite. Therefore, considerable mismatch is evident between coatings of these materials and the graphite mold surfaces. This mismatch handicap, however, was not considered to be serious enough to prevent an evaluation of the coatings, since the geometry of the coated graphite mold surfaces was a simple cylindrical cavity.

PREPARATION OF EXPERIMENTAL MOLDS

In order to simplify various problems concerned with coating graphite test mold surfaces and to facilitate the experimental work of casting and subsequent examination of the results, a cylindrical casting geometry was employed. The mold configuration consisted of split hollow graphite cylinder inserts held in a segmented graphite block, hollowed out for the inserts and for sprues and gates for bottom feeding the cylindrical castings. The design concept is illustrated in the drawing of Fig. 2, in the detail of Fig. 3, and, as assembled ready for casting, in Fig. 4. This arrangement facilitated the coating work and permitted casting a heat of titanium into four test cylinders at one time.

The graphite inserts were fabricated by coring cylinders from a block of ATJ grade graphite. These cylinders were split longitudinally into two equal parts and then machined into hollow cylinders with a 3.75-in. O.D., a 6-in. length and a 0.375-in. wall. Considerable care was exercised in machining the inside diameter of the hollow cylinder so as to minimize the formation of microcracks in this surface. The finish of the inside surface was initially threadlike with 92 threads per inch, 3 mils deep. This finish was found to be too smooth for obtaining good mechanical adhesion of the coatings and was replaced with a rougher finish obtained by light blasting of the surface with sharp gain ZrO_2 .

The fabricated graphite test inserts were given a preparatory heat treatment in hydrogen followed by degassing in high vacuum before being coated. The primary purpose of the hydrogen treatment was to remove the residual graphite dust from surfaces to be coated. The presence of this dust was considered to be a potential source of undesirable carbonaceous gaseous contaminants occurring as absorbed or adsorbed gases and as gaseous products from possible reaction between coating and the finely divided dust.

Hydrogen reacts with heated graphite to form methane (CH_4) according to the reaction $\text{C} + 2\text{H}_2 = \text{CH}_4 + 17.6 \text{ kcal}$. The reaction is exothermic. In the range of 1000°C to 1250°C , methane is the only stable product to be formed from carbon and hydrogen at 1

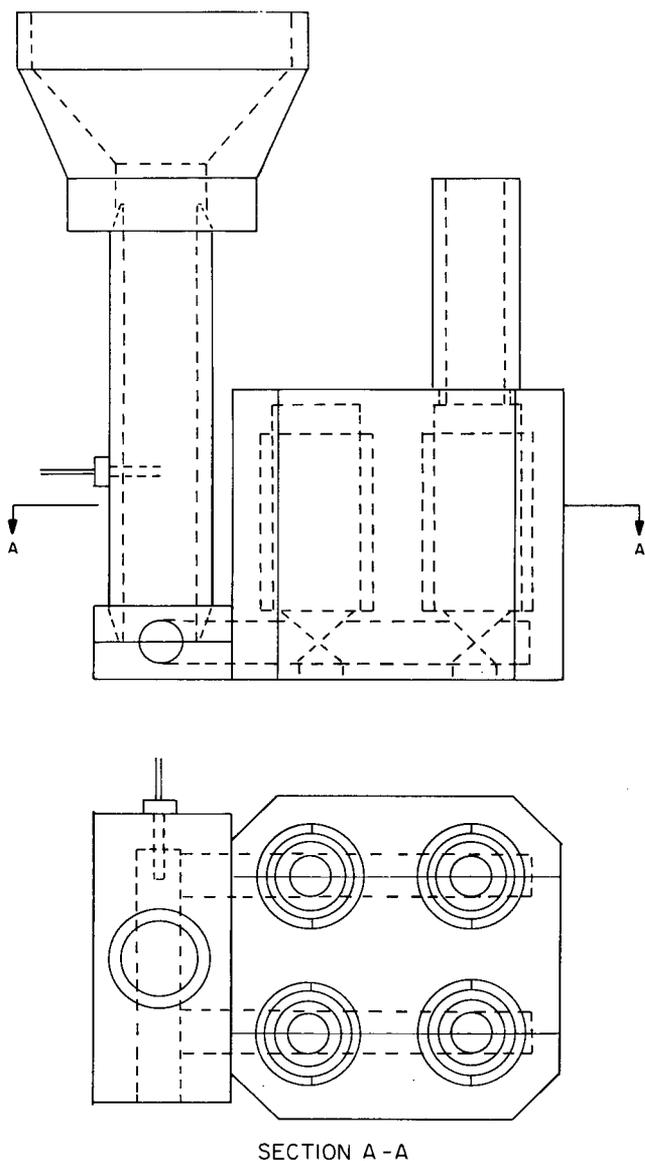


Fig. 2 - Schematic diagram of segmented block mold assembly

atmosphere of pressure as may be seen from Fig. 5, a plot of the Gibbs free energy of formation of CH_4 , C_2H_6 , and C_2H_2 vs temperature.

The rate of methane production from carbon and hydrogen may be determined by the equation

$$\frac{dn_{(\text{CH}_4)}}{dt} = k_m \quad m \quad c_{\text{H}_2} \quad (\text{mole/sec})$$

where

k_m = rate constant per unit mass of carbon ($\text{cm}^3/\text{gm-sec}$),

m = mass of carbon,

c_{H_2} = concentration of hydrogen (mole/cm^3),

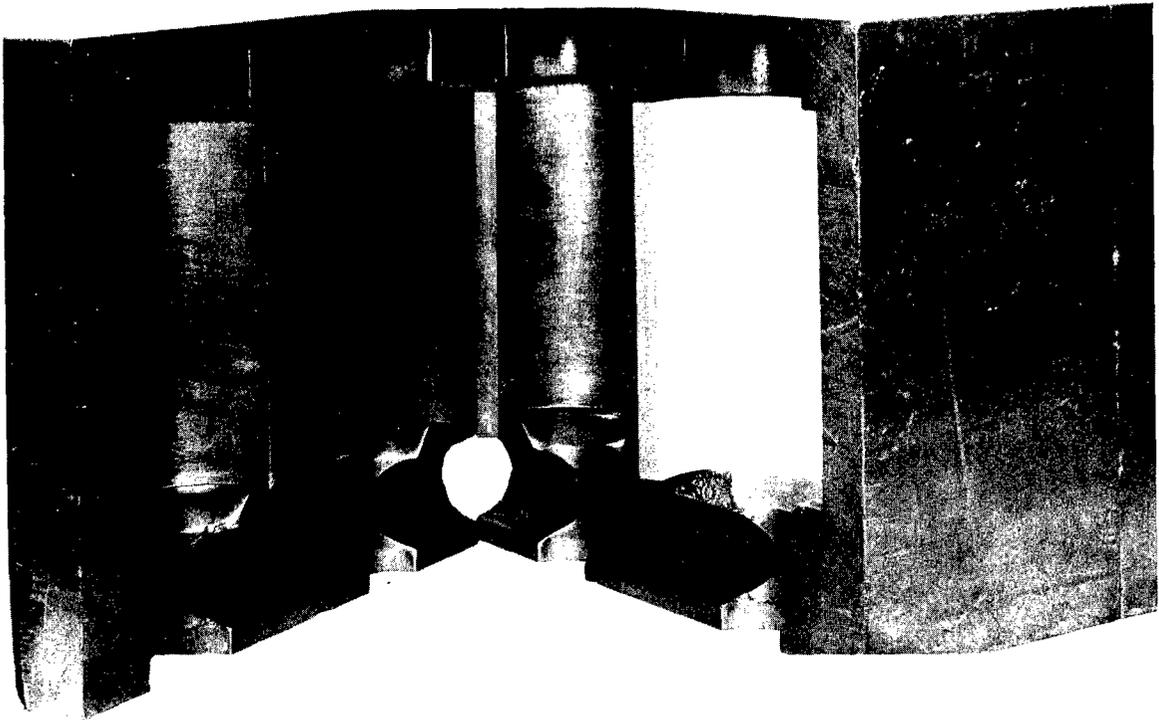


Fig. 3 - Detail of graphite block mold showing position of experimental inserts and runner for bottom feed of castings

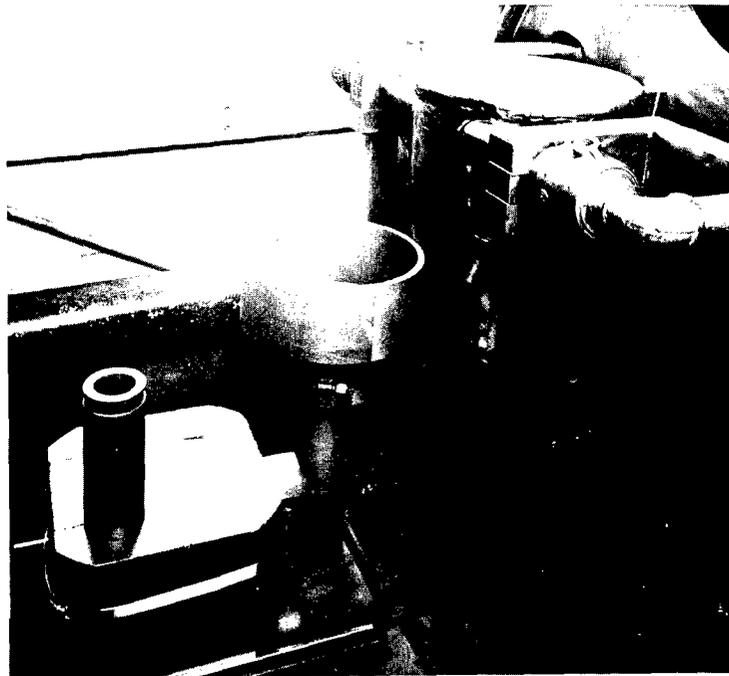


Fig. 4 - Assembled block mold in position for pouring melt in casting furnace

assuming no back reaction occurs with decomposition of methane. The rate constant of methane production was estimated to be about $0.00075 \text{ cm}^3/\text{g-sec}$ at 1000°C .

Hydrogen heat treatment of the graphite mold inserts was conducted in an Inconel muffle approximately 5 ft long, having a cross section of 6-1/4 in. by 4-1/2 in. One end was permanently blanked off while the opposite end was flanged and closed off by a water-cooled spring-loaded cover fitted with an O-ring seal. The cover was held against the flanged end by spring pressure of about 5 psi for safety. The permanently blanked off end was fitted with one tube for inlet of hydrogen and one exhaust tube. The inlet tube extended to the front end of the muffle so that gas flow was from front to back. The exhaust gases passed out of the muffle through a mercury trap before being released to the atmosphere.

Source hydrogen was passed over a platinum catalyst to remove oxygen and the water formed was removed with activated alumina. Hydrogen flow rate was controlled with a floating ball type flowmeter.

The procedure used in the hydrogen heat treatment was as follows. The graphite mold inserts were carefully cleaned of free dust with a vacuum cleaner, placed on nickel sheet, and loaded into the muffle. After securing the access port, the muffle was purged with helium for approximately 10 min, followed by flushing with hydrogen for 15 min. The muffle was then heated and maintained at 1000°C for 3 hrs under a hydrogen flow of 10 cu ft/hr. The muffle was then allowed to cool to room temperature under the same rate of hydrogen flow. Before opening the muffle to extract the treated graphite mold inserts the hydrogen was purged from the muffle with helium.

Microscopic examination of the inside diameter surface of the mold inserts indicated a clean surface free of dust.

There was an indication at 50X magnification that a very slight burnoff of solid graphite had also occurred from the surface that showed up as minute pitting.

Following the hydrogen treatment the graphite mold inserts were wrapped in 2-mil-thick molybdenum sheet, loaded into a stainless steel boat, and inserted into an 8-in.-diameter stainless steel tube vacuum furnace for a degassing treatment. The furnace tube was evacuated to at least 0.1 micron before applying heat. During heating the temperature rise was controlled so that the outgassing pressure did not exceed 1 micron. Evacuation was continued at a terminal temperature of 1000°C until the pressure stabilized below 0.01 micron. The tube furnace was cooled to room temperature under vacuum and brought to atmospheric pressure with argon before opening the tube furnace to extract the graphite mold inserts. The degassed inserts were immediately sealed in plastic bags protected with a desiccant and maintained in this manner until they were coated.

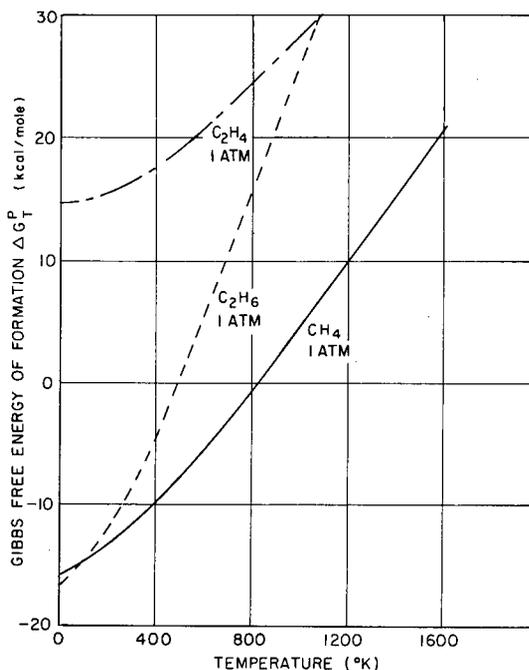


Fig. 5 - Stability diagram of CH_4 , C_2H_4 , and C_2H_6 at 1 atmosphere

METHODS OF APPLICATION OF BARRIER COATINGS

The manner of applying a barrier coating to graphite mold surfaces for casting titanium was considered to be as important as the selection of the coating material itself. Although barrier coatings may be applied in many ways, it was considered necessary to select those methods as would produce the most refractory and effective barrier between graphite and molten titanium. The deposition of a coating involves a large number of variables such as coverage, porosity, thickness, texture, adhesion, interparticle bond strength, particle surface characteristics, and integrity of particle composition during deposition. Some of the older ceramic methods were tried for depositing coatings on graphite from slurries, by dipping, spraying and painting, but these methods were discarded because they did not produce a coating having suitable characteristics. In order to obtain coatings on graphite which would have a smooth surface, low porosity, good adherence, and high mechanical strength, it was considered essential to employ methods of deposition based on fusing the coating material and spraying it molten on the graphite surface at a rate that would produce a continuous uniform layer.

Coatings of CaZrO_3 and of the $\text{MgO} \cdot \text{ZrO}_2$ solid solution were applied to graphite mold surfaces by an oxyacetylene flame spray technique.* The method consisted of feeding powdered coating material through an oxyacetylene flame and blowing the molten particles onto the graphite surfaces as illustrated schematically in Fig. 6. The powdered

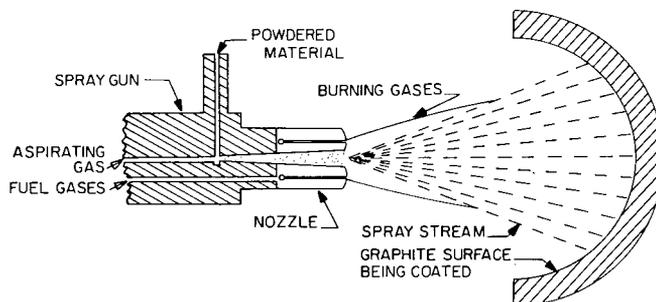


Fig. 6 - Schematic of oxyacetylene flame spray process for powders

material was fed into the spray gun from a reservoir and injected into the flame by means of an aspirating gas under pressure. The fuel gases (oxygen and acetylene) entered the nozzle through a separate line and burned at the tip. In passing through the flame, the powdered material melted and was sprayed molten onto the surface being coated. The maximum temperature that can be produced in an oxyacetylene flame is about 3140°C which limits the use of this method to those materials which can be effectively melted and sprayed molten under the thermal conditions existing in the flame.

The sesquioxides Y_2O_3 and Gd_2O_3 were applied to graphite mold surfaces by a plasma flame spray process.† This process consisted of passing an inert gas through an electric arc and exciting the gaseous atoms to produce a plasma of ionized gas ranging in temperature from about $15,600^\circ\text{C}$ to as low as about 1650°C , which depends upon the power input used. Powdered coating material was introduced into the plasma with an

*Coated at Titanium Alloy Mfg. Co., Niagara Falls, N.Y., through courtesy of Dr. Steve Urban.

†Applied by Plasmadyne Corp., Santa Ana, Calif.

inert carrier gas under pressure. The powdered material was instantaneously melted by the intense heat of the plasma and sprayed onto the graphite base. The process is illustrated schematically in Fig. 7. Advantage of this process over the oxyacetylene method was that practically any material in the periodic table could be spray coated at exceptionally high velocities in an inert atmosphere, thus avoiding contamination in the sprayed coating.

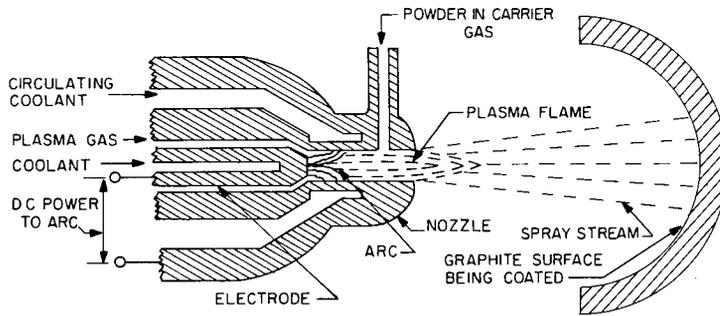


Fig. 7 - Schematic of plasma flame spray process for powders

Typical examples of coated inserts are shown in the following illustrations. The two adjacent inner insert halves of Fig. 8 were flame sprayed with CaZrO_3 , while the two outer insert halves were uncoated. The surface characteristics of flame sprayed CaZrO_3 coatings at 50X magnification showed a globular type surface with some porosity extending

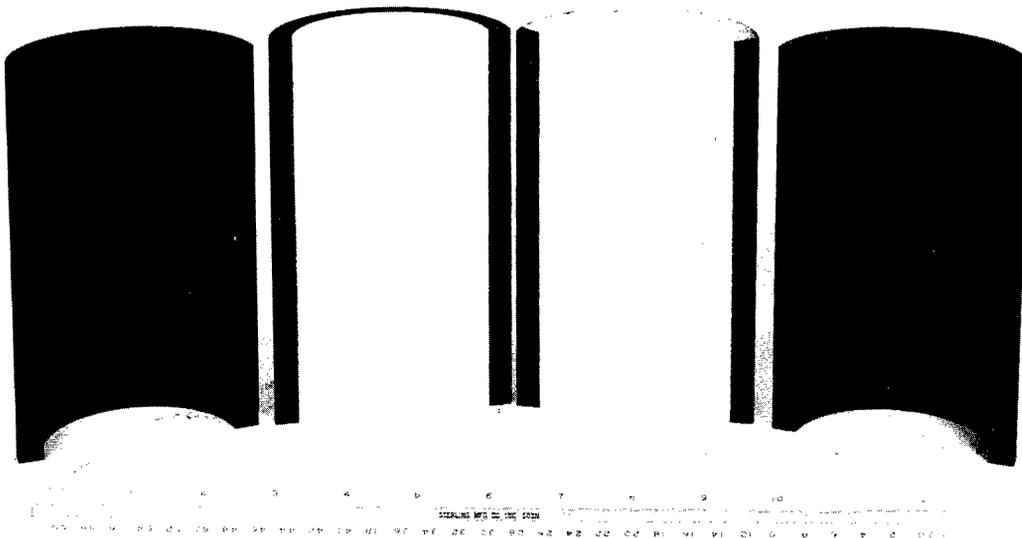


Fig. 8 - Example of CaZrO_3 coating on graphite mold inserts (left to right: insert 37(a), uncoated; insert 39(b), coated with CaZrO_3 ; insert 39(a), coated with CaZrO_3 ; and insert 37(b), uncoated)

below the surface. The inserts shown in Fig. 9, proceeding from left to right, include uncoated insert 47, insert 46 coated with Gd_2O_3 , insert 57 also coated with Gd_2O_3 , and insert 49 coated with Y_2O_3 . These coatings were deposited by the plasma flame method. A closeup of insert 57 coated with Gd_2O_3 is shown in Fig. 10. The coatings appeared to be nonporous, with good surface finish and good adherence as indicated by the top edge of Fig. 10.

Although the powdered coating materials were carefully sized and presumed to be free flowing and in a satisfactory condition for flame spraying, some difficulty was experienced during the deposition process which required retreatment of the powdered

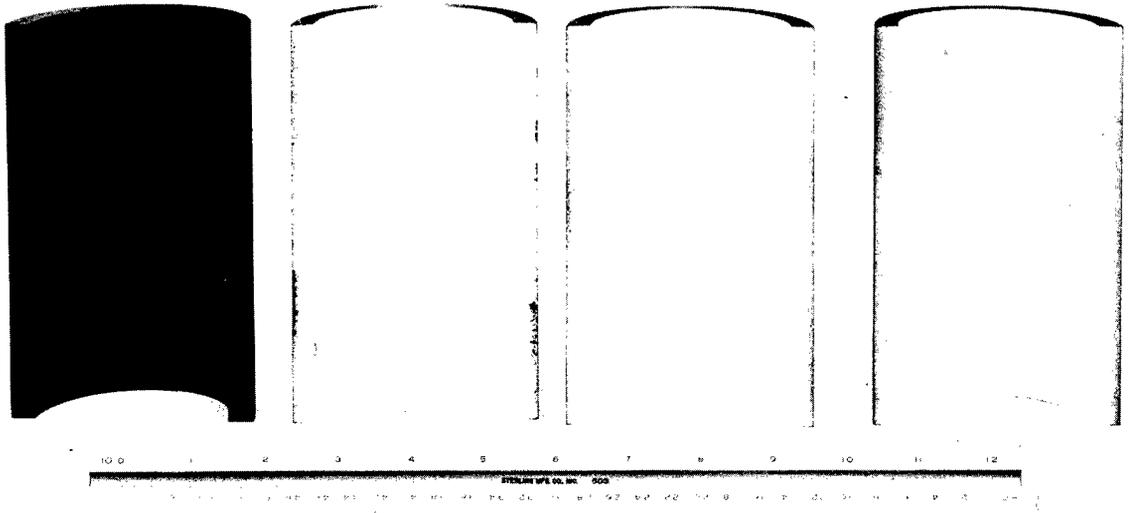


Fig. 9 - Typical Gd_2O_3 and Y_2O_3 coatings on graphite mold inserts (left to right: insert 47, uncoated machine finish; insert 46, Gd_2O_3 coated; insert 57, Gd_2O_3 coated; and insert 49, Y_2O_3 coated)



Fig. 10 - Closeup of insert 57 coated with Gd_2O_3

materials used for plasma flame spraying. The retreatment consisted of sintering the Y_2O_3 and Gd_2O_3 powders above $1400^\circ C$, followed by fine grinding and wet screening to obtain an optimum particle size distribution. The result of this treatment was an improvement in coating uniformity and adherence to the graphite substrate.

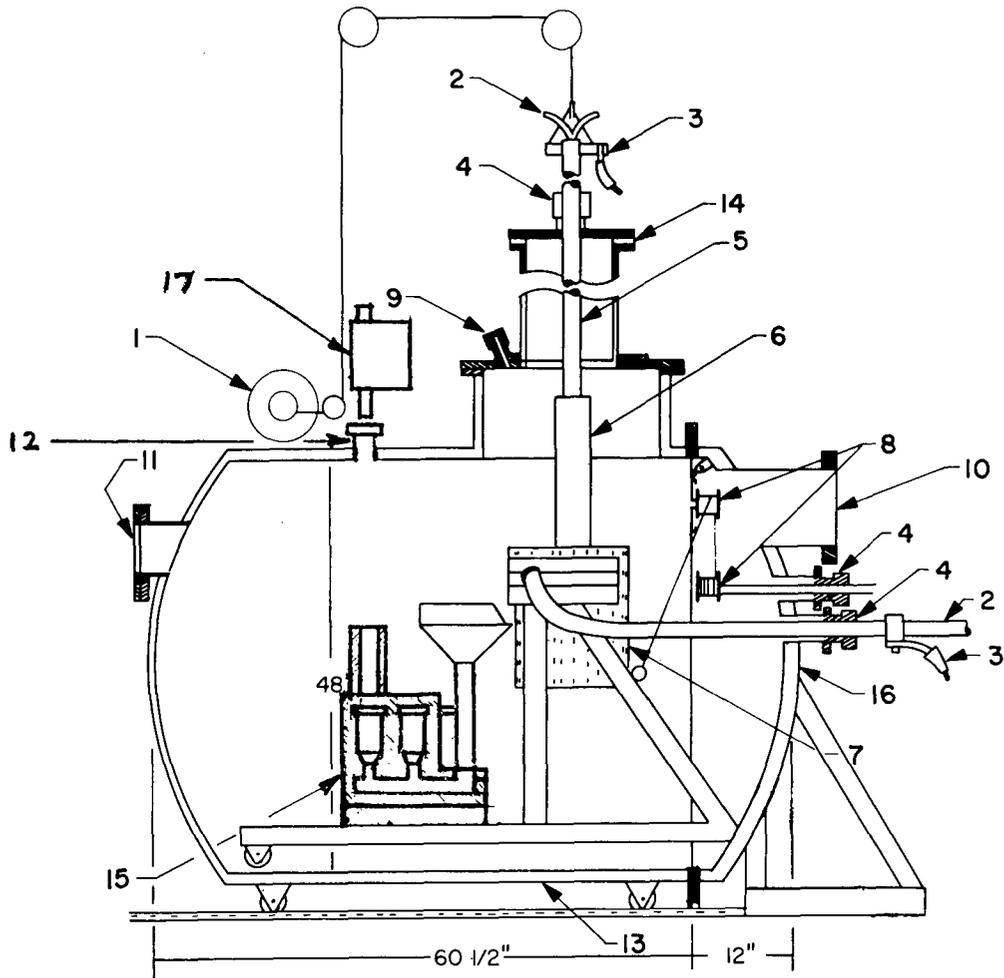
MELTING AND CASTING PROCEDURE

The casting furnace used in this investigation is illustrated schematically in Fig. 11. The details and operation of this equipment were previously described elsewhere (3), and need not be repeated. A typical heat included the following steps: initial vacuum in the furnace before ignition of arc was about 0.01 micron; arc was ignited using about 4000 amps at 30 volts dc and pressure immediately increased to about 0.4 micron; after melting was established, power was increased to about 6000 amps at 30 volts dc and held at this level for filling crucible with molten metal and pressure increased to nearly 1 micron during this stage; prior to finish of melting cycle, power was increased to 7600 amps at 30 volts dc to provide superheat and pressure did not increase; prior to pouring of the melt, power was cut off and consumable electrode stub retracted from crucible and pressure during casting of the melt remained at about 0.5 micron, dropping rapidly as mold and casting began to cool. The mold was permitted to cool to nearly room temperature before removing it from the furnace for disassembly. A typical melt after casting is illustrated in Fig. 12, which shows the filled mold and the skull remaining in the copper crucible. The tube extending above the mold on the left side was for sighting into the mold with a two color pyrometer for temperature measurements during casting. The metal used in the casting work was unalloyed titanium in the form of 6-in.-diameter consumable electrodes which had been prepared from ingot material produced first by arc melting high-quality sponge compacts in an ingot furnace under a partial pressure of inert gas and then remelting in a skull furnace under vacuum and casting into graphite ingot molds. About 30 mils thickness was machined off from the outside diameter of the remelted ingot material to remove surface carbon contamination acquired from casting in graphite. The ingot ends were machined flat and drilled and tapped on one end for a titanium stud for fastening the ingots together. The outside edge of the resulting joint was welded under an inert atmosphere of helium. From the consumable electrodes thus formed about 60 lb of molten titanium was cast per heat.

The range of interstitial content (in weight percent) of the consumable electrodes used for casting work was as follows: 0.0867-0.0965% oxygen; 0.00042-0.00058% H_2 ; 0.007-0.013% C; 0.007-0.009% N_2 .

Attempts to measure the temperature of molten metal during pouring using thermocouples based on tungsten-molybdenum and tungsten-iridium were unsuccessful. The need to employ thick graphite protection tubes caused a serious temperature lag in the thermocouple response which resulted in gross inaccuracy in the temperature measurement. A two-color pyrometer was tried on two melts with some success of ascertaining molten metal temperature during casting. The tube shown on the left side of the mold assembly in Fig. 12 was used for sighting the two-color pyrometer onto the molten metal as it entered the mold cavity.

The two-color pyrometer was an automatic instrument that produced a continuous signal that could be recorded. The time response of the instrument was approximately 0.3 second and since this type of instrument was not significantly affected by changes in emissivity or nonblackbody conditions, the results obtained were considered fairly representative of the temperature conditions of the molten metal during casting. The oscillogram trace of Fig. 13, for melt C225, showed that the temperature of the molten titanium was about $1797^\circ C$ as it entered the mold cavity occupied by insert 56 coated with Y_2O_3 . The top surface of the casting in this cavity apparently solidified at about $1705^\circ C$ in approximately 5.4 seconds after the metal entered the cavity. The cooling rate prior



LEGEND

1. Motor operated cable system for lowering or raising the consumable electrode
2. Cooling water supply to "Stinger"
3. DC power connection for consumable electrode (cathode)
4. Sliding vacuum seal
5. "Stinger" (heavy wall copper tube)
6. Consumable electrode
7. Water cooled copper crucible
8. Tilting mechanism for pouring melt
9. View port
10. Exhaust port to vacuum system
11. View port
12. Sight port for temperature measurement
13. Movable section of casting furnace
14. Electrical insulator
15. Pouring funnel and mold assembly
16. Fixed section of casting furnace
17. Two color pyrometer

Fig. 11 - Schematic diagram of NRL "Skull" furnace



Fig. 12 - Typical melt after casting showing filled mold and solid "Skull" in copper crucible

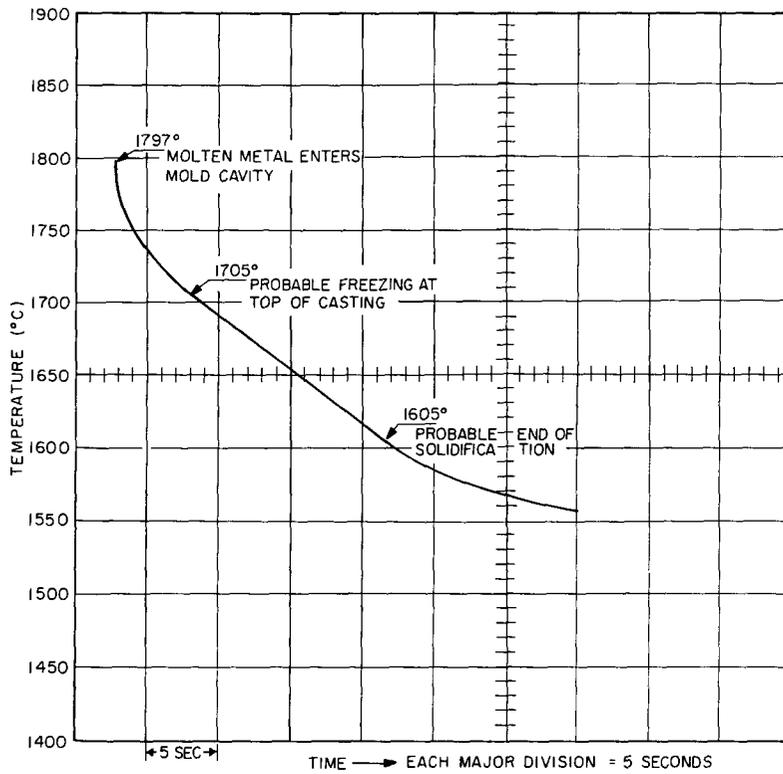


Fig. 13 - Oscillogram trace of melt C225 showing temperature of metal during casting

to the initial freezing was about $17.5^{\circ}\text{C}/\text{sec}$. Cooling progressed linearly below the first inflection point for nearly 14 seconds at a rate of about $7.5^{\circ}\text{C}/\text{sec}$. to the second inflection point, where the end of solidification apparently occurred within the casting. The oscillogram trace of Fig. 14, for a subsequent melt C226, showed that the temperature of the molten titanium was about 1807°C as it entered the mold cavity under observation with the two-color pyrometer. This cavity was occupied by insert 57 coated with Gd_2O_3 . In this case the mold was overfilled and molten metal spilled over from the top of the mold sight tube. The cooling rate up to an apparent initial freezing at the top of the casting was indicated to be considerably faster in Fig. 14 than that indicated in Fig. 13. The

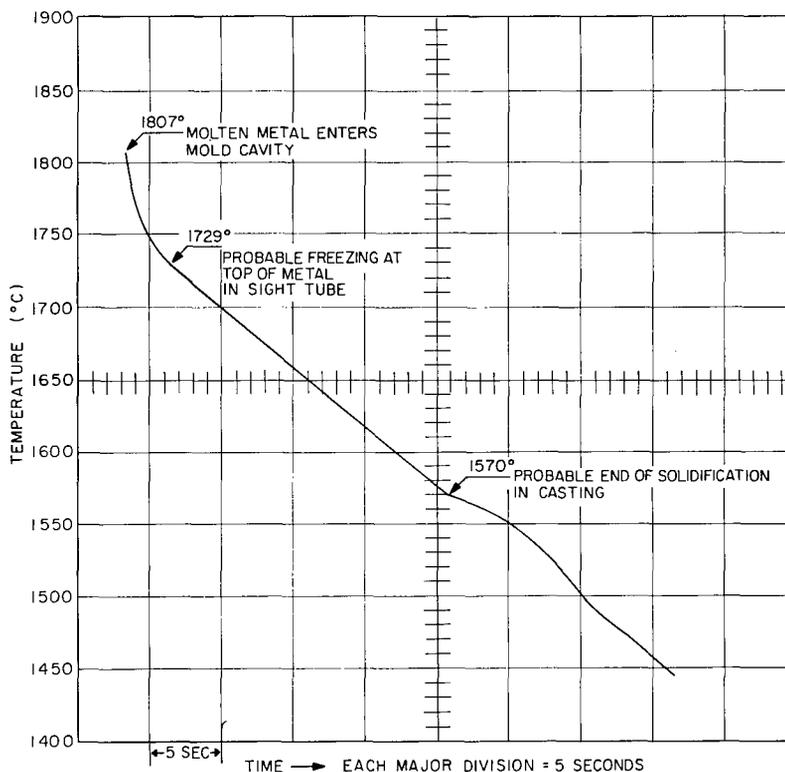


Fig. 14 - Oscillogram trace of melt C226 showing temperature of metal during casting

heat losses from the surface of the metal under observation in melt C226 were considerably greater in view of the fact that the metal was at the top of the mold sight tube. The important result obtained from the temperature measurements with the two-color pyrometer was the information on the approximate amount of superheat contained in the metal as it filled the mold cavity. The melting point of the titanium used in this work was considered to be about 1680°C , based on its quality. Thus, the superheat observed was about 120°C as the metal entered the mold cavity. Since pouring of a melt of about 60 lb of metal was completed in about 5 sec after interruption of the arc, the mold was filled very rapidly as a result. Even though the molten metal was transferred from the crucible to the mold at high speed, a considerable amount of the initial superheat was lost in view of the steep thermal gradients existing in the crucible during melting and the high extraction of heat by the mold.

The mold configuration, illustrated in the drawing of Fig. 2, accommodated four complete cylindrical experimental mold inserts. In each melt cast, one insert set was used uncoated and the resulting casting from this insert served as a control or reference. The uncoated graphite insert set was positioned at the left side of the mold assembly away from the hottest incoming metal.

ANALYTICAL PROCEDURE

The coatings were examined after casting by spectrochemical, x-ray diffraction, and metallographic methods to determine: the extent of any reaction between titanium on one side and/or graphite on the other side; the nature of reaction products; any structural changes; penetration by molten metal. The cast cylinders produced in coated and uncoated mold inserts were analyzed for carbon, oxygen, hydrogen, and nitrogen content, and for the base metals of the coatings.

The method of determining the depth and amount of contamination in the surface layers of the cast cylinders was by obtaining samples cut at various depth increments. The first cut was 5 mils deep, the second cut was another 5 mils deep below the first cut, the third cut was 10 mils deep below the second cut, the fourth cut was 10 mils deep below the third cut, and the fifth cut was 10 mils deep below the fourth cut. Thus, the sampling sequence involved the following surface layers: 0-5 mils, 5-10 mils, 10-20 mils, 20-30 mils, and 30-40 mils. A sample was obtained from the center of each cast cylinder by drilling it to a depth of about 3 in. Sampling was done dry without the use of lubricants or coolants. This method appeared to be satisfactory for determining carbon contamination in surface layers of cast ingots but was not satisfactory for determining oxygen contamination and had to be modified.

The above method of sampling to determine the oxygen contamination was found to give values that were too high and not representative of the actual oxygen content. The fine turnings picked up oxygen in the process of machining which introduced an unpredictable blank correction for oxygen. This method of sampling was superseded in later experiments by cutting out small block samples from various parts of the cast ingots to a depth of 1/8 in. The solid block sample method reduced the sample surface area to an extent that the blank correction could be ignored. Solid block samples were also obtained from the center of the cast ingots by cutting up the ingots.

Oxygen and hydrogen values were obtained by a vacuum fusion method. Carbon was determined by a combustion method in which the resulting CO_2 was absorbed in an electrically sensitive medium making it possible to determine the carbon by means of electroconductivity measurements. Nitrogen was determined by the Kjeldahl method. Metallic contaminants in the cast metal were detected and their relative amounts determined by spectrochemical analysis.

RESULTS AND DISCUSSION

MgO · ZrO₂ Coatings

X-ray diffraction examination of the magnesium zirconate powder used in flame sprayed coatings, disclosed that this was not a true compound oxide but a solid solution of MgO and ZrO₂ with some free MgO also present. When this material was flame sprayed onto graphite, the resulting coating corresponded to the same mixture that was found in the powdered material.

When titanium was cast against these coatings, the coatings were found to be attacked in spots by the molten metal, with metallic droplets, identified to be metallic

magnesium, occurring in affected areas. This indicated that the MgO phase had been attacked and reduced to metal by the titanium.

A typical example of the casting experiment involving magnesium zirconate coated inserts is shown in Fig. 15. The block mold is shown in opened position with the cast ingots and one half of each insert adhering to each ingot appearing on the left side, while

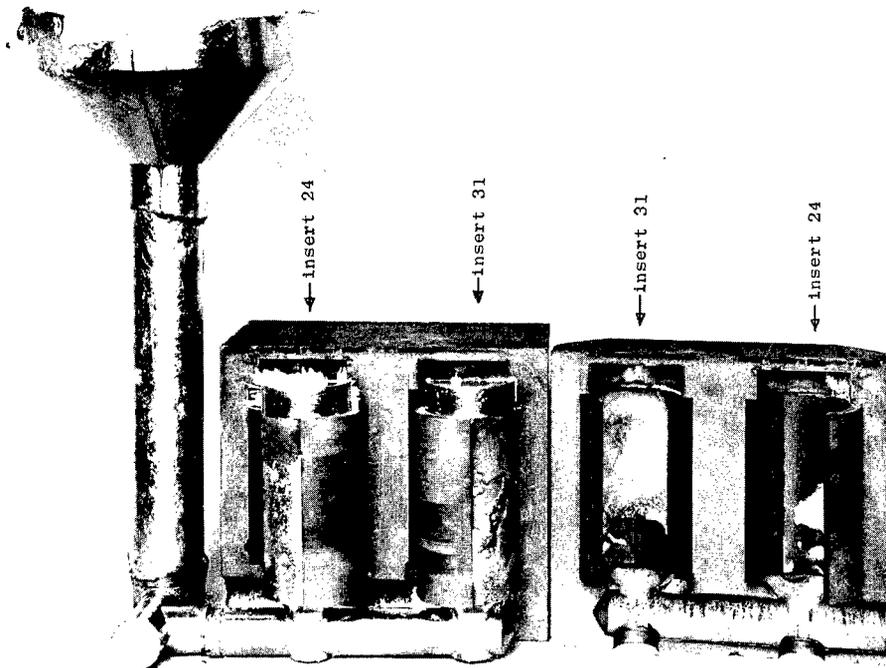


Fig. 15 - Cylinders 24 and 31 cast in $\text{MgO} \cdot \text{ZrO}_2$ coated inserts

the mating insert halves appear on the right side. The average thickness of coating was 0.016 in. on insert 24 and 0.025 in. on insert 31. The coatings of both inserts were attacked locally by titanium; however, the attack appeared to be greater in the case of the thicker coating with a greater amount of metallic droplets present. The coating on insert 24 fractured into large segments when the insert was separated from the cast ingot and most of the pieces adhered to the graphite substrate. Some of the coating adhered near the top of the ingot farthest away from the mold runner. The thicker coating on insert 31 fractured into smaller pieces upon separation from the cast ingot. The surfaces of the coatings of both inserts showed evidence of reaction with titanium during casting. The surfaces of the cast ingots were roughened somewhat from this reaction. The coatings were white before casting as illustrated in Fig. 8 but were gray throughout their thickness after casting, indicating penetration by the titanium. Spectrographic analysis of the coating adjacent to the graphite substrate gave a positive indication that titanium had permeated the coating.

An examination of the surface contamination of the cast titanium ingots showed that the oxygen content was 0.280 wt-% in the outside 5-mil-thick layer, and 0.184 wt-% in a 5 mil-thick layer ending 10 mils below the surface. The oxygen content at the center was

0.189 wt-%. The ingot cast into uncoated graphite mold insert 36 in the same casting experiment showed an oxygen content of 0.190 wt-% at the center. As previously mentioned, these values were suspected of being too high because of the error introduced in the analyses by the character of the samples. The results show, however, that the first-5-mil surface layer was significantly contaminated by oxygen.

The carbon content of the ingot cast into the uncoated graphite mold insert 36 ranged from 0.083 wt-% for the outside 5-mil-thick layer to 0.046 wt-% for a 10-mil-thick layer ending 30 mils below the surface and to 0.026 wt-% at the center. The carbon gradient thus appeared to extend more than 30 mils below the surface and probably reached 50 mils before the concentration became equal to that at the center.

The ingots cast into magnesium zirconate coated mold inserts 24 and 31 showed a carbon gradient from 0.041 wt-% for the outside 5-mil-thick layer to about 0.025 wt-% in a 10-mil layer ending 30 mils below the surface. In this case, the gradient did not appear to extend below 30 mils from the surface. Normally, a coating would be expected to act as a barrier between the substrate and the metal being cast and there should be no contamination generated from the substrate. In this case, however, sufficient reaction appeared to occur between substrate, coating, and the cast metal to produce surface contamination of the cast metal with oxygen and with carbon. Since this coating material consisted of a solid solution of magnesium oxide and zirconium oxide and an included magnesium oxide phase, its chemical stability was apparently insufficient to prevent some reaction between metal and the constituents of the coating during casting. Although MgO is relatively stable up to about 1800°C in contact with graphite, it develops significantly high vapor pressure above 1600°C in vacuum. This characteristic probably was a contributing factor to the local attack of the coating and its reduction to magnesium metal. MgO reacts with carbon at about 1900°C to form Mg metal and CO in accordance with the reaction $\text{MgO} + \text{C} \rightarrow \text{Mg} + \text{CO}$. Since titanium has a high affinity for both carbon and oxygen at elevated temperatures it would be expected to getter any CO produced under the conditions of casting even though the casting operation was conducted under high vacuum conditions. This probably explains the occurrence of the carbon gradient found in the surface layers of titanium cast in magnesium zirconate coated mold inserts. Molten titanium reduces MgO to metal and will absorb the oxygen in solid solution, liberated from the reaction.

The casting experiments involving the coatings composed of a solid solution of MgO and ZrO₂ and a separate MgO phase indicated that this material was not sufficiently chemically stable to provide an effective barrier between graphite and molten titanium. Although the carbon contamination pickup in the surface layers of cast metal did not appear to be excessive, the oxygen contamination pickup was considered to be serious enough to significantly affect the ductility and toughness of cast titanium.

Calcium Zirconate (CaZrO₃) Coatings

The calcium zirconate coating material was identified by x-ray diffraction to be a true oxide compound with no change occurring in its composition after deposition as coatings. Spectrochemical check of the material indicated the presence of the following impurities and their approximate amounts: <1 wt-% silicon; <0.1 wt-% each of manganese, aluminum, and iron; <0.01 wt-% each of vanadium and molybdenum.

The first CaZrO₃ coated mold insert, No. 25, to be tested was included in the casting experiment involving melt C-136 which included two magnesium zirconate coated inserts and one uncoated insert as shown in Table 1. This initial trial of the integrity of the CaZrO₃ coating indicated that the coating material displayed resistance to molten titanium. The results of this trial, shown in Fig. 16, include a close-up of the ingot cast in the CaZrO₃ coated mold insert on the left side and the ingot cast in an uncoated mold

Table 1
Summary of Analytical Results for Metal
Cast in Coated Mold Inserts

Experimental Melt	Ingot and Insert No.	Coating		Oxygen Content at Various Depths (wt-%) Depth (inch)				Carbon Content at Various Depths (wt-%) Depth (inch)					
		Mat'l	Aver. Thick. (inch)	0.-0.005	0.005-0.010	0.020-0.030	Center	0.-0.005	0.005-0.010	0.010-0.020	0.020-0.030	0.030-0.040	Center
C136	24	MgO · ZrO ₂	0.016	0.280	0.184	-	0.189	0.041	0.037	0.032	0.027	-	0.027
	25	CaZrO ₃	0.025	0.231	0.206	0.136 (1/8")	0.138	0.046	0.033	0.031	0.025	-	0.025
	31	MgO · ZrO ₂	0.025	-	-	-	-	0.041	0.033	0.028	0.024	-	0.024
	36	None	-	-	-	0.195 (1/8")	0.190	0.083	0.059	0.046	0.046	-	0.026
C145	26	CaZrO ₃	0.025	-	-	0.141 (1/8")	0.142	0.067	0.056	0.037	0.035	-	0.029
	27	50-50 mix. CaZrO ₃ & MgO · ZrO ₂	0.017	-	-	0.146 (1/8")	0.138	0.036	0.036	0.041	0.035	-	0.034
	29	MgO · ZrO ₂	0.030	-	-	-	-	0.048	0.039	0.035	0.035	-	0.032
	44	None	-	-	-	0.190 (1/8")	0.189	0.086	0.064	0.050	0.047	-	0.033
C151	37	None	-	-	-	-	-	0.073	0.047	0.036	0.032	0.028	0.022
	38	CaZrO ₃	0.022	-	-	-	-	0.048	0.032	0.020	0.031	0.022	0.023
	39	CaZrO ₃	0.033	-	-	-	-	0.053	0.042	0.031	0.030	0.018	0.018
	41	None	-	-	-	-	-	0.079	0.036	0.032	0.025	0.021	0.016
C225	52	Y ₂ O ₃	0.035	-	-	-	0.095	0.046	0.020	0.026	0.017	0.016	0.015
	51	Gd ₂ O ₃	0.032	-	-	-	0.094	0.026	0.018	0.016	0.018	0.014	0.018
	56	Y ₂ O ₃	0.037	-	-	-	0.090	0.056	0.030	0.026	0.025	0.019	0.019
	48	None	-	-	-	-	0.093	0.136	0.055	0.043	0.040	0.027	0.017
C226	49	Y ₂ O ₃	0.032	-	-	-	0.093	0.044	0.031	0.024	0.019	0.018	0.021
	46	Gd ₂ O ₃	0.032	-	-	-	0.093	0.041	0.030	0.028	0.024	0.019	0.016
	57	Gd ₂ O ₃	0.037	-	-	-	0.092	0.053	0.036	0.030	0.021	0.017	0.014
	47	None	-	-	-	-	0.091	0.166	0.099	0.077	0.057	0.038	0.015



Fig. 16 - Closeup of ingots cast in CaZrO_3 coated mold insert 25 and in uncoated mold insert 36

on the right side. A portion of the CaZrO_3 coating is shown lightly adhering to the right half of the ingot. It will be noted that there was no visible evidence of any reaction between the graphite substrate or the cast metal. There was likewise no evidence of titanium soaking through the coating. The lower portion of the coating was broken to illustrate this aspect; it will be noted that the broken edge of the coating remained white and unaffected through its thickness. Further evidence to illustrate the nonpenetrating aspect of the CaZrO_3 coating with respect to molten titanium during casting is shown in Figs. 17 and 18. The ingot on the right side of the mold shows the condition of the coating after casting in insert 38, melt C151 listed in Table 1. The broken edges on the coating appear as white lines, further indicating the resistance of the coating to penetration by molten titanium during casting. The as-fractured section of the coating taken from CaZrO_3 coated mold insert 39 after casting experimental melt C151 is shown in Fig. 18. This section was taken from near the bottom of the coated insert where the entering molten metal would be expected to be hotter and probability greater for reaction between coating and metal. The upper dark band represents the side in contact with molten metal during casting, while the opposite edge is the side in contact with the graphite substrate. The thickness of coating on insert 39 was about 33 mils which is magnified about 30 diameters in Fig. 18. The dark band in the coating adjacent to the cast metal was estimated to be about 5 mils thick and represented the extent of titanium penetration into the coating.

The coatings on inserts 25 and 26 were deposited on a smooth graphite substrate. This provided very little mechanical adhesion to the graphite substrate. In order to obtain better coating adhesion to the graphite, subsequent mold inserts 38 and 39 were blasted with sharp grain zirconia (ZrO_2) at a 45° angle to the surface prior to coating. This procedure improved the mechanical adhesion of the coatings to the graphite substrate.

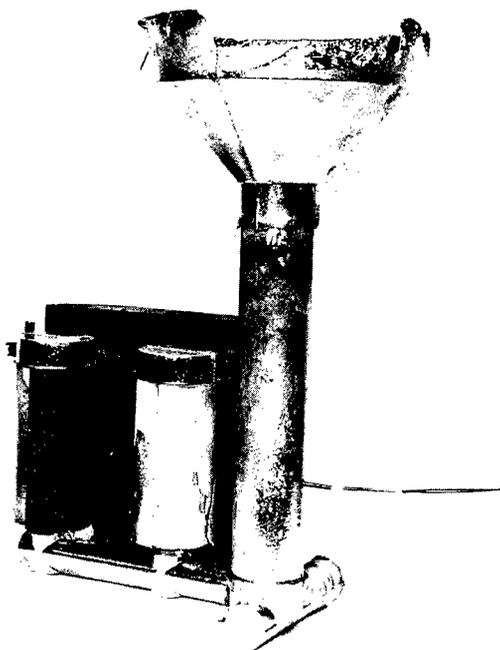


Fig. 17 - Ingots cast in CaZrO_3 coated inserts 38 (right) and 39 (left)

The surfaces of ingots cast in coated CaZrO_3 mold inserts were smooth and reflected to a large degree the surfaces of the coatings against which the metal was cast as illustrated in Fig. 16. The as-cast grain size of the metal cast in CaZrO_3 coated inserts was not as sharply delineated as was metal cast in uncoated graphite inserts such as the ingot on right side of Fig. 16. The shiny surface and prominent as-cast grain structure is characteristic of titanium cast in machined graphite molds.

The oxygen content of ingots cast in CaZrO_3 ranged in one case from 0.231 wt-% for a 5-mil-thick surface layer to 0.206 wt-% for the second 5-mil layer below the surface to 0.138 wt-% at the center of the ingot. The oxygen values were again probably higher than were actually present in the surface layers for reasons discussed previously. A relative indication of some oxygen contamination in the first two 5-mil-thick surface layers, however, is shown by the values.

Oxygen values determined from the 1/8 in.-thick-solid block samples taken

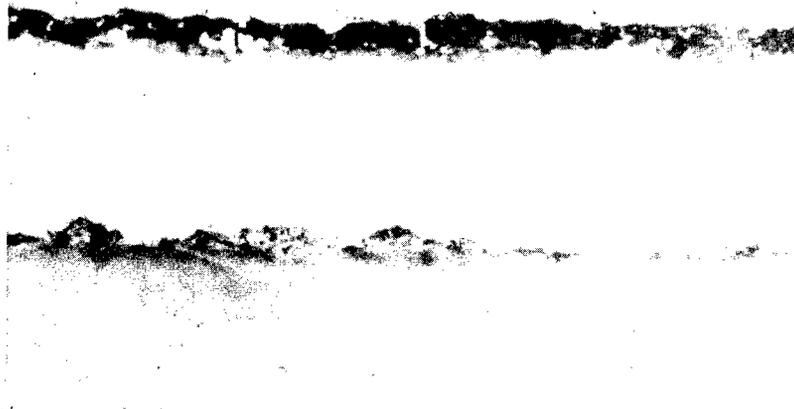


Fig. 18 - Cross section of CaZrO_3 coating taken from mold insert 39 after casting. The dark upper band indicates the depth of penetration of titanium into the coating. Magnification 30X.

from the surface layer of the cast ingots showed little or no difference between the oxygen content in the surface layer and at the center of the ingots. This seemed to indicate that the reaction between the CaZrO_3 coating and the cast metal was only superficial.

Since oxygen increases the hardness of titanium, attempts were made to determine if oxygen gradients were present in the surface layers of the cast ingots by making hardness measurements. The microhardness values obtained, although random in nature, did not vary much from the surface to the center of the cast ingots. From this, it was concluded that very little oxygen contamination was transferred from the CaZrO_3 coatings into the surface layers of the cast titanium.

The problem of determining differences of carbon content in the surface layers and in the center of the cast ingots by hardness measurements was not successful. Low concentrations of carbon apparently do not harden titanium sufficiently to make hardness measurements meaningful.

The analytical results for carbon content in ingots cast in CaZrO_3 coated mold inserts are listed in Table 1. It will be noted that a gradient in carbon content occurred in all of the surface layers of these ingots. A similar gradient also occurred in the ingots cast in uncoated mold inserts. It appears to be easier to explain the carbon content gradient in the metal cast in uncoated mold inserts than in metal cast in CaZrO_3 coated inserts since the cast metal was in direct contact with the mold insert. Under these conditions, surface contamination by carbon would be expected since molten titanium is known to react with carbon. The depth of the carbon gradient in these ingots was about 40 mils. The reason for a carbon gradient in ingots cast in the CaZrO_3 coated inserts is somewhat obscure since the CaZrO_3 coating appeared to provide an effective barrier between the graphite substrate and the cast metal. Under these conditions the surfaces of the ingots were not in direct contact with a source of carbon in the final stage of casting within the mold inserts. Some carbon pickup occurred in the molten metal when it was poured into the block mold and came into contact with exposed graphite parts along the channels leading to the mold inserts. The carbon pickup, however, did not increase progressively in the metal as the metal advanced along the runners to the final stage of entry into the coated inserts. A thin skin of metal undoubtedly solidified quickly after coming in contact with the relatively cold graphite mold parts due to the high thermal conductivity of graphite. Therefore, some of the metal during its transit in the mold runners to the final entry into the experimental mold inserts was virtually out of contact with graphite but in contact with the frozen skin mentioned above. The mold was designed so as to eliminate turbulence in the final entry of the cast metal into the experimental inserts by introducing the molten metal from below and causing it to rise without turbulent movement. The transit of this metal into the experimental mold inserts, however, was exceedingly rapid since the casting operation of pouring the entire melt from the copper crucible of the casting furnace into the block mold did not exceed about 5 seconds. In view of the assumed relatively quiescent advance of the molten metal into the experimental inserts, it appeared that the carbon picked up from the walls of the runners did not distribute itself into the molten metal but remained as an enriched layer at the outer edges of the molten column. Since freezing undoubtedly occurred quickly at the coating-cast metal interface and progressed fairly rapidly toward the center of the ingot there was little time for effective distribution of the carbon by diffusion. This is considered to be a plausible explanation for the carbon gradient found in the surface layers of ingots cast in CaZrO_3 coated mold inserts.

Another possible source of carbon pickup that may have contributed somewhat to the carbon gradient in the ingot surfaces was from the coating reacting with the graphite substrate during the time that the interface was at maximum temperature during casting. An odor of acetylene was noted each time the casting furnace was opened to remove the casting experiment for examination. The acetylene odor was traced to the coatings, which indicated that a carbide had formed that was capable of producing acetylene (C_2H_2) upon

UNCLASSIFIED

coming into contact with moisture. Of the constituents present in the casting experiments, capable of producing a carbide that would produce acetylene upon hydrolysis, calcium appeared to be the only likely source. Calcium carbide can be obtained from the reaction $\text{CaO} + 3\text{C} = \text{CaC}_2 + \text{CO}$ at temperatures above 2000°C in vacuum. Although there did not appear to be any visible reaction between the coatings and the graphite substrate the presence of acetylene strongly indicated that a superficial layer of CaC_2 may have formed at the interface. Since the coatings were not pore free, the CO generated from the reaction between the coating and graphite would pass through the coatings and be immediately taken up in the surface layers of the hot titanium. The temperature of the molten metal entering the coated experimental mold inserts was probably sufficiently high to promote the carbide-forming reaction mentioned above.

A superficial reaction between coating and cast metal was also suspected although there was virtually no visible evidence of this on the surfaces of either the coating or the cast metal. Spectrochemical examination indicated, however, traces of calcium to a depth of 10 mils below the surface of cast metal. The effects of this slight reaction probably introduced some oxygen contamination into the outside surface layer of the cast metal but probably no CaC_2 was formed since the amount of carbon contained in the titanium was insufficient to that required for carbide formation.

Comparing the carbon results obtained for metal cast into CaZrO_3 coated mold inserts with those for metal cast into uncoated mold inserts under the same conditions it will be noted from Table 1 that a lesser amount of carbon contamination occurred in surface layers of metal cast in the coated inserts and the contamination did not penetrate as deeply. The fact that molten metal acquired some carbon contamination from contact with uncoated graphite before its entry into the experimental mold inserts may have obscured somewhat the barrier effect of the coatings.

The CaZrO_3 coatings exhibited good thermal shock resistance and did not crack under the severe temperature gradient from room temperature initially, to a virtually instantaneous temperature of at least 1900°C when suddenly brought into contact with molten titanium during casting. Despite this desirable characteristic the other factors seemed to indicate that CaZrO_3 would not be sufficiently chemically stable under casting conditions to qualify it as an entirely satisfactory and reliable coating material on graphite mold surfaces for the casting of titanium.

50-50 Mixture of $\text{MgO} \cdot \text{ZrO}_2$ and CaZrO_3

One mold insert, No. 27, was flame spray coated with a 50-50 blended mixture of magnesium zirconate and calcium zirconate to explore the merit of the combination of the CaZrO_3 compound and the solid solution of magnesium and zirconium oxides. This coating was 17 mils thick and was tested in the experimental casting experiment involving melt C145 (see Table 1). The coating prior to casting appeared to be similar in appearance to those of magnesium zirconate and calcium zirconate.

Upon separation of the ingot from the coated insert after casting the coating remained attached to the graphite substrate with the exception of a small piece of the coating which adhered to the ingot. There were several brownish gray areas in the coating which appeared to penetrate through its thickness to the graphite substrate. Outside of these areas the coating showed about a 5-mil penetration of titanium into the thickness of the coating.

The surface of the cast ingot was similar to that observed on the ingots cast in CaZrO_3 with some dull gray areas distributed among the predominantly bright metal. Where the coating adhered to the ingot some reaction had apparently occurred between coating and metal but reduction of the coating as occurred in the case of the $\text{MgO} \cdot \text{ZrO}_2$

coatings appeared to be absent. The coating appeared to resist thermal shock under the conditions of casting.

The oxygen content in a 1/8-in.-thick surface layer of the ingot was found to be 0.146 wt-% and 0.138 wt-% at the center. Since the oxygen content of the consumable electrode material was under 0.1 wt-% of oxygen and there was no source of oxygen contamination during casting other than that of the coating it was concluded that some reaction must have occurred between the metal and the coating. This contamination occurred both in the surface layers and in the bulk of the cast metal.

The carbon content of the ingot appeared to be nearly the same from the surface to the center. This indicated that the coating acted as an effective barrier between the graphite substrate and the cast metal. Despite the lack of a carbon gradient in the cast ingot, the condition of the coating indicated somewhat more attack by the molten titanium than was observed in the case of the CaZrO_3 coatings and therefore the 50-50 mixture was considered to be less effective as a coating material than the CaZrO_3 .

Gadolinium Sesquioxide (Gd_2O_3) Coatings

In view of the high melting points of Gd_2O_3 , and that of Y_2O_3 to be discussed in the next section, it was considered necessary to employ a plasma flame method for applying the coatings onto the graphite in order to obtain complete fusion of the coating material during deposition. The typical plasma coated mold inserts were illustrated in Fig. 9 and the coating thicknesses obtained are listed in Table 1.

The gadolinia (Gd_2O_3) powdered coating material was identified to be of cubic structure before plasma flame spraying. After coating, the crystal form of the oxide could not be positively identified but was considered to be a high temperature crystal form reported to occur at temperatures above 1300°C (4). The high temperature form apparently did not revert to the low temperature cubic modification but was retained upon cooling to room temperature.

The Gd_2O_3 coating on insert 51 was observed to have poor adherence. This was attributed to the oxide powder not having the necessary characteristics for satisfactory plasma flame spraying. This condition was corrected by calcining the powder at 1400°C to presinter it, followed by crushing and wet screening to obtain the required mesh size and free flowing characteristics. Coatings applied to inserts 46 and 57 (see Table 1) were of pinkish white color and exhibited excellent surface characteristics and excellent adherence to the graphite.

In order to obtain a better evaluation of the effectiveness of the Gd_2O_3 and Y_2O_3 coatings in preserving the quality of titanium cast into molds coated with these oxides, it was considered necessary to determine in some detail the amount of carbon and oxygen in the consumable electrode melting stock for reference purposes. Since the electrode stock had been previously cast into uncoated machined graphite ingot molds, it was necessary to machine about 30 mils from the top, bottom, and sides of each electrode to remove surface carbon contamination. Samples for oxygen analysis were obtained by cutting out solid pieces of approximately 0.4 gram each from the top, bottom and sides of each electrode. Samples for carbon determination were obtained from drilling the center of the top and the bottom and chips from end milling the sides at top, midsection, and bottom. The analytical results obtained for electrodes C210 and C211 used in melts C226 and C225 respectively are listed in Tables 2a and 2b, respectively. Each of these melts included mold inserts coated with Gd_2O_3 and with Y_2O_3 in the casting experiments as shown in Table 1.

Table 2a
Summary of Analytical Results for Consumable Electrode No. C210
Melting Stock

Part of Electrode Sampled*	Analysis No.		Oxygen		Hydrogen		Part of Electrode Sampled	Analysis No.	Carbon	
			ppm	Average Wt-%	ppm	Average $\times 10^{-6}$ Wt-%			Wt-%	Average Wt-%
Top-sampled on opposite sides	T241 one side	A1	937	0.095	6	5.3	Top-center-drilled	T253	0.012	0.011
		A2	979		4				0.009	
		B1	892		4		Bottom-center drilled	T254	0.012	
		B2	989		7				0.011	
	T242 opposite side	A1	986	0.105	6	7.5	Top-circumference end milled	T255	0.013	0.013
		A2	1032		8				0.013	
		B1	1086		6		Midsection circumference end milled	T256	0.013	
		B2	1098		10				0.011	
Midsection-sampled on opposite sides	T243 one side	A1	1010	0.098	9	6.8	Bottom circumference end milled	T257	0.009	0.008
		A2	905		5				0.007	
		B1	980		5		Overall Average Content	0.011 wt-%		
		B2	1032		8					
	T244 opposite side	A1	990	0.095	4	4.3				
		A2	1018		6					
		B1	882		4					
		B2	903		3					
Bottom-sampled on opposite sides	T245 one side	A1	901	0.094	6	5.5				
		A2	954		2					
		B1	985		5					
		B2	916		9					
	T246 opposite side	A1	916	0.092	3	5.8				
		A2	910		5					
		B1	932		9					
		B2	916		6					
Overall Average Content			0.097 wt-%		5.9×10^{-6} wt-%					

*Solid samples approx. 0.4 g each.

Table 2b
Summary of Analytical Results for Consumable Electrode No. C211
Melting Stock

Part of Electrode Sampled*	Analysis No.		Oxygen		Hydrogen		Part of Electrode Sampled	Analysis No.	Carbon	
			ppm	Average Wt-%	ppm	Average $\times 10^{-6}$ Wt-%			Wt-%	Average Wt-%
Top-sampled on opposite sides	T247 one side	A1	685	0.085	3	5.0	Top-center drilled	T258	0.012 0.011	0.012
		A2	970		5		Bottom-center drilled	T259	0.012 0.009	0.011
		B1	908		6		Top-circumference end milled	T260	0.011 0.011	0.011
		B2	825		6					
	T248 opposite side	A1	852	0.086	3	6.0	Midsection circumference end milled	T261	0.011 0.013	0.012
		A2	855		8		Bottom circumference end milled	T262	0.017 0.009	0.013
		B1	904		8					
		B2	830		5					
Midsection sampled on opposite sides 90° to sampled areas of top	T249 one side	A1	946	0.094	6	5.8	Overall Average Content			
		A2	990		7					
		B1	948		6					
		B2	887		4					
	T250 opposite side	A1	1024	0.091	3	3.5	0.012 wt-%			
		A2	907		4					
		B1	867		3					
		B2	835		4					
Bottom-sampled on opposite sides	T251	A1	848	0.081	2	1.5	Overall Average Content			
		A2	810		1					
		B1	830		1					
		B2	760		2					
	T252	A1	860	0.083	2	3.3	4.2 $\times 10^{-6}$ wt-%			
		A2	745		3					
		B1	880		4					
		B2	841		4					
Overall Average Content			0.087 wt-%		4.2 $\times 10^{-6}$ wt-%					

*Solid samples approx. 0.4 g each.

NAVAL RESEARCH LABORATORY

The surface condition of the ingot cast in Gd_2O_3 coated insert no. 51 appeared to be relatively smooth with some grain structure visible on the surface of the metal. The overall appearance of this ingot was somewhat smoother than the best appearing ingot cast in a $CaZrO_3$ coated insert.

The Gd_2O_3 coating remained nearly intact but separated from the graphite insert during casting. The coating adhered to the ingot near its top and could not be readily separated from it causing the coating to break up when an attempt was made to remove it. The coating appeared discolored on the side in contact with graphite and on the side in contact with metal, however the penetration of the coating by titanium appeared to be superficial. A segment of the coating is shown attached to the inner surface of insert 51 at the extreme right side of Fig. 19. The insert cracked during casting, apparently because of a too tight fit in the block mold. There was no odor of acetylene observed in the

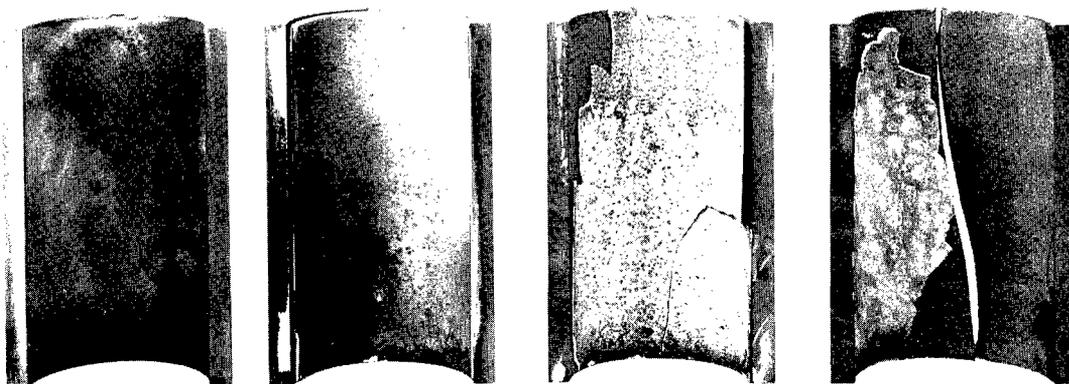


Fig. 19 - Half sections of inserts after casting (left to right: No. 48 uncoated, No. 56 Y_2O_3 coated, No. 52 Y_2O_3 coated, and No. 51 Gd_2O_3 coated)

casting experiment involving melt C225. This indicated that there were no rare earth or yttrium carbides formed during casting and, therefore, an absence of a carbon-coating reaction. The white color of the fractured edge of the coating shows that metal did not penetrate the coating to any significant depth during casting.

The surface of the ingot cast in Gd_2O_3 coated insert 46 (melt C226) appeared to be smooth but of a rather dull luster with a grayish color toward the top of the ingot. The coating was intact but separated from the graphite insert during casting. Approximately 25% of the coating was found to be firmly bonded to various spots of the upper part of the ingot and had to be tapped with a hammer to separate it from the metal. The surface condition of the ingot and the appearance of the casting are shown on the right side of Fig. 20. There was no penetration of metal through the coating.

The ingot cast in Gd_2O_3 coated insert 57 shown on the left side of Fig. 20 was included in the same casting experiment with the ingot cast in insert 46. The surface of the ingot had a smooth dull luster but somewhat brighter than the ingot from insert 46. The coating showed to be firmly bonded to the ingot only in isolated spots, one such spot is shown in Fig. 20 at the parting line of the mold insert. The broken edges of the coating

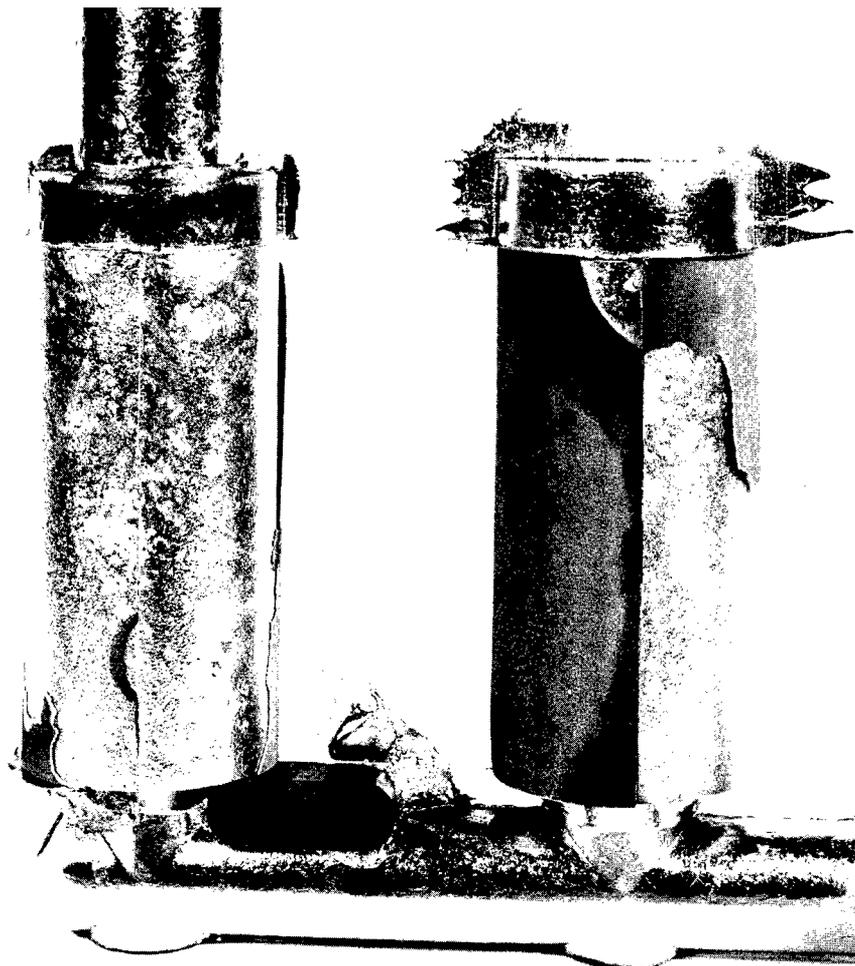


Fig. 20 - Ingots cast in Gd_2O_3 coated inserts: right side, insert 46; left side, insert 57

show by their white color that there was no significant attack of the coating by the molten metal during casting.

Melt C226 was apparently somewhat hotter than melt C225, when poured, since the power input into melt C226 was 1.2 kilowatts higher than that in melt C225 at the finish. This may have accounted for the increase in reactivity between coating and metal. As insert 46 was positioned in the block mold closer to the pouring funnel than was insert 57, the metal entering insert 46 during casting was undoubtedly also somewhat hotter than that entering insert 57.

X-ray diffraction analysis of the Gd_2O_3 coatings after plasma flame spraying showed the oxide to be entirely in a high-temperature crystal form. After casting, an analysis of the oxide coatings next to the cast metal showed, however, that some of the oxide had reverted to the low-temperature cubic crystal form. This seemed to indicate that the

transformation to a high-temperature crystal form was not strictly irreversible as was indicated previously. This situation may be related to the oxide being slightly deficient in oxygen on the surface next to the cast metal as a result of a slight reaction between the oxide and the metal while the latter was molten in which some oxygen may have been transferred from the oxide to the titanium. If this should be the case then stoichiometry of oxygen content in the oxide could be expected to influence the crystallographic transition behavior of the oxide.

X-ray diffraction analysis did not detect any reduction of the oxide Gd_2O_3 as a result of molten titanium being cast against it. Spectrographic analysis of the cast metal surface which had been in contact with the oxide likewise did not show any gadolinium content, further indicating the absence of any significant reduction of the oxide. Likewise, there were no gadolinium carbides detected, indicating that there was no detectable reaction between the oxide coating and the graphite substrate. The absence of any odor of acetylene upon exposure of the casting experiments to atmospheric air involving melts C225 and C226 provided further evidence that no detectable acetylide carbides were present. The acetylide carbides of the rare earths hydrolyze, producing a mixture of gases consisting of 70-80% acetylene, about 20% methane, and some hydrogen and ethylene. These results indicated that the oxide Gd_2O_3 had remained relatively stable with respect to molten titanium on one side and with respect to graphite on the other side during casting.

From samples taken at the top and bottom of the ingot cast in Gd_2O_3 coated insert 51 the oxygen content was found to be 0.094 wt-% in both parts of the ingot. The overall oxygen content of the consumable electrode C211 used in melt C225 was 0.087 wt-%. Assuming that no oxygen contamination occurred during the melting operation the increase of 0.007 wt-% of oxygen in the cast ingot apparently was derived from the surface reaction between the Gd_2O_3 coating and the metal during casting.

The carbon content of the ingot cast in Gd_2O_3 coated insert 51 was found to be 0.026 wt-% in the outside 5-mil surface layer and 0.018 wt-% in the next 5-mil layer below the outside layer and 0.018 wt-% at the center of the ingot. The small difference of 0.008 wt-% between the content of the 5-mil-thick outside layer and the content of the bulk of the ingot indicated that the coating had provided an effective barrier between the graphite insert and the cast metal. The overall carbon content of the consumable electrode C211 used in the casting experiment melt C225 was 0.012 wt-%. The bulk carbon content of the ingot cast into the uncoated graphite mold insert 48 was 0.017 wt-%. There was a carbon content increase during casting of 0.006 wt-% in the ingot cast in Gd_2O_3 coated mold insert 51 and of 0.005 wt-% in the ingot cast in the uncoated mold insert 48. The small difference in these values is considered to be within the analytical precision for carbon determination.

In the case of the ingots cast in Gd_2O_3 coated mold inserts 46 and 57, the average oxygen content of each ingot was found to be 0.093 wt-% and 0.092 wt-% respectively, whereas, the overall oxygen content of consumable electrode C210 was found to be 0.097 wt-%, a difference of about 0.004 wt-%. This difference was probably not due to any removal of oxygen from the metal during the melting operation but attributable to the sampling and analytical precision. In view of this discrepancy there was no positive indication that the oxygen content of the cast metal had been increased as a result of its contact with the Gd_2O_3 coatings.

The carbon content of ingots cast in Gd_2O_3 coated mold inserts 46 and 57 was found to range from 0.041 wt-% and 0.053 wt-% respectively in the outside 5-mil surface layer to 0.019 and 0.017 wt-% respectively in a 10-mil layer 40 mils below the outside surface and to 0.016 and 0.014 wt-% respectively at the center. The carbon content of the ingot cast in uncoated mold insert 47 included in the same casting experiment was found to range from 0.166 wt-% in the outside 5-mil surface layer to 0.038 wt-% in a 10-mil layer

40 mils below the outside surface, to 0.015 wt-% at the center. The carbon content of consumable electrode C210 used in this casting experiment was found to have an overall average carbon content of 0.011 wt-%. Thus, the amount of carbon picked up in the bulk cast metal over its initial content before pouring appeared to be about 0.005 wt-%. The presence of a small carbon content gradient in the surface layers of the ingots cast in Gd_2O_3 coated mold inserts is somewhat puzzling since the coatings appeared to provide a good barrier between the graphite mold inserts and the cast metal. In addition, the small increase in the carbon content found in the bulk metal of the cast ingots indicated no great pickup of carbon contamination by the molten metal in traversing uncoated parts of the block mold. The carbon enrichment of the surface of the ingot cast into the uncoated mold 47 is easy to explain since the metal was in direct contact with the source of carbon during casting. In the case of the ingots cast in the Gd_2O_3 mold inserts, however, there was no direct contact between the graphite mold inserts and the ingot. Since there was a severe temperature gradient in the ingots during casting there appeared to be a plausible explanation that carbon bearing liquid metal would solidify in accordance with the amount of carbon present, the higher content solidifying first. The phase relationships between titanium and carbon indicated such a process to be feasible.

In summarizing the experimental work on the effectiveness of Gd_2O_3 as barrier coatings on graphite mold surfaces for casting of titanium it may be stated that Gd_2O_3 was found to be superior to the best $CaZrO_3$ coatings tested. The best Gd_2O_3 coatings were found to be those in which the material had been presintered by calcining at $1400^\circ C$, followed by crushing and wet screening to obtain a free flowing powdered material of required particle size. The absence of any significant reactivity between the coatings and the cast metal or between the coatings and the graphite substrates was reflected in the very low amounts of oxygen and carbon contamination that occurred in the cast metal. Although good adherence of the coatings was obtained on the graphite mold inserts during plasma spray coating, the coatings appeared to separate from the mold inserts during casting. Such coatings would, therefore, be useful only for a single use; however, since the graphite substrates did not appear to undergo any deterioration they could be re-coated and reused. The extent of such utility, however, cannot be estimated from this work.

Yttrium Sesquioxide (Y_2O_3) Coatings

The initial attempt to spray coat Y_2O_3 powder onto graphite mold inserts in the as-received powder condition gave somewhat inferior results, similar to those obtained on Gd_2O_3 coated insert 51 already discussed. A comparison of the quality of these coatings is shown in Fig. 21 which shows: second from left, insert 56 coated with treated Y_2O_3 powder; third from left, insert 52 coated with as-received Y_2O_3 powder; fourth from left, insert 51 coated with as-received Gd_2O_3 powder. The Y_2O_3 powdered oxide was given the same treatment used to condition the Gd_2O_3 powdered oxide to obtain a free flowing material. The Y_2O_3 coatings were tan colored, which appeared to be characteristic of this oxide. The coating on insert 52 like that of insert 51 coated with Gd_2O_3 , was considered to be rather inferior in quality and showed poor adherence to the graphite inserts. The coatings obtained on inserts 56 and 49 after treating the oxide were of excellent quality and showed good adherence to the graphite substrates.

The ingot cast into mold insert 52 was smooth with a slightly dulled luster near the top but appeared bright on the rest of its surface, with as-cast grains showing. The coating remained intact during casting and there was no visual evidence of titanium soaking through the coating. Half of the mold insert broke during casting apparently because of too tight a fit in the block mold cavity. The coating in contact with the cast metal was metallic gray, indicating that titanium penetration into the coating was very superficial. The coating in contact with the graphite was gray colored by graphite smeared on it, but there was no evidence of any chemical reaction between the coating and the graphite.

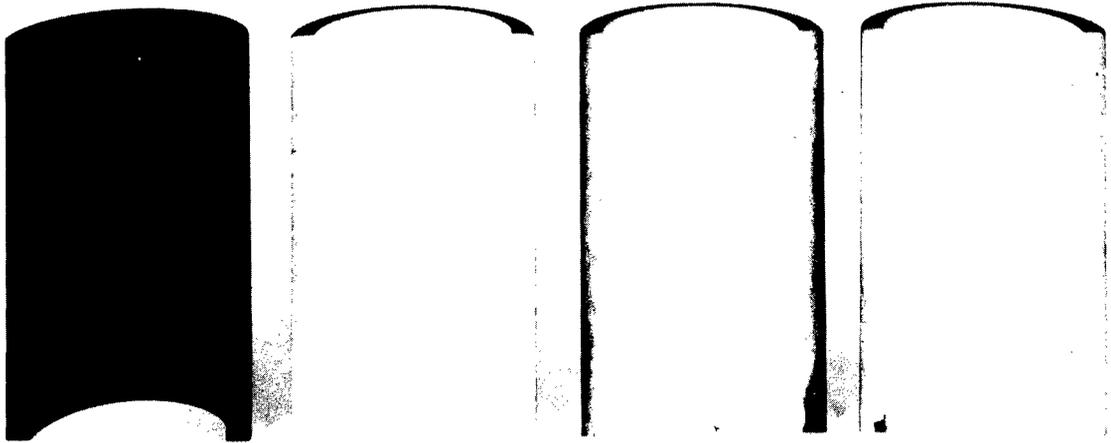


Fig. 21 - Comparison of coating quality (left to right: insert 48 uncoated, insert 56 coated with treated Y_2O_3 , insert 52 coated with as-received Y_2O_3 , and insert 51 coated with untreated Gd_2O_3)

There was no odor of acetylene observed, indicating the absence of carbide formation. The coating separated cleanly from the cast ingot showing that the oxide Y_2O_3 had good resistance toward molten titanium.

The condition of the Y_2O_3 coatings on inserts 56 and 52 is shown by the second and third half sections from the left side of Fig. 19. Insert 52 was coated with as-received Y_2O_3 powdered oxide and insert 56 with treated Y_2O_3 powdered oxide. The coating on insert 52 showed a slightly greater amount of superficial metal penetration near the top of the insert than occurred in the rest of the coating surface. This situation probably reflected the somewhat inferior quality of the coating surface of insert 52. The coating was broken to expose the edges in order to show that the metal penetration of the coating was superficial. In comparison, the condition of insert 56 (second from left) is completely intact and the surface of the coating shows virtually no metal penetration, reflecting the quality of the coating and its high resistance to molten titanium during casting. The broken edge at the bottom of the left side of the insert shows the absence of metal penetration and of any reaction with the graphite. The coating, however, separated from the graphite during casting. The difference in coefficients of thermal expansion of the graphite and of the oxide, Y_2O_3 , is too great, making it virtually impossible to prevent separation of the coating from the substrate during casting. Thus, these coatings would be useful for a one time use only; however, the graphite substrate could probably be recoated and reused many times since the condition of the graphite insert appeared to be unaffected.

The ingot cast into insert 49 which was included in casting experiment involving melt C226 was similar in appearance to the ingot cast in insert 56 in casting experiment involving melt C225. In the case of the ingot cast in insert 49, there appeared to be, however, slightly more metal penetration into the coating near the top of the ingot. This same situation was observed to occur in the case of ingots cast in Gd_2O_3 coated mold inserts. The only explanation that can be advanced is that the proximity of the uncoated

portion of the graphite block mold above the coated inserts may have enriched, somewhat, the cast metal with carbon and caused a slightly greater reaction to occur between coating and cast metal at that point. The condition of the ingot and of the Y_2O_3 coated insert 49 is shown on the left side of Fig. 22. The integrity of the coating is clearly shown. The ingot on the right side of Fig. 22 was cast in uncoated insert 47 and shows the characteristic surface condition of titanium cast in machined graphite molds.

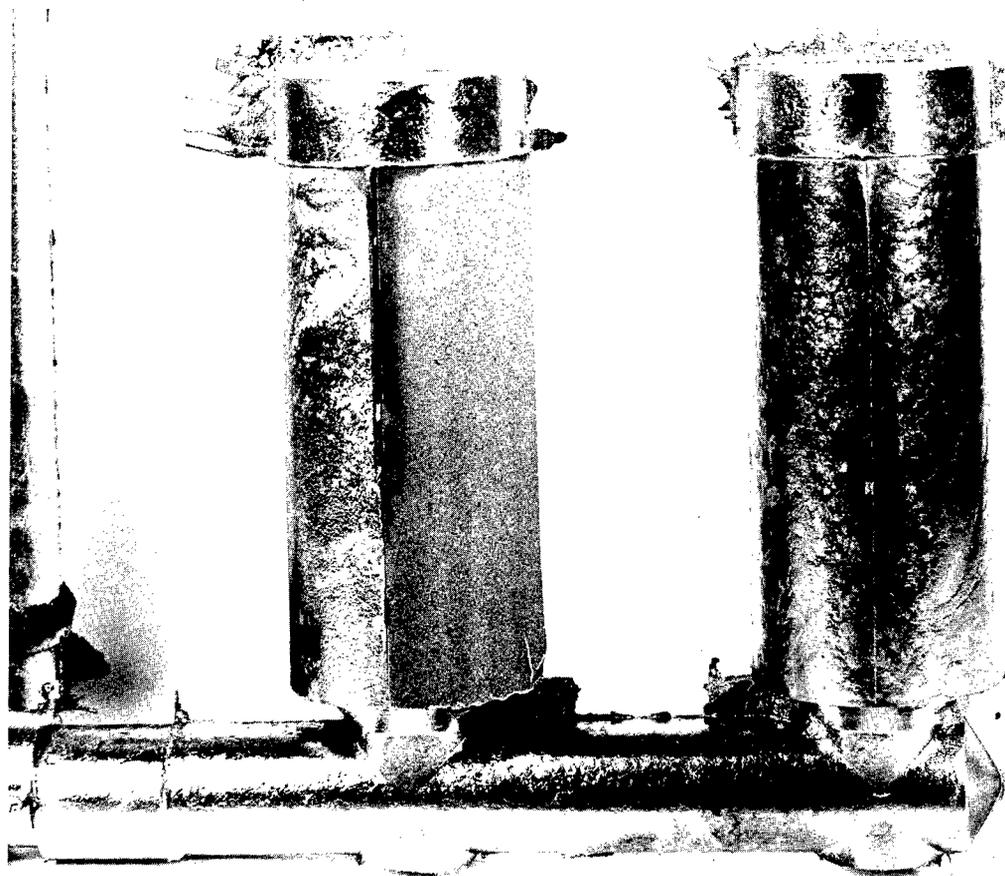


Fig. 22 - Ingots cast in Y_2O_3 coated insert 49 and uncoated insert 47 (casting experiment melt C226)

The condition of half sections of the mold inserts included in the casting experiment involving melt C226 are shown in Fig. 23. These are, from left to right, uncoated insert 47, Gd_2O_3 coated inserts 46 and 57, and Y_2O_3 coated insert 49. The integrity of the coatings is clearly shown. The uncoated graphite insert shows a metallic film of titanium, while the coated inserts are uniformly gray colored by a superficial metallic film. It will be noted that the coatings on inserts 46 and 49 cracked during casting. This was caused by cracking of the graphite substrate, probably because the inserts fitted too tightly in the block mold cavity.

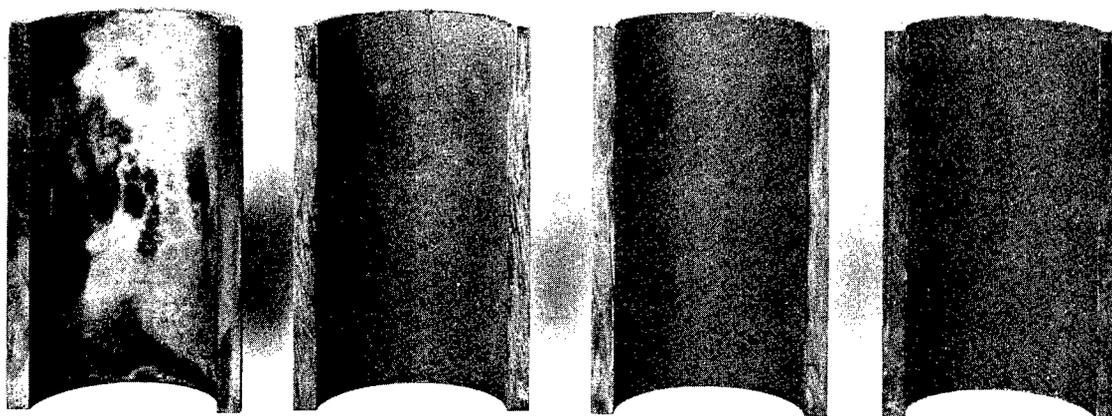


Fig. 23 - Half sections of mold inserts included in casting experiment melt C226 (left to right: uncoated insert 47, Gd₂O₃ coated inserts 46 and 57, and Y₂O₃ coated insert 49)

The oxygen content of ingots cast in oxide Y₂O₃ coated inserts was listed in Table 1. In the case of ingots cast in inserts 52 and 56 in casting experiment melt C225 the oxygen content was found to be 0.095 wt-% and 0.090 wt-% respectively, whereas, the overall average oxygen content of the consumable electrode C211 was 0.087 wt-%. Thus, a small increase of oxygen occurred in the metal during casting. From the condition of the coatings after casting, it is unlikely that there was any significant contribution of oxygen from reaction between molten titanium and the oxides. It is more likely that the metal picked up the oxygen from the graphite as it flowed through the uncoated channels of the block mold. The molds were heated to about 130°C and outgassed under vacuum in the casting furnace to a pressure of about 1×10^{-5} torr and then cooled under vacuum to room temperature. This treatment, however, only removed residual water vapor and did not remove the oxygen absorbed in the graphite. It would have been necessary to heat the graphite mold to very high temperatures to remove residual oxygen from it and such treatment would have caused difficulties with the coatings.

In the case of the ingot cast in insert 49 in casting experiment melt C226 the oxygen content was found to be 0.093 wt-%, whereas, the oxygen content of the consumable electrode C210 was 0.097 wt-%. This discrepancy is similar to that already discussed in the case of ingots cast into Gd₂O₃ coated inserts 46 and 57 for this melt and the only explanation that can be advanced is that the sampling and/or the analytical precision were somehow inaccurate.

The carbon content of ingots cast in Y₂O₃ coated inserts 52, 56, and 49 was found to be somewhat greater in surface layers than it was in the bulk of the metal as was found in the case of metal cast in Gd₂O₃ coated inserts (see Table 1). There was also a small increase in the carbon content in the bulk of the cast ingots over that found in the consumable electrode melting stock. As previously discussed, the increase of carbon content in the bulk of the cast metal can be explained by the exposure of molten metal during casting to uncoated graphite mold channels. The only plausible explanation for a surface gradient in carbon content as previously advanced is that the carbon bearing metal being of higher melting point would solidify first followed by metal containing lesser and lesser amounts of carbon. The condition of the coatings appeared to exclude any possibility of carbon pickup by the cast ingots.

In general the heat transfer characteristics of the coated graphite hollow cylinder mold inserts were analogous to the case involving two or more concentric cylinders of different materials. The coated cylinders acted as a heat sink, while the cast titanium acted as a heat source. Since the titanium, the coating, and the mold inserts were in intimate contact during casting, heat transfer was principally by conduction with some radiant energy being transferred to the graphite substrate by means of pores in the coating.

In view of the rather poor thermal conductivity of the coating materials it appeared as if there should have been some reduction in the strong chilling effect that bare graphite has on metal during casting. Metallographic examination of the grain size of ingots cast in coated and uncoated mold inserts, however, did not reveal any significant differences in grain size. The as-cast grain size was large and well developed in both cases with no apparent differences in the solidification pattern in the ingots or any indication that the problem of center line shrinkage had been altered or reduced. Apparently the thin coatings did not provide a sufficiently effective thermal barrier to produce any drastic change in the heat extraction capability of the graphite mold parts. With thicker coatings the heat extraction capability of the graphite mold parts could probably be reduced but at the expense of promoting chemical reactivity between coating and cast metal. Reducing the rate of heat extraction from the cast metal would cause the metal to remain in contact with the coating for a longer period at a higher temperature. This would result in deeper surface contamination of the metal, drastically affecting its quality and mechanical properties. It was therefore concluded, that the thin barrier coatings employed did not effectively alter the heat transfer characteristics of the graphite mold parts during casting of titanium. Thus, such coatings could not be expected to provide a feasible means for controlling as-cast grain size or center line shrinkage. The coatings of Gd_2O_3 and Y_2O_3 did, however, show that they could be employed effectively as barrier coatings on graphite and inhibit carbon pickup in titanium during casting.

CONCLUSIONS

1. Of the two spray coating methods employed to coat the experimental graphite mold inserts the plasma spray method appeared to produce the best quality and density of coating. Although all sprayed coatings are somewhat porous because the spraying process is unable to eliminate all the pores and joints between the sprayed particles, this porosity can be a very important physical characteristic of the coating because it provides the lower modulus of elasticity and the extra "flexibility" required to absorb the differential thermal expansion stresses and the thermal shock stresses. The mass and thermal conductivity of graphite are important factors controlling coating quality. The high conductivity of the graphite substrate quenches the sprayed molten particles rapidly, limiting flow and coating density. In addition, the density and microphysical characteristics of the coating deposit depend on the viscosity, specific heat, and thermal conductivity of the molten coating material. The thermal conductivity of the graphite substrate determines the flow of the deposited molten particles before solidification. If droplet viscosity is low the individual particles blend into one another which promotes the formation of dense coatings. When the liquid particles are more viscous, flow is inhibited and micropores do not fill. The oxyacetylene flame spray method is limited in the amount of heat that can be imparted to a particle traversing the hottest part of the flame cone. Particle velocities are in general from 100 to 150 ft/sec. Thus some particles may not be completely molten in passing through the flame even though they are of from 200 to 325 mesh in size. This situation can be better understood when the residence time of a particle in the flame and the transit time to a substrate of about 20 cm away is considered. The residence time of a particle is about 4.6 milliseconds and the transit time is about 1.6 milliseconds. Thus large particles with poor thermal conductivity and/or low hemispherical emissivity are unlikely to be completely molten on striking the substrate. This situation was observed in the case of the coatings of $MgO \cdot ZrO_2$ and $CaZrO_3$. Some of the particles appeared not to be completely molten upon impact but in

a plastic state from the flattened shape of these particles. In the plasma spray process the high temperatures created in the plasma arc potentially assures that all particles are in a molten state. The particle velocities in this spray process range from 1000 to 2000 ft/sec. Thus, the Gd_2O_3 and Y_2O_3 coatings produced by the high velocity and very fluid sprayed particles were less porous and of better quality than those produced by the oxyacetylene flame spray method.

Any material that will melt without decomposition can be sprayed by the arc plasma process. For materials that dissociate or decompose the coating will not be the same as the starting material. In the attempts to plasma spray thoria (ThO_2) it was found that the oxide decomposed in the plasma and resulted in a coating of poor quality and contaminated with reaction products both from the substrate and the atmosphere. Thus, dissociation, decomposition, or sublimation of materials during spray deposition are the greatest limitations of the plasma spray process.

Adhesion of the sprayed coatings on graphite was generally rather poor. The bond of the coating to the substrate and between the particles was almost entirely mechanical although chemical bonds were believed to exist in the case of plasma sprayed coatings of Gd_2O_3 and Y_2O_3 .

Feeding of fine powdered material to be sprayed by either the oxyacetylene or plasma spray methods is difficult. The powders must be free flowing so that the powders can be supplied into the spray gun at a uniform rate, otherwise intermittent excess and deficiency of spray particles causes difficulty in obtaining a uniform deposit while coarse particles may not be completely melted. It is therefore important to exercise control over the condition of the raw materials. This was found to be the case in attempting to spray the Gd_2O_3 and Y_2O_3 oxides in the as-received condition. These powders had to be presintered at about $1400^\circ C$, then crushed and wet classified to obtain a free flowing material of 200-325 mesh.

2. The coatings consisting of the solid solution of MgO and ZrO_2 were found to be insufficiently stable chemically to resist reduction by molten titanium. Therefore, this compound oxide was considered to be of no potential value as a barrier coating material on graphite mold parts for the casting of titanium.

3. The coatings composed of the true oxide compound $CaZrO_3$ appeared to exhibit considerable resistance to the highly reactive molten titanium under casting conditions. The presence of calcium and oxygen contamination detected in surface layers of the metal and the presence of acetylene gas noted after exposure of the casting experiments to the atmosphere indicated that some chemical attack of the oxide had occurred. The presence of acetylene gas indicated that calcium carbide CaC_2 had been formed which hydrolyzed in the presence of atmospheric moisture to produce the gas. This contamination appeared to be superficial and probably did not seriously affect the quality of the cast metal. Increases in oxygen content detected in both surface layers and in the bulk metal over that existing in the consumable electrode melting stock however is undesirable contamination which could be expected to have an adverse effect on the ductility and impact properties of titanium castings. Therefore, this oxide, although a seemingly effective barrier coating material for graphite molds, was not considered to be sufficiently stable chemically against molten titanium to qualify it as a potentially useful coating material for use under casting conditions.

4. The coatings composed of the rare earth oxide Gd_2O_3 , exhibited good chemical stability in contact with molten titanium and with the graphite substrate during casting. Some superficial reaction occurred in local areas between the coatings and the metal which caused wetting of the oxide and bonding to the metal in these areas. There was, however, no evidence of carbide formation or of any significant increases in the oxygen content of surface layers or in the bulk of the metal as a result of the slight superficial

reaction noted. There was no evidence of molten titanium soaking into or through the thickness of the coating, indicating that the oxide coatings were relatively dense and provided an effective barrier between cast metal and the graphite substrate. These oxide coatings were observed to remain intact and not crack during casting indicating good resistance to thermal stresses and to thermal shock under the severe temperature gradients generated by casting molten titanium against them. Due to mismatch in the respective coefficients of thermal expansion between the oxide coating and the graphite substrate, the coatings separated from the substrate since adhesion between them was relatively very weak. This circumstance limits the use of Gd_2O_3 coatings to a one-time application; however, from the protection that the graphite substrate received during casting it would be expected that the mold could be recoated and reused without any significant deterioration of mold surfaces or loss of mold dimensions.

5. The coatings consisting of the oxide Y_2O_3 exhibited the best overall chemical stability of any of the oxides examined. The ingots cast in graphite mold inserts coated with this oxide exhibited good surface characteristics of finish, luster, and freedom from bonding to the coating. The coatings separated readily from the cast metal. The coatings showed only a superficial film of metal on the side in contact with the cast ingots with no evidence of any local attack or penetration of the metal into the coating, which demonstrated the dense quality of the plasma sprayed coating. The coatings were observed to remain intact during casting with no cracks occurring from the severe thermal stresses and thermal shock prevailing under the casting conditions. The coatings separated readily from the graphite inserts due to the poor adhesion and to the mismatch in thermal expansion coefficients between the coatings and the graphite substrate.

There was no significant increase of oxygen content detected in either the surface layers or in the bulk of the cast titanium ingots, showing that the oxide coating had successfully resisted chemical attack by the molten titanium during casting.

Although a gradient in carbon content was detected in the surface layers of the cast ingots, this could not be attributed to any pickup of carbon from the coated graphite substrate since the oxide coating appeared to provide an effective barrier between molten titanium and the graphite substrate during casting. The gradient in carbon content was attributed to the pickup of carbon by the molten metal traversing uncoated graphite mold parts prior to its entry into the coated mold inserts and to the enrichment of surface layers in carbon content during the process of solidification. The evidence obtained demonstrated that the oxide Y_2O_3 plasma spray coated onto graphite mold substrates was potentially useful as a barrier coating to inhibit carbon pickup in titanium during casting.

6. The use of barrier coatings on graphite mold parts for altering the heat transfer characteristics of graphite during casting of titanium does not appear to be feasible. In order to obtain any significant improvement in the problem of center line shrinkage such coatings would necessarily have to be thicker than those employed in the experimental work reported here. Increasing the thickness of the coatings would promote chemical reactivity between molten metal and the coating since the temperatures at the interface of coating and metal would be maintained for a longer period. The success of the thin coatings obtained in this work is probably due to the ability of the graphite substrate to keep the temperature at the coating-molten metal interface below the point where significant reaction would be likely to occur.

REFERENCES

1. Chapin, E.J., U.S. Patent 2,977,219, Mar. 28, 1961
2. Chapin, E.J., and Friske, W.H., "A Metallurgical Evaluation of Refractory Compounds for Containing Molten Titanium, Part I—Oxides," NRL Report 4447, Nov. 1954
3. Chapin, E.J., Huber, R.W., and Lane, I.R., Jr., Foundry 87(No. 6):88-93 (June 1959)
4. Curtis, C.E., and Johnson, J.R., J. Am. Ceram. Soc. 40:15-19 (1957)

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) U.S. Naval Research Laboratory Washington, D.C. 20390		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
		2b. GROUP	
3. REPORT TITLE AN INVESTIGATION OF BARRIER COATINGS ON GRAPHITE MOLDS FOR CASTING TITANIUM			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) A final report on the problem.			
5. AUTHOR(S) (Last name, first name, initial) Reaves, W.A., and Chapin, E.J.			
6. REPORT DATE October 13, 1965		7a. TOTAL NO. OF PAGES 42	7b. NO. OF REFS 4
8a. CONTRACT OR GRANT NO. NRL Problem M01-17		9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6295	
b. PROJECT NO. RR 007-01-46-5419 and RR 011-03-41-6068		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c.			
d.			
10. AVAILABILITY/LIMITATION NOTICES Unlimited availability - Available at CFSTI -			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Dept. of the Navy (Office of Naval Research)	
13. ABSTRACT <p>The feasibility of employing barrier coatings on graphite molds for inhibiting carbon pickup in titanium and for possible control of solidification shrinkage during casting was investigated. Oxide coating materials whose known thermal properties appeared to be potentially useful were selected. These oxides included: a solid solution of MgO and ZrO₂; a true oxide compound, CaZrO₃; and two single oxides, Gd₂O₃ and Y₂O₃. The compound oxides were applied to specially cleaned ATJ grade graphite-mold hollow-cylinder inserts by an oxy-acetylene flame spray method, and the single oxides were applied in similar inserts by a plasma spray technique. Coatings composed of the solid solution of MgO and ZrO₂ were attacked by molten titanium during casting with some reduction of the MgO phase to metal and contamination of the cast metal with oxygen. These coatings were considered to be insufficiently stable against molten titanium. Coatings composed of the zirconate CaZrO₃ were found to be fairly resistant to molten titanium, however, sufficient reaction occurred between metal and coating to introduce undesirable contaminants into the cast metal. These coatings were also considered to be insufficiently resistant under casting conditions to qualify as satisfactory barrier coatings. The rare earth oxide Gd₂O₃ was found to be resistant to molten titanium during casting and to provide a good barrier between the graphite mold substrate and the cast metal, with no significant increases in either oxygen or carbon content. The oxide Y₂O₃ was found to have the best characteristics as a barrier coating. This oxide did not appear to be wetted by the molten metal cast against it nor to introduce any significant amounts of contaminants into the cast metal.</p> <p>The barrier coatings were not effective in altering the high heat extraction capability of the graphite substrate and thus did not provide any improvement in solidification center line shrinkage.</p>			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Titanium Casting Coatings Flame spraying Castings Holding materials						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.
- 2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.
- 2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.
3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.
4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.
5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.
6. **REPORT DATE:** Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.
- 7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.
- 7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.
- 8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.
- 8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.
- 9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.
- 9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).
10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.
12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.
13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.