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MANUFACTURING PROCESS FOR PREMIUM QUALITY TITANIUM CASTING

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Manufacturing Technology Division
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FOREWORD

This Final Technical Report covers all work performed under Contract AF33(615)-2557 from 15 February 1966 to 15 April 1966. The manuscript was released by the authors in May 1966 for publication as an RTD Technical Report.

This contract with Mitron Research and Development Corporation, Waltham, Massachusetts, was accomplished under the technical direction of Lt. James D. Gerber of the Metallurgical Processing Branch (MATB), Manufacturing Technology Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, and was initiated under Manufacturing Methods Project 8-298, "Manufacturing Process for Premium Quality Titanium Castings."

This program was supervised by Dr. R. A. Rosenberg, Director of Mitron's Applied Sciences Division. Messers. K. J. Pulkonik, R. D. Regan, and W. E. Lee cooperated in the research and in the preparation of this report.

This project has been accomplished as a part of the Air Force Manufacturing Methods program, the primary object of which is to develop on a timely basis manufacturing processes, techniques, and equipment for use in economical production of USAF materials and components. The program encompasses the following technical areas:

Metallurgy - Rolling, Forging, Extruding, Casting, Fiber, Powder.
Chemical - Propellant, Coating, Ceramic, Graphite, Nonmetallics.
Fabrication - Forming, Material Removal, Joining, Components.
Electronics - Solid State, Materials and Special Techniques, Thermionics.

Suggestions concerning additional Manufacturing Methods development required on this or other subjects will be appreciated.

This Final Technical Report has been reviewed and is approved.

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ABSTRACT

A chemically inert binder for producing water soluble rammed graphite molds and cores for producing titanium castings has been developed and tested under commercial foundry conditions. Mechanical property tests, chemical analyses, and the quality of the castings produced demonstrated the applicability of the developed process for producing premium quality titanium castings.

Although several methods of applying the non-reactive flux to molds and cores were investigated, the most effective means was to incorporate the flux in the mold as one of the constituents. By varying mold and core processing times and composition, a simplified mold processing technique was developed for producing a chemically inert, water soluble mold and core material. The water solubility of the mold system permits the casting of intricately cored shapes not currently attempted. Intricate castings having a finish weight of 5-25 pounds were cast successfully utilizing this chemically inert binder.

The feasibility of casting titanium in zircon sand molds using the non-reactive flux as a binder, was demonstrated. No gross reaction between the titanium and the shell mold was evidenced.

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I. INTRODUCTION

The potential for application of titanium and titanium alloys to commercial and aerospace usage has yet to be fully realized. Titanium is a very attractive material for a great number of applications because of its high strength to weight ratio, good fatigue resistance, and extraordinary immunity to corrosive environments over a large temperature range when compared with the more commonly employed metals. However, when heated above 1200°F, titanium becomes highly reactive requiring the presence of an inert environment to avoid deleterious modification of its properties. Molten titanium is particularly troublesome because it approaches being the universal solvent, dissolving or reacting with almost every element or compound it contacts.

Many fabrication techniques require heating titanium above 1200°F. At these temperatures, proper precautionary measures must be employed to prevent contamination of the titanium by atmospheric elements. This complicates the use of many processing techniques as either an inert or vacuum environment must be maintained requiring specially designed equipment. The problem of contamination is of paramount importance in casting and welding, both of which require heating of titanium above its melting point. These factors contribute to the relatively high cost of titanium materials and end products and restrict the application of titanium to a small percentage of its potential.

Titanium castings are expensive to produce because of the costly procedures required for melting and producing molds. Consumable electrode melting in vacuum is inherently a costly operation. Titanium reacts with all known refractory mold materials to some degree. To date the most satisfactory mold material is graphite though some dissolutions occurs. Machined graphite molds have limited life and are very costly to produce, while rammed graphite molds are considerably more expensive to produce than rammed sand molds used for steel and other metal castings. However, cast titanium parts have appeal because of their high strength-to-weight ratios and their good corrosion resistance.

MITRON proposed to improve current titanium molding practice by application of a proprietary "flux" material which is essentially non-reactive with titanium. As the MITRON flux is essentially non-reactive, it differs from conventional fluxes which typically are formulated to promote specific reactions between it and the material being processed. The objectives of the program were to improve the quality of titanium castings, to substantially reduce the cost of producing titanium castings, to allow more complex shapes to be cast commercially and to permit the adoption of more commonly practiced molding techniques for the production of titanium castings. These modifications were based on the incorporation of the non-reactive flux material as a mold coating and/or a constituent in mold mixtures for titanium castings.

The nonreactivity of the flux and its applicability to titanium processing was demonstrated under contracts AF33(615)-1384(27) and N140-(131)-74050B(X).(28) The results of both investigations definitely established that the flux is not chemically reactive with molten titanium. Although both programs were welding investigations, the use of the flux in conjunction with casting was a logical extension.

The first phase of the casting program was the use of the flux as a mold coating. The presence of a flux mold coating will act as a barrier to prevent contamination of the molten metal by deleterious elements present in the mold. The effectiveness was evaluated for permanent metal and graphite molds, and also for rammed graphite mold of the type presently employed in the commercial production of titanium castings. The second phase of the program was the development of a rammed graphite mold composition employing the flux as a binder material for a graphite aggregate. The program also included limited study of flux applicability to zircon and graphite shell molding procedures, and as a mold wash constituent for rammed graphite molds.

Throughout the course of the program, promising laboratory developments were further evaluated under actual foundry conditions at Oregon Metallurgical Corporation, Albany, Oregon.

II. HISTORY OF THE DEVELOPMENT OF TITANIUM FOUNDRY PRACTICE

Though titanium was discovered in 1790, it was not until 1945 that elemental titanium was found to be ductile instead of brittle as previously assumed. Recognizing the extreme usefulness of titanium, an extensive processing development effort was launched by government and industry. The effort in casting development was split primarily in two directions--the development of melting techniques and the development of molding techniques. To fully appreciate the magnitude and complexity of the problems of obtaining premium quality titanium castings, a summary of the work performed by other investigators to develop suitable melting and molding systems is presented.

A. DEVELOPMENT OF MELTING TECHNIQUES

The development of melting techniques has been hampered and restricted by the high reactivity of molten titanium with almost all materials. One of the first published melting techniques (1) employed a permanent electrode in a controlled atmosphere avoiding titanium contamination by restricting contact of the molten titanium to powdered titanium. This technique was employed solely for laboratory applications. Subsequent developmental work for titanium melting attempted to either modify existing melting techniques or develop new techniques to avoid the problem of contamination.

Induction Melting

Much effort has been expended in the modification of induction melting for use with titanium. This system offers many advantages including single stage melting, uniformity of temperature and composition within the melt, and the ability to melt scrap, ingot or sponge together without prior electrode fabrication. However, a crucible must be employed, and this is the main problem. As early as 1949, researchers at DuPont(2) reported the development of a unit for induction melting and casting 10 pound ingots of titanium. The first crucibles used were machined from high purity graphite, but the molten titanium was able to flow through the pores in this material. Satisfactory results were obtained with denser, less pure graphite (CS). Ingots obtained using this process contained from 0.4 to 0.7% carbon, and it appears that the deleterious effects associated with the high carbon levels were not clearly recognized by early investigators.

A very similar program was conducted by Westinghouse, (3) but the emphasis was on finding a suitable refractory crucible material for use with induction melting. Of the refractories investigated, thoria was considered the most successful. A variety of titanium alloys were prepared by vacuum induction melting in thoria crucibles and the results were described as "fairly satisfactory providing the metal was not heated too far above the melting point". Results for thoria were not considered successful enough to warrant continued evaluation as a crucible material for induction melting of titanium.

In 1950 DuPont (4) reported that they had scaled up their induction melting apparatus for the production 650 pound ingots. In 1951, the Titanium Alloy Manufacturing Division of the National Lead Company (5) reported that it was using vacuum induction melting in a graphite crucible to produce 25 pound ingots of titanium. Much of the early work utilizing graphite crucibles was negated when it was determined that the carbon content of the ingot produced was much too high, resulting in a deleterious effect on the properties of the titanium.

In 1956, Watertown Arsenal (6, 7, 8) reported on a modified induction melting technique which minimized contact between the molten titanium and the graphite crucible. A CS grade graphite crucible was modified by putting a solid titanium skull in the bottom of the crucible. The lowest turn of the induction coil was raised above the level of the skull reducing the energy input to the skull to a minimum. A high power input rapidly melts the titanium, and the vigorous stirring action maintains a very steep meniscus. The metal is molten for a short time and is then tilt poured into a graphite mold. This melting technique results in a significant reduction in carbon pickup. Carbon content of the sponge charge was .025%; carbon in an ingot melted under optimum conditions was 0.066%. Other ingots analyzed 0.11 and 0.15% carbon which is well below that reported in other investigations. This carbon content is acceptable for a limited number of titanium castings, but in general is much too high.

More recently (9) cold-wall crucibles for induction melting were studied. In general, results were unsuccessful. Of the melting attempts made, the most encouraging results were obtained using a BeO coated two segment crucible (segmented to inhibit the effects from the induction field on the crucible). Recommendations stated segmented crucibles offered little commercial potential because of problems of electrical shorting, mechanical difficulties and electrical isolation problems.

To date, the unsuccessful quest for a suitable crucible material or suitable procedure modification has precluded employment of induction melting for the production of commercial titanium castings.

Permanent Electrode Arc Melting

As early as 1949, permanent electrode arc melting was used extensively for the production of experimental titanium alloy ingots.(10) Battelle reported the development of a unit capable of melting 5 pound ingots.

The first permanent electrode skull-melting furnance for casting titanium was built by Rem-Cru Titanium, Inc. (now Crucible Steel Co.) (11, 12, 13). The unit consisted essentially of a tungsten-tipped electrode and a machined graphite crucible with a hole in the base which could be plugged. Casting was accomplished by increasing the power to bore a hole through the molten metal and the plug in the base of the skull. The limiting factor on the amount of metal which can be poured by this technique is the depth of the molten pool which can be pierced by the arc to initiate the pouring cycle. This technique produced titanium castings of excellent purity with the exception of tungsten inclusions, but obviously had limitations which would prevent its application to casting titanium on a production basis.

To circumvent the problem of reactivity of molten titanium with all known crucible materials, several attempts have been made to eliminate the crucible from the melting operation. Drip melting (17) of titanium has been attempted. The principle of the drip melting process is to vertically feed a bar of the material to be melted into an induction coil so that the end is melted off continuously.

"Auto-crucible" is another melting technique developed not requiring a crucible. It consists of holding a flat induction coil near the surface of a horizontal block of the metal to be melted. The intense eddy currents directly under the coil build up a liquid pool which is forced toward the center of the induction coil.

A third melting technique which does not require a crucible is levitation melting. (18) The principle of this process is to suspend metals in an electro-magnetic field produced by induction coils which surround but do not touch the melt. All of the described processes have been used for melting titanium. Because of the many difficulties associated with these processes, their usefulness has been limited to melting small quantities of titanium for laboratory application.

Vacuum Consumable Electrode Melting

In the early 1950's, the Bureau of Mines Station in Albany, Oregon developed arc melting practices for producing zirconium ingot, and as a result of this work Watertown Arsenal (13) funded a program in 1953 for the development of a skull melting furnace that used a consumable electrode. At this time, four separate permanent electrode units were in operation, but none were capable of producing a sufficiently large quantity of molten titanium to produce a reasonable size casting.

The program to develop consumable electrode skull-casting techniques was extremely successful. The main components of the skull castings furnace consist of an electrode and a water cooled copper crucible in a vacuum chamber. The water cooled copper crucible is charged with a previously produced skull and a quantity of scrap prior to evacuating the chamber. A diffuse, nonconsuming arc is struck at approximately 2500 amperes. The current is then raised to the operating level of approximately 1000 amperes per inch of diameter of the crucible and the melting begins immediately. Melting current is maintained at the desired level until the electrode is consumed and the molten pool adequately superheated. The arc is then raised to the maximum power level to melt through the base of the skull for a bottom pour, or the arc is extinguished, the electrode extracted and the crucible tilt poured.

In 1955, (14) it was reported that titanium castings of up to 100 pounds had been produced by this technique. This weight includes risers and ingates and represents a significant quantity of metal, because titanium castings require extensive risering. Although a completely acceptable technique had not yet been developed, the results were extremely encouraging and a definite solution for producing cast titanium parts was taking shape.

The most serious problems encountered for the bottom pour apparatus were associated with either removing or inserting the stopper from the tap hole in the base of the crucible.(15) In some cases, the stopper stuck to the base of the skull and could not be removed; also if the thickness of the skull exceeded 1 inch, there was not sufficient power to melt through the skull to pour. In many instances, a single heat was poured because drips from the tap hole prevented the stopper from being reseated properly. These problems resulted in the investigation and development of over-the-lip pouring in conjunction with consumable electrode melting.

The intial over-the-lip unit was very successful. A skull could be used at least 10 times before trimming was necessary, rapid recycling was possible and the developed techniques eliminated the problems associated with the bottom pour apparatus. The unit was scaled up to take a 165 pound charge with an 80 to 90 pound pour weight. A total cycle time of 2 hours was required for a heat with only 15 minutes required for melting time.

The high melting rate (9 lb./min.) and high power input insured a large super heated volume of titanium. In some cases, over 60% of the charge was molten. A number of castings were poured using the consumable electrode over-the-lip technique and the results were very satisfactory. The metal was free from contamination, had excellent fluidity, and the process in general was acceptable from an industrial viewpoint. Although this work was completed late in 1955, it was not until 1958 than an Air Force program was initiated (16) to develop a commercially feasible process for the production of titanium castings on a non-proprietary basis. This program, with Boeing as the prime contractor was aimed at developing titanium alloy castings for aircraft application. Oregon Metallurgical Corporation was seclected as subcontractor and conducted the research and development work. The equipment used for this program was patterned after the Bureau of Mines furnace with certain modifications and improvements in the mechanism and controls. The furnaces were equipped for either centrifugal or static casting. The techniques established during this investigation are essentially the same as those currently in use at Oremet, the only organization currently producing large titanium castings commercially.

The consumable electrode skull melting technique is currently the only acceptable method of melting titanium on a commercial basis. Although it is used, it has been described as expedient and has a great many disadvantages. It is a difficult process to control; the molten pool has a nonuniform temperature distribution and cools rapidly when the arc is extinguished. Alloys melted by this technique are not completely homogeneous. High power inputs are required and the yield is low. The process is also dangerous because the high intensity arc can rapidly penetrate the cooling coils causing an explosion. Centrifugal casting is generally used to rapidly fill the graphite molds currently in use. The lack of precise superheat control, the rapid heat extraction of the graphite molds and residual mold gas dictate this requirement, although static castings can be poured.

B. DEVELOPMENT OF CRUCIBLE MATERIALS

Initially the principal crucible material used for containing molten titanium was graphite, but as was pointed out, there is appreciable carbon contamination from the crucible which is slowly dissolved by the titanium. The extreme reactivity of molten titanium has resulted in extensive research programs in an attempt to find a material which is not reactive with titanium. All of the known refractories have been investigated and attempts have been made to produce new or modified refractory compounds specifically for containing molten titanium. As early as 1948, Brace(19) reported that of the oxides investigated, only thoria (ThO_2) offered some promise, but this material was not regarded as inert to molten titanium. To date, the situation has not changed. No ideal crucible material has been found. Materials which cannot be used, however, are well documented.

In June 1950, Battelle(20) reported the results of an extensive investigation which included the following general categories of crucible materials: metals, carbon and carbides, oxides, nitrides, sulphides, borides and silicides. The results established that with the possible exception of zirconia, all of the investigated materials react with, or are appreciably soluble in molten titanium. None of the materials investigated offered more promise than graphite. Even the zirconia, which was not wetted by the titanium, produced a high hardness as a result of the increased oxygen content, but the zirconium content of the melt was relatively low. As a result, attempts were made at reusing the oxygen depleted zirconia crucible, but the crucibles failed as the ingot cooled. No suitable crucible materials were established.

Several years after the Battelle report was published, a program with Armour Research Foundation(21) was initiated by the Air Force to study methods of producing new refractory materials which would be sufficiently inert to titanium. Two possible directions were suggested: the development of a nonoxide, noncarbide, nonnitride refractory or the development of a means of stabilizing a refractory containing some of these normally objectionable ingredients.

Theoretically, it was determined that the most promising series of complex oxyfluorides would be those containing relatively large amounts of zirconium. Attempts were made to prepare several synthetic as well as new oxyfluoride compounds. Although fluoride refractories with softening points over 1800°C were prepared, they were deficient in fluorine and were not a completely stable or stoichiometric product. The lack of stability of the refractories reduced their resistance to molten titanium, but several of the complex oxyfluoride refractories were better crucible materials for titanium than zirconia, although hardness surveys indicated contamination was excessive. The developed materials were not suitable for industrial application, and it appears that no further research was performed in this area.

Recognizing the fact that titanium could be expected to react to some degree with any known material, Alfred University,(22) under the supervision of Watertown Arsenal, investigated the possibility of intermetallic materials as crucibles for titanium. Metals which could be useful as alloying elements with titanium were selected because, if a reaction occurred during the melting cycle, the titanium would not be adversely affected. Of the materials tested,

Mo_3Al offered the most potential. Crucibles of this compound contributed only a small and constant amount of molybdenum and aluminum to the titanium melt. Although this work appeared to be successful, nothing further has been reported in this area.

In November and December of 1954 and January 1955, three reports were published by Chapin and Fiske of the Naval Research Laboratory. The reports were entitled "A Metallurgical Evaluation of Refractory Compounds for Containing Molten Titanium" and were divided as follows:

Part I:	Oxides (23)
Part II:	Carbon, Graphite and Carbides (24)
Part III:	Borides and Sulphides (25)

Although many of the materials investigated were known to react with molten titanium, the purpose of this study was to re-examine some of the more promising materials in a comprehensive manner. Alumina, beryllia, thoria, stabilized zirconia, gadolinia, carbon, graphite, the monocarbides of Ti, Zr, Nb, Vi, Ta and W, borides of Ti, Zr and Cr and CeS were studied.

It was generally concluded from the Naval Research Laboratory investigation that all of the investigated materials lacked the desirable inertness since they all reacted with titanium to some degree. The melts were generally contaminated by reaction products which caused hardness increases, embrittlement, and the presence of duplex-microstructures.

Weber et al. (26) completed a research program in 1956 which appears to be the last published effort to develop a crucible material for titanium. Based upon the result of previous investigations as well as free energy of formation and heat of formation data for zirconia, the most promising system appeared to be stabilized zirconia. An oxygen deficient zirconia crucible was produced by adding titanium metal to zirconia and sintering. This material was claimed to be thermally stable and inert to attack by molten titanium with two qualifying conditions rendering the developed material impractical for industrial application; super heating and/or long soaking times resulted in contamination.

The development of skull melting techniques to a degree which was and is commercially applicable, virtually ended further attempts to develop a suitable crucible material for titanium. Nevertheless, if a suitable crucible material were developed, it would have a profound effect on the titanium industry and the degree of application of titanium to commercial products and equipment.

C. MOLD MATERIALS

Permanent Molds - Metal

Metal molds for production of titanium castings have been found to be satisfactory only for the simplest of shapes (16, 29). Any restriction of contraction during cooling of the titanium will cause rupturing of the restricted areas. Steel,(30) copper, aluminum(29) and bronze(31) molds have been used. The copper and aluminum molds produced very smooth surface finishes, but the results were not reproducible because of the severe chilling effect or high heat extraction of the mold. If the titanium is superheated to avoid folds on the casting surface, the titanium will dissolve the mold surface, particularly where the pour impinges on the mold. This was found to be true for both copper and aluminum.

The dissolution of the mold surface did not appear to be a problem for the steel molds used in conjunction with the Impel process developed by TMCA. It was reported that as many as 100 parts could be produced from a single mold. Since one of the major objections to the permanent mold is economic, provided the casting is simple enough to apply this technique, a considerable decrease in price is realized as a result of the extended mold life. Any casting which has a re-entrant angle, a complex curved surface or a cored section cannot be made by a completely permanent mold. In many instances, the mold would have to be destroyed to remove the casting.

Permanent Molds - Machined Graphite

During all stages of titanium casting development, machined graphite molds have been employed. Although reasonable quality castings can be produced, the molds have essentially the same limitations described for metal molds. They are expensive, although not as expensive as metal molds, produce laps and rippled casting surface finishes, and are subject to erosion or tearing. The high hot strength of titanium can cause cracking or crushing of mold corners at re-entrant angles. Mold life can be extended by the use of replaceable mold inserts in the areas subject to damage, however, machined graphite molds with adequate draft, simply shaped with no re-entrant angles, and designed to take expendable inserts in critical areas have a life of about 50 castings. An added problem which results from the use of graphite molds is carbon contamination. The maximum depth of surface contamination in castings from machined graphite molds is approximately 0.010 inch/inch of section thickness. Although this contamination is not serious when the cast part is to be used in a non-critical area such as chemical processing equipment, it does represent a serious problem for the application of titanium castings in the aerospace industries where quality and reliability are necessary.

Currently, a limited number of machined graphite molds are being used by Oregon Metallurgical Corp. to produce castings on a commercial basis, but the majority of titanium castings are made in rammed graphite molds.

In an attempt to reduce or inhibit carbon pickup from graphite molds, researchers at NRL(32) investigated barrier coatings. In addition to the problem of surface contamination, the high heat extraction of graphite causes rapid solidification and this interferes with adequate feeding of the casting during solidification. Gross porosity and centerline shrinkage are frequently found in the heavy sections of titanium castings which are not heavily risered. In an attempt to remedy the problem of carbon contamination and the steep thermal gradient at the mold-metal interface, various oxide coating materials were investigated. Various oxide barrier coatings did not alter the heat transfer from the molten titanium to the graphite mold, but Gd_2O_3 and Y_2O_3 did exhibit good chemical stability in contact with molten titanium with the Y_2O_3 being the better of the two. There was no significant increase in oxygen content of the titanium in contact with the Y_2O_3, and the coating did prevent or inhibit carbon contamination.

In order to reduce center line shrinkage, a very thick barrier coating is necessary, but increasing the thickness of the coating promotes chemical attack because the interfacial temperature at the coating-metal interface is maintained for a longer period of time. The thin coatings used reduced carbon pick-up, but not center line shrinkage because the graphite removed the heat from the casting rapidly enough to keep the coating-molten metal interface temperature below the point where a significant reaction would occur.

Although the Y_2O_3 coating is capable of reducing or eliminating carbon contamination, its application to producing titanium casting is not very practical. Yttria is rare, expensive and can be applied only by plasma spray techniques. The coating is readily separated from the mold and this would require a fresh coating for each casting.

Expendable Molds - Rammed Graphite

The majority of commercial titanium castings made to date have been poured in rammed graphite molds. Since no refractories are completely inert to molten titanium, the choice of mold materials is obviously limited to the material which will cause the minimum contamination in contact with the molten metal. Since machined graphite molds yielded reasonable quality castings, the use of graphite in a granular form would circumvent the disadvantages of the machined molds as well as make the material adaptable to common foundry techniques. An extensive program to investigate granular graphite and bonding agents was carried out by Feild(33,34) at DuPont. The results of this work were published in 1956. After an extensive evaluation of organic and inorganic binder materials, the following composition was determined to be the most suitable:

53%	electric furnance graphite powder (-20 + 100 mesh)
10%	dry corn starch
10%	pulverized pitch
8%	carbonaceous cement
1%	surface-active agent (Duponol G fatty alcohol amine sulphate)
18%	water

Mold processing consisted of air drying from 8 to 72 hours followed by oven drying gradually increasing the temperature from 140 to 250°F over a 48-hour period. The mold was then fired at 1200 to 1650° F for 1 to 2 hours enclosed in a steel box with a graphite lid to prevent oxidation during firing. Although the 18% water content was high, it was necessary to reduce mold spalling and cracking. Molds made by this process were hard and permeable and produced reasonable quality titanium castings.

Subsequent literature referring to a continuation of this effort at Frankford Arsenal (35,36) reported on a comprehensive study of some of the variables of graphite material on its foundry characteristics. It was determined that permeability, strength, thermal conductivity, surface finish and shrinkage of graphite molds can be varied by controlling water content and molding pressure. Satisfactory molds were produced with a water content of 6%. This work provided a starting point for the development of a rammed-graphite mold mixture suitable for producing titanium castings. The development of rammed graphite molds did not achieve a level suitable for commercial application until a comprehensive development program sponsored by the Air Force was undertaken by Boeing and Oremet (16). Numerous combinations of unused graphite, reclaimed graphite, laundry starch, corn flour, carbonaceous cement, raw linseed oil, water, Duponal G, petroleum calcined coke, coal calcined coke, petroleum raw coke, coke flour, amino-aldehyde, urea and phenoformaldehyde were evaluated. In addition, numerous types of graphite and grain sizes as well as a variety of processing cycles were investigated. The following composition was determined to be optimum:

Graphite Powder	70%
Laundry Starch	5
Black Foundry Pitch	10
Carbonaceous Cement	8
Water	7

The mold processing technique established consists of:

1. air dry for 16 hours
2. oven dry at 200° F for 24 hours
3. pack mold in steel box and cover with 4 inches of graphite
4. place packed molds in furnace at 1200° F, raise temperature to 1650° F, hold 3 hours
5. Cool in furnace to 1100° F
6. remove and unpack when molds reach 700° F
7. store at 250° F until about 2 hours before assembly

There are variations in this processing technique, but they do not deviate to any great degree. Deviations are related primarily to the size of the molds being processed. Core processing also differs slightly. Cores are usually given a longer high temperature bake to insure the complete removal of all volatiles.

Although this composition and processing of rammed graphite molds has been extensively employed for commercial castings, limitations restrict the use of this process.(37) The primary limitation is core knockout. Although the expendable molds do not produce hot tearing in titanium castings, the fired molds and cores are extremely hard and strong. Cores must be chipped out and this can be accomplished in a short time, only for the simple shapes. Any casting which has a small opening through which a large core must be removed, cannot be made economically because core removal times are extreme. The geometry of cored castings is limited to those which are accessible for removal. This is a serious limitation because it eliminates a large number of castings from consideration. In addition to core removal, the rammed graphite mold presents a problem in dimensional control because the mold shrinkage resulting from the high temperature processing cycle is difficult to control. This shrinkage causes mold cracking particularly when the mold has thick and thin sections which shrink at a different rate. Mold processing is lengthy and costly.

Recently the results of a study to develop a more practical mold composition were published by the Bureau of Mines.(38) The blend consists of powdered graphite, cornstarch, dextrose, cereal binder, linseed oil, and carbowax - 4000. The mixture is completely waterfree. The facts that the mix is waterfree and applicable to core blowing or hand ramming appear to be the only advantages. The composition must be mulled in a carbon dioxide atmosphere, cured at 93° C (up to 300 hours are required for large molds), and baked in gradual 100° C stages up to 960° C. Satisfactory titanium castings could be produced only with some compromise in surface finish.

In essence, rammed graphite molds are commercially applicable for the production of titanium castings because of the limited reactivity of graphite with titanium. The graphite aggregate, binder system and the processing techniques developed are suitable for the production of titanium castings, but limitations with the present system result in high cost and limited application as a result of the difficulties associated with core removal. This was essentially the state of development of the rammed graphite mold system when MITRON proposed the incorporation of its nonreactive flux material.

III. EXPERIMENTAL PROGRAM

During the early stages of this program, prior to evaluation under commercial foundry conditions, titanium was melted in a vacuum induction furnace using a graphite crucible. Though carbon contamination was introduced by the graphite crucibles, this melting technique was economically satisfactory for evaluating and eliminating many mold processing variables and experimental mold compositions prior to evaluation of the most promising systems under actual commercial foundry conditions where vacuum consumable electrode melting was employed. Figure 1 illustrates a typical vacuum induction-melting set-up with molds positioned on the turntable with a pouring cup placed over each mold. In this manner, several experimental mold systems could be evaluated for each heat poured.

The crucibles were machined from AUC grade graphite having a low ash content, and had a maximum capacity of approximately 30 lbs. of titanium. It should be noted again that though carbon was picked up in these melts due to reaction with the graphite crucible, the ready availability of this melting equipment permitted the evaluation and elimination of many variables, because examination of the surface condition of castings reflected any catastrophic reaction between titanium and the mold ingredients.

Mold Design

The three mold configurations employed in the laboratory phase of this program were used to evaluate flux coatings and associated variables for coated molds of machined graphite and steel. The three mold configurations, Figures 2, 3, and 4 have somewhat different functions. The rectangular test step mold in Figure 2 is used for evaluating the effectiveness of mold coatings and/or flux-mold mixtures in reducing mold-titanium reactions as a function of casting thickness. Since this mold is directly fed with molten metal, mechanical erosion of mold coatings by the molten metal can be evaluated. The cylindrical test step mold exhibited in Figure 3 is used for evaluating the effectiveness of gating and risering for two or more solid cylinders for each mold material used. The top section of the casting is a riser. The flat plate test mold illustrated in Figure 4 is used for evaluating the fluidity of molten titanium as a function of mold coating thickness.

Mold Materials

Molds were machined from a high density reactor grade (ATJ) graphite in the three mold configurations described. A rectangular step mold and cylindrical step mold were also machined from a low carbon mild steel (C-1018). The specific geometry of the steel molds was altered slightly because of machining difficulty, but this alteration did not reduce the significance of the results obtained with these molds, or their comparability to the graphite molds.

Flux Mold Coatings

The initial effort to improve the quality of titanium castings was in the application of the nonreactive flux as a mold coating. This phase of the program evaluated the effects of flux coatings on permanent steel molds, permanent machined graphite molds, rammed graphite molds, and zircon and graphite

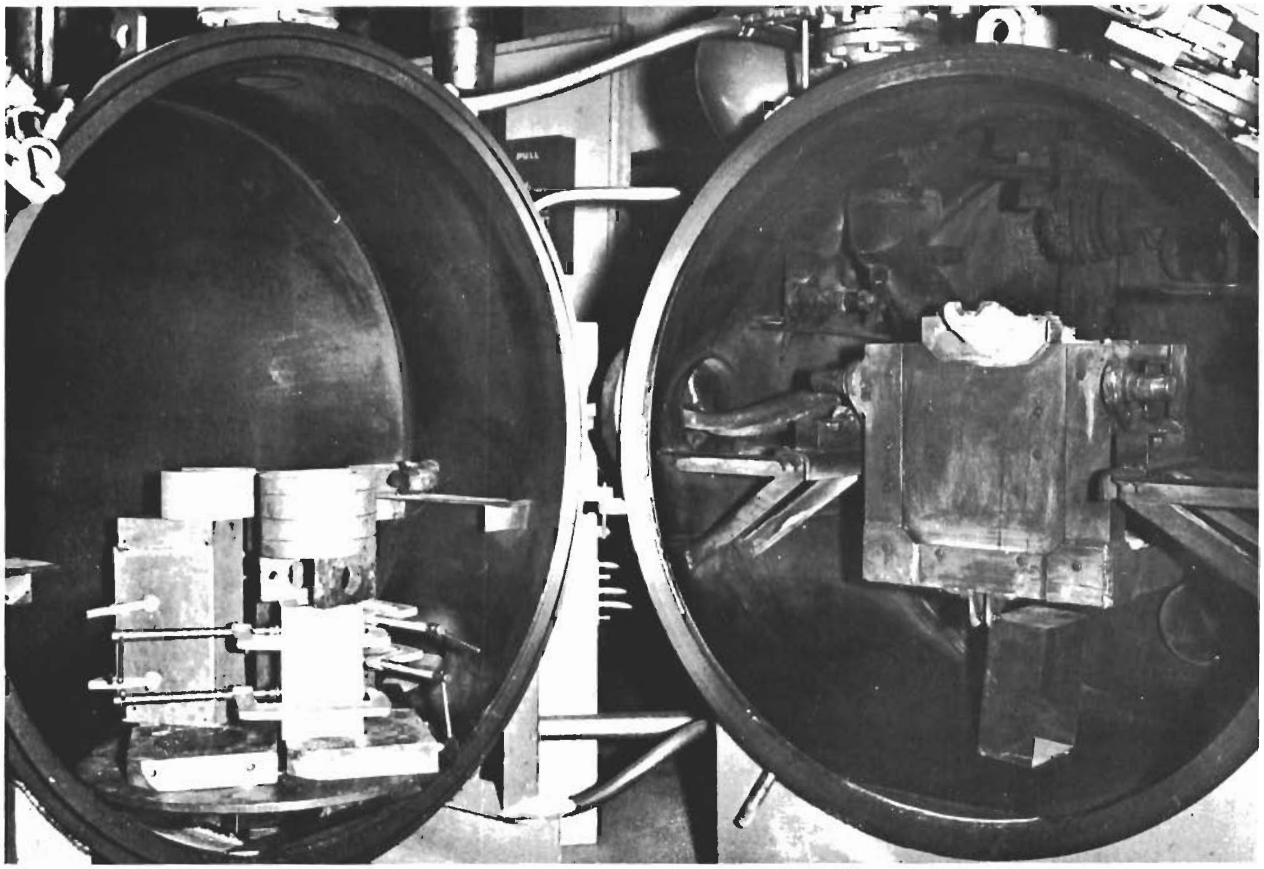


Figure 1 - Vacuum Induction Equipment When Open
Exhibiting Molds and Melting Equipment

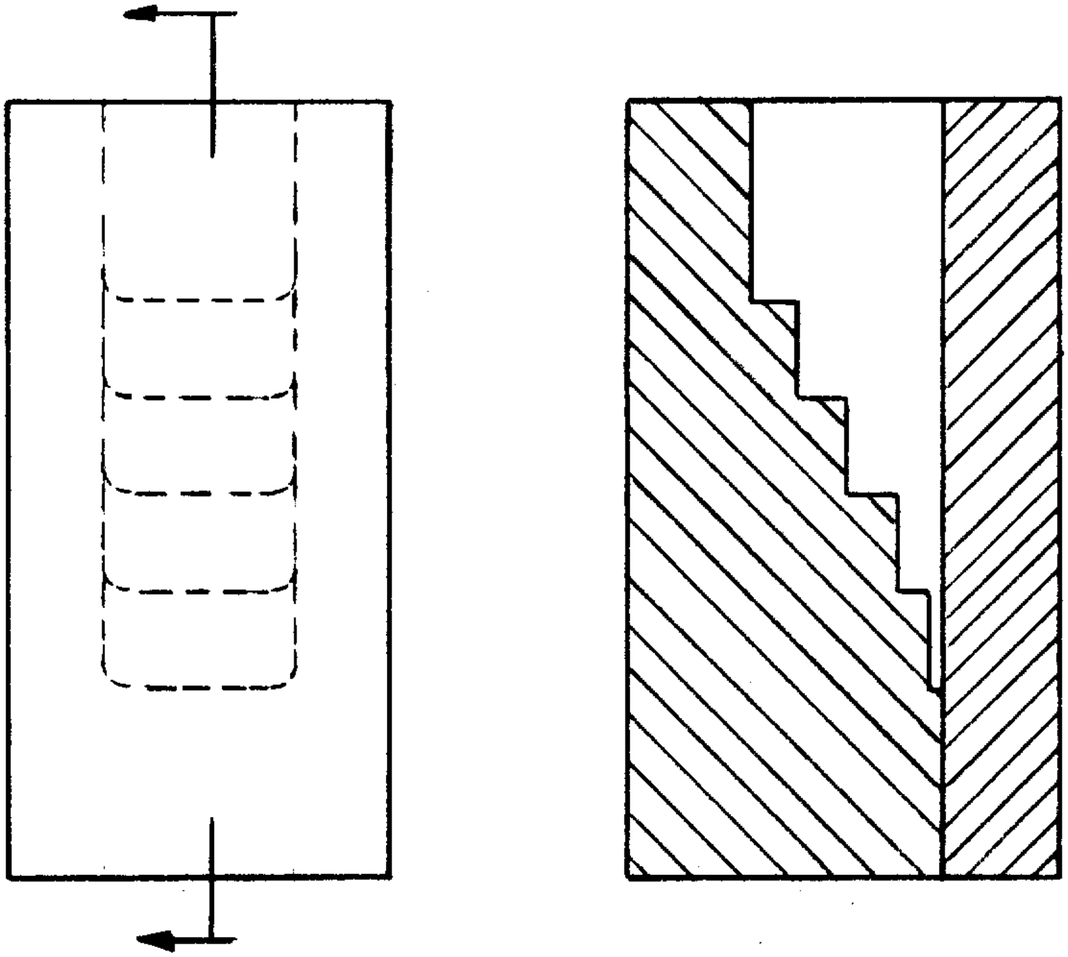


Figure 2 - Test Step Mold Schematic

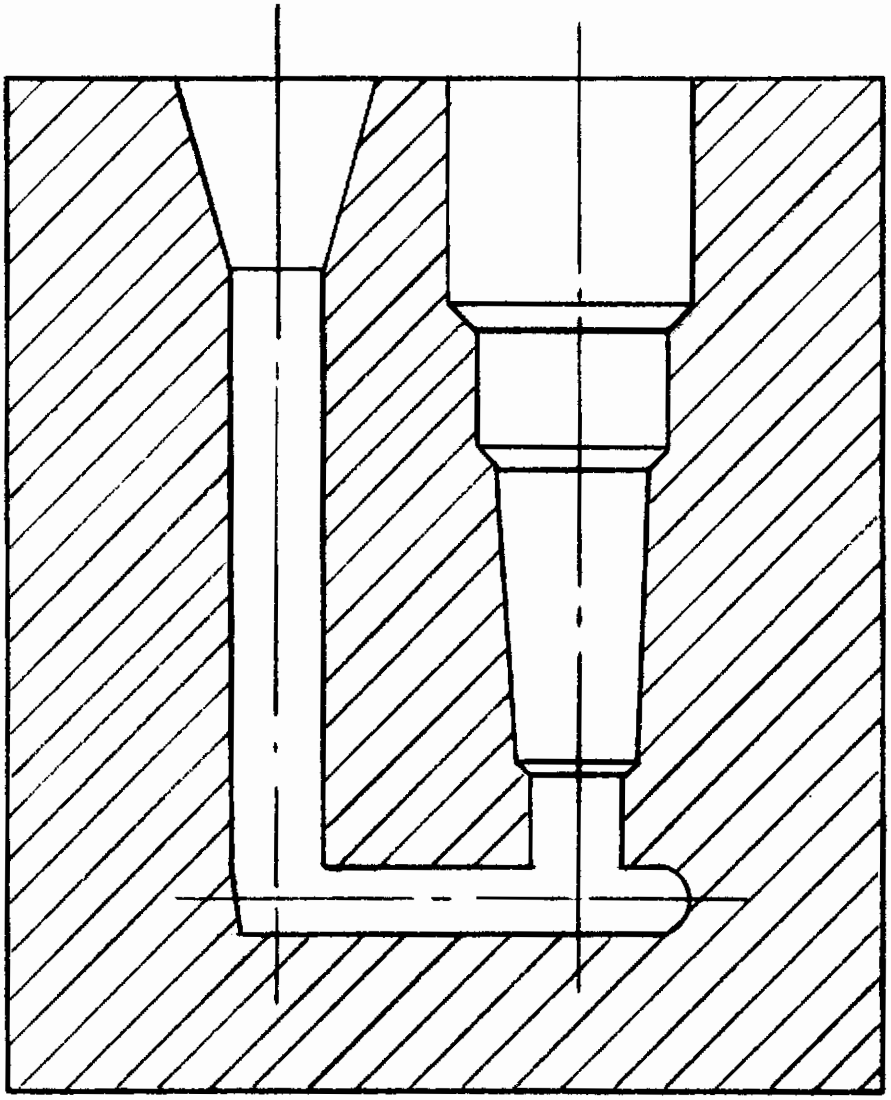


Figure 3 - Test Mold to Determine Effect of Gating & Risering

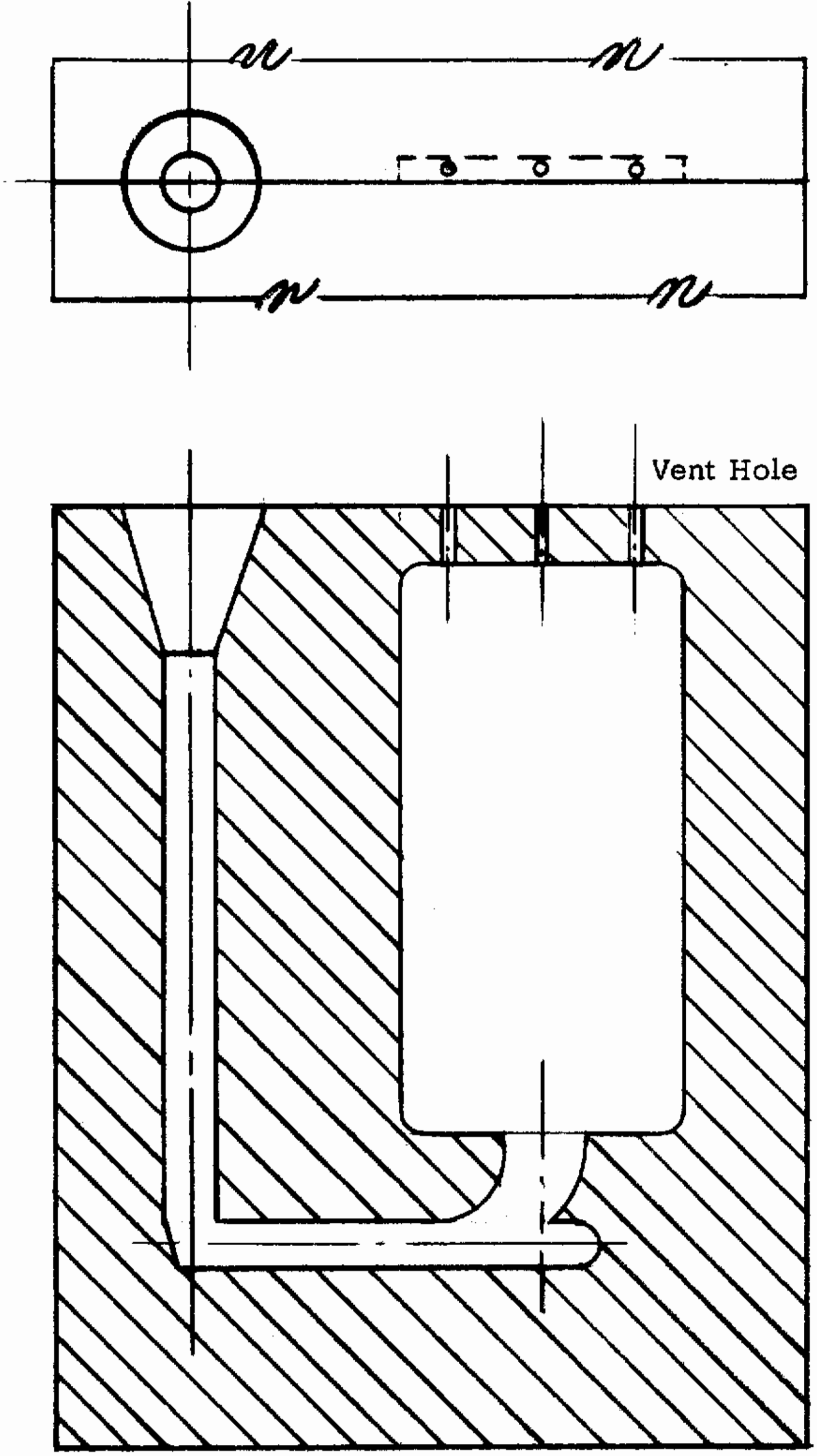


Figure 4 - Flat Plate Bottom Fed Mold

shell molds.

In order to determine the effectiveness of flux coated machined graphite and steel molds with respect to titanium casting quality, the following experimental procedure was followed:

A. Obtain reference castings from uncoated graphite and steel molds by the vacuum induction melting process.
B. Cast titanium by procedures used to obtain reference castings into molds coated to various thicknesses by several techniques.
C. Evaluate coating procedures.
   1. Visual examination of castings taken from flux coated molds to determine surface appearance.
   2. Evaluation of dimensional retention and reproducibility of castings.
   3. Metallographic examination of sectioned castings.
   4. Chemical analyses of material poured and material taken from casting surfaces.
   5. Examination of cross section of castings to determine defects which might be present from possible flux-metal reactions such as pin hole porosity, blowholes, etc.
   6. Evaluation of data and determination of optimum coating techniques.

D. Evaluation of the optimum coating technique developed by casting consumable electrode skull melted CP titanium into molds coated by the optimum process.

Sample castings of vacuum induction melted CP titanium were poured into uncoated machined graphite and steel molds to optimize the gating system, to ensure proper melt superheat, and to obtain sample castings of each design for use as standards of reference for evaluating castings poured into flux coated molds. Melt temperature was measured with an optical pyrometer. While this technique does not accurately measure temperatures, the amount of superheat could be determined by a measurement at the point when all the charge was molten and also at the point when heating ceased just prior to pouring. It was determined that approximately 130°F superheat was sufficient and this amount of superheat was used for all heats; standard induction melting procedures were employed. A typical heat log is presented in Figure 5. Figures 6, 7 and 8 are photographs of test castings which were taken from uncoated machined graphite molds. The surfaces of these castings were silvery as was expected, but "cold shuts" resulting from the rapid chilling of the molten metal by the graphite molds were common.

It was noted that in all of the step mold castings which were taken from uncoated graphite molds, the last step of each casting did not fill. The combination of rapid chilling by the graphite mold and the lack of mold preheat indicated that for the particular superheat, or pouring temperature used, the thickness of the last step was not sufficient for filling. In addition, some erosion was observed at the mold surface along the in-gate section of the cylindrical step and plate test castings, but no defects were observed within the actual mold cavity in these two particular molds.

Flux coating thicknesses ranging from less than 0.001 inch to greater than 0.100 inch were considered for purposes of this evaluation. The flux was

HEAT LOG

DATE 6/25/65 HEAT 12

Time	Power, KW	Pressure	Temp. F	Remarks
9:35 A.M.				Pump down
10:00 A.M.	5 KW	20 microns		Power on
10:05 A.M.	10 KW	15 microns		
10:10 A.M.	15 KW	10 microns		
10:15 A.M.	20 KW	6 microns		
10:20 A.M	25 KW	7 microns		
10:25 A.M.	30 KW	8 microns		
10:30 A.M.	37 KW	9 microns		
10:34 A.M.	37 KW	20 microns		Press Rising
10:45 A.M.	37 KW	65 microns		
11:00 A.M	37 KW	150 microns	2750° F	All melted
11:02 A.M.	37 KW	150 microns	2830° F	Argon added
11:07 A.M.	37 KW		2880° F	Pour

Figure 5: Typical Heat Log for Experimental Induction Melting Heats

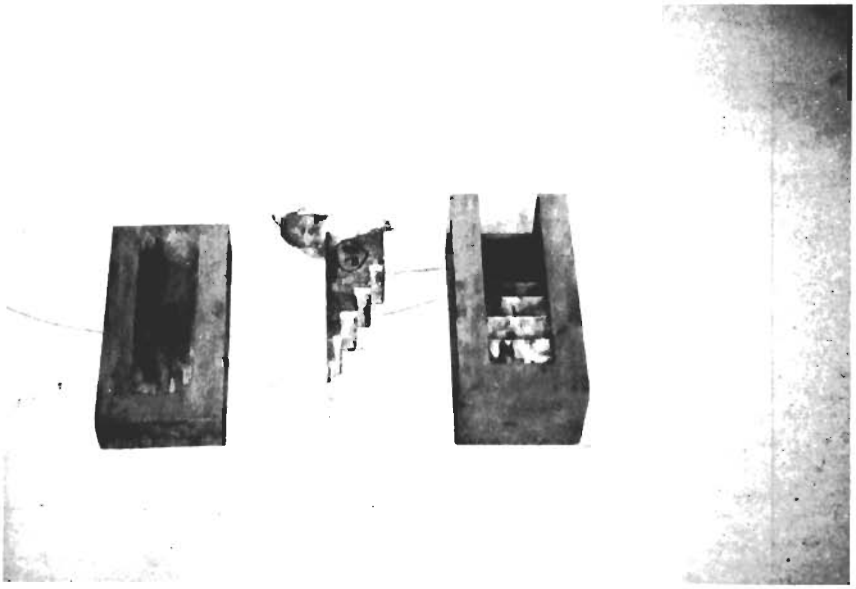


Figure 6 - Step Casting From Graphite Mold

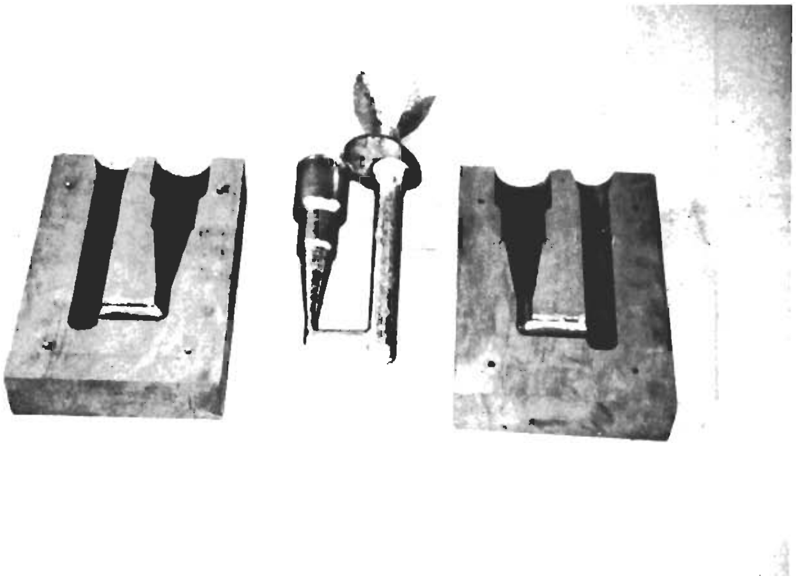


Figure 7 - Step Cylinder Casting From Graphite Mold

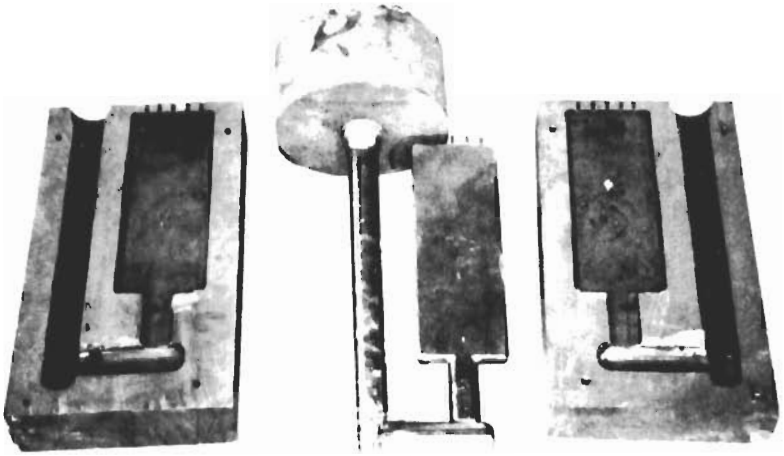


Figure 8 - Flat Plate Casting From Graphite Mold

initially applied as a slurry using methyl alcohol as a binder. Once the slurry was applied to the mold walls, the alcohol was evaporated by either air or oven drying. Both drying techniques are satisfactory, though the latter technique can obviously be carried out faster. The flux with a methyl alcohol carrier was sprayed on with a simple paint sprayer to produce thin coatings. Coating thickness could be varied by varying spraying time per unit area to be coated. Coatings thicker than 0.020 inches were brushed on with a small camel's hair brush.

Visual examination of castings taken from coated molds indicated that all thicknesses of coatings afforded equivalent chemical inertness to the titanium as expected. Since the castings were poured in an inert environment, contamination by oxygen, nitrogen, and hydrogen was not probable. Also, the surface appearance of the castings poured into molds with coatings thinner than 0.020 inches was not deleteriously affected by being exposed to the flux. However, since the flux does melt at a substantially lower temperature than titanium, castings taken from molds with coatings thicker than 0.020 inches exhibited imperfect surfaces and dimensional tolerances could not be held.

Figure 9 shows a flat plate casting which was poured into a mold with the surface covered with a heavy* coating of flux. The variations in smoothness are quite evident. Figure 10, on the other hand, shows the opposite side of the same casting which was exposed to a light* flux coating. This second side is far smoother, though cold shuts are visible on this surface. As expected, light coatings are the most desirable as coatings for machined graphite.

The flux does not produce any deleterious chemical effects on the graphite molds. However, flux coatings appeared to accelerate oxidation or rusting the steel molds at room temperature. The latter effect can be minimized if required, by employment of proper precautionary measures such as cleaning and wire brushing of the steel molds immediately after removal of the casting.

Numerous techniques for applying the flux to the molds were evaluated for both steel and machined graphite molds. Ease of application, uniformity of coating, and smoothness of resultant casting surfaces were used as criteria for evaluation of the various coating techniques. As mentioned previously, light flux coatings are most desirable so that hereafter all coating procedures described will refer to light coatings.

Dusting the molds with flux in the powder form, a technique commonly used in some foundry practices, yields a uniform, smooth coating. However, this procedure is not practical for vacuum melting procedures. The molds are held in vacuum prior to pouring and the fines would be drawn into the vacuum system. To overcome this problem, the coating must adhere to the mold in order to prevent it from being drawn into the vacuum system. Accomplishing this requires the employment of a binder which is not harmful to the mold properties or reactive with the titanium. Borrowing from previously described techniques, a slurry of methyl alcohol plus flux is satisfactory and the described procedures for applying this mixture proved satisfactory from this particular aspect.

* Reference to light coatings is to those 0.0005 - 0.003 inches in thickness. Heavy coatings are greater than 0.020 inches in thickness. Medium coatings are between 0.003 and 0.020 inches in thickness.

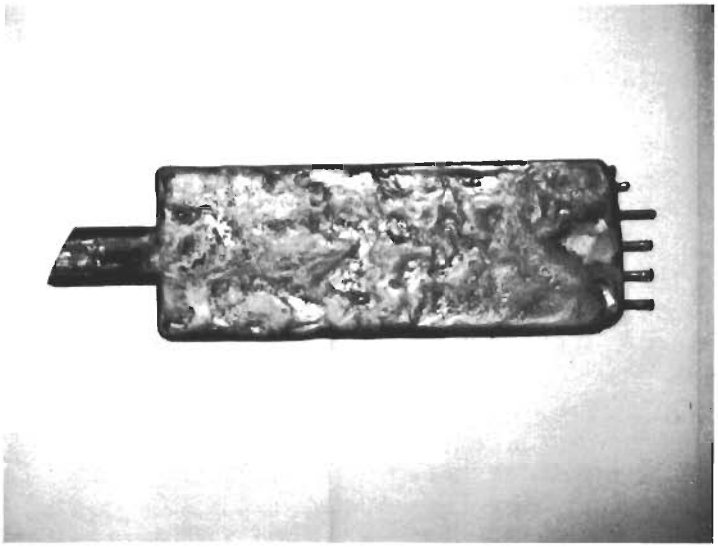


Figure 9 - Surface on Flat Plate Casting Exposed to Thick Coating of Flux on Mold Surface

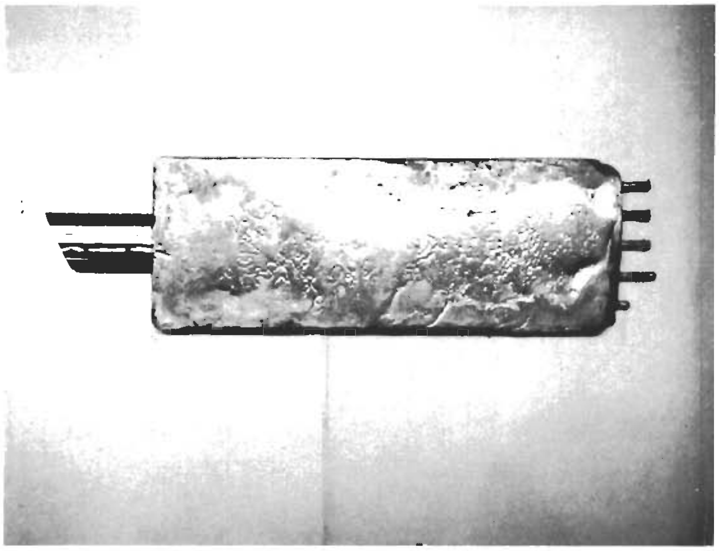


Figure 10 - Surface on Flat Plate Casting Exposed to Thin Coating of Flux on Mold Surface

Note that the methyl alcohol itself has no effect upon either the steel or graphite molds and that it is completely removed by evaporation either in air or in the oven prior to pouring.

The most successful application technique used was the spraying of the slurry onto the mold. Very uniform coatings are quickly deposited and the coatings adhere to the molds upon alcohol evaporation. The resultant titanium castings have smooth surfaces, which are at least equivalent to those cast into uncoated molds. Preheating both the coated graphite and steel molds improved the uniformity of the coating as the alcohol evaporated on contact with the mold and did not "run". This problem sometimes occurs when the flux slurry is rapidly sprayed onto molds at room temperature. In general, the spraying technique appears quite adequate from all considerations.

A modification of the spray procedure for coating graphite molds incorporates heating of the coated molds until the coating melts to form a "glazed" surface. The technique used to "glaze" the molds consists of spray coating the molds at room temperature, followed by heating the coated molds at about 1450°F for a few minutes until a glaze is formed. The resultant coating completely covers the graphite and penetrates the mold surface, since machined AUC-grade graphite is somewhat porous. These glazed coatings are smoother than sprayed-on coatings which are not postheated, and castings from glazed graphite molds exhibit smoother surfaces then those from either coated or uncoated molds. A typical resultant casting, taken from a mold which was coated and glazed as described above is shown in Figure 11. The few surface defects present were the result of improper mold gating and were unavoidable. However, the quality of the surface is superior to that of any casting taken from uncoated molds of the same design poured under the same conditions.

Other flux-alcohol slurry application techniques have been found inadequate. Included in these unsatisfactory techniques is the dipping of the mold into a flux-alcohol slurry. This does not yield as smooth a coating as would be desired and is also difficult to apply consistently. Painting the slurry onto the molds does not produce smooth coatings or smooth casting surfaces, thus proving to be an insufficient coating technique.

The protectiveness and chemical inertness of the flux with reference to molten and heated titanium has been demonstrated previously both in theory through thermodynamic calculations and in practice when applied to titanium welding. As noted previously, the purpose of this work is to apply the basic nonreactivity and protectiveness of the flux to titanium foundry practice in order to obtain superior castings. Chemical analyses of some of the castings were been made and these are tabulated in Table 1. Samples 6B, 6D1 and 6D2 were taken from castings poured in the same heat. Note that the halide content is very low indicating no measureable flux pickup or flux degradation or reaction between flux coating and the titanium. The casting from a steel mold, 6B, has the lowest carbon content for the same heat. A specimen taken from the surface of a casting from a thinly coated graphite mold, 6D2, exhibits a carbon content that is about equal to the carbon content from a sample taken from the center of the same casting, 6D1, but somewhat greater than the carbon content of the casting taken from the steel mold.

CASTING 10A

Figure 11 - Casting Poured into Graphite Molds Coated with a Glazed Flux Surface

TABLE 1

CHEMICAL ANALYSES OF VARIOUS TITANIUM CASTING SAMPLES

Specimen	Mold Material	Coating	%Carbon	% Halides	Remarks
6B	steel	none	1.21	0.001	
6D1	graphite	light flux	1.23	0.001	Sample from casting center
6D2	graphite	light flux	1.25	0.001	Sample from casting surface
5BF	graphite	flux	0.95	-----	Sample from casting surface
5BG	graphite	none	1.01	-----	Sample from casting surface

Specimens 5BF and 5BG were taken from a single casting but a different heat from the previously mentioned specimens. This casting was made in a graphite mold with one-half lightly coated with flux and the other half uncoated graphite. Note that specimen 5BF taken from the flux side exhibits a lower carbon content than specimen 5BG taken from the uncoated side.

Though all specimens in Table 1 exhibit a high carbon content indicative of extensive carbon pickup during melting, it can be seen that some carbon is being picked up from reaction of titanium with uncoated mold walls. Based on the data obtained, it appears that the flux does reduce carbon pickup. It should be noted that the carbon content of the stock melted ranged between 0.02 and 0.03 percent and it was not possible to sample the molten titanium just prior to pouring to obtain a carbon analysis of the material poured. The chemical inertness and protectiveness of the flux seems to be apparent by the essential nonexistence of halides at the casting surfaces and by the absence of gross blow holes or porosity. In summary, light coatings of flux on permenent molds were found to be of some benefit, but it was felt that the effectiveness of the flux would be more apparent if it were applied to rammed graphite molds either as a coating or a mold constituant. Therefore, emphases was shifted to the study of the applicability of the flux to rammed graphite molds.

The evaluation of flux coatings on rammed graphite molds was extensively studied as rammed graphite molds are commercially employed in the production of most commercial castings. The casting configuration used for this portion of the program was the cylindrical step mold. The rammed graphite molds used for this work were made by employing the shell mold pattern plate with variations as exhibited in Figure 12. The primary advantages of rammed graphite molds over machined graphite molds include economy of process, and the ability to produce large molds readily with complicated geometric configurations. Also, ordinary wood or metal patterns can be used in rammed graphite molding operations.

All mixing of mold ingredients was accomplished in a Hobart mixer. The dry ingredients were preblended for approximately 3 minutes. The wet ingredients were premixed until they were homogeneous and then added to and mixed with the dry ingredients. Several castings from lightly flux coated rammed graphite molds were obtained. These exhibited little cold shut and somewhat smoother surfaces than those from uncoated graphite molds.

Based on these results, an arrangement was made with Oregon Metallurgical Corp., Albany, Oregon to cast high purity titanium into coated test molds under normal foundry conditions to evaluate developments made in the laboratory. The first heat at Oremet was used to evaluate various flux coating techniques described previously for applicability to commercially produced rammed graphite molds. To facilitate this evaluation, a small casting of relatively simple design was chosen. This test casting, however, does exhibit sufficient variation in thickness to allow for wide variation in solidification rates at various sections of the casting. The test casting employed is shown in Figure 13.

As noted above, commercially processed rammed graphite molds were employed. Figure 14 shows the cope and drag sections prior to casting.

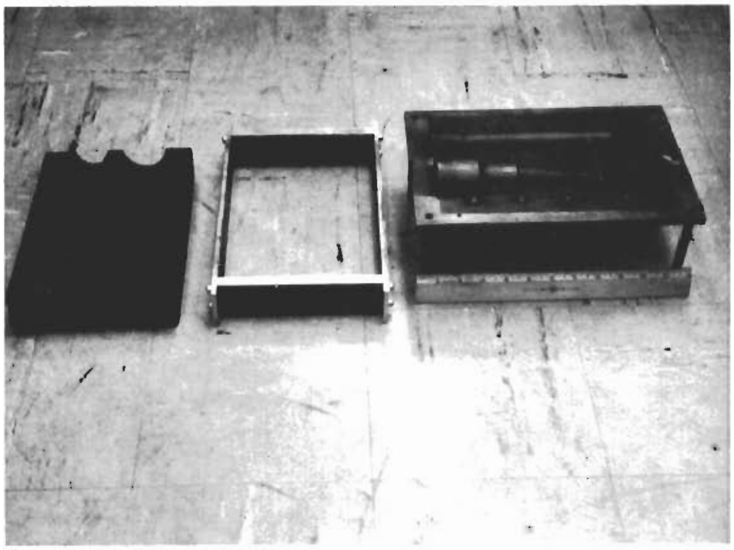


Figure 12 - Cast Iron Pattern Plate with Experimental Flask and Rammed Graphite Mold Half

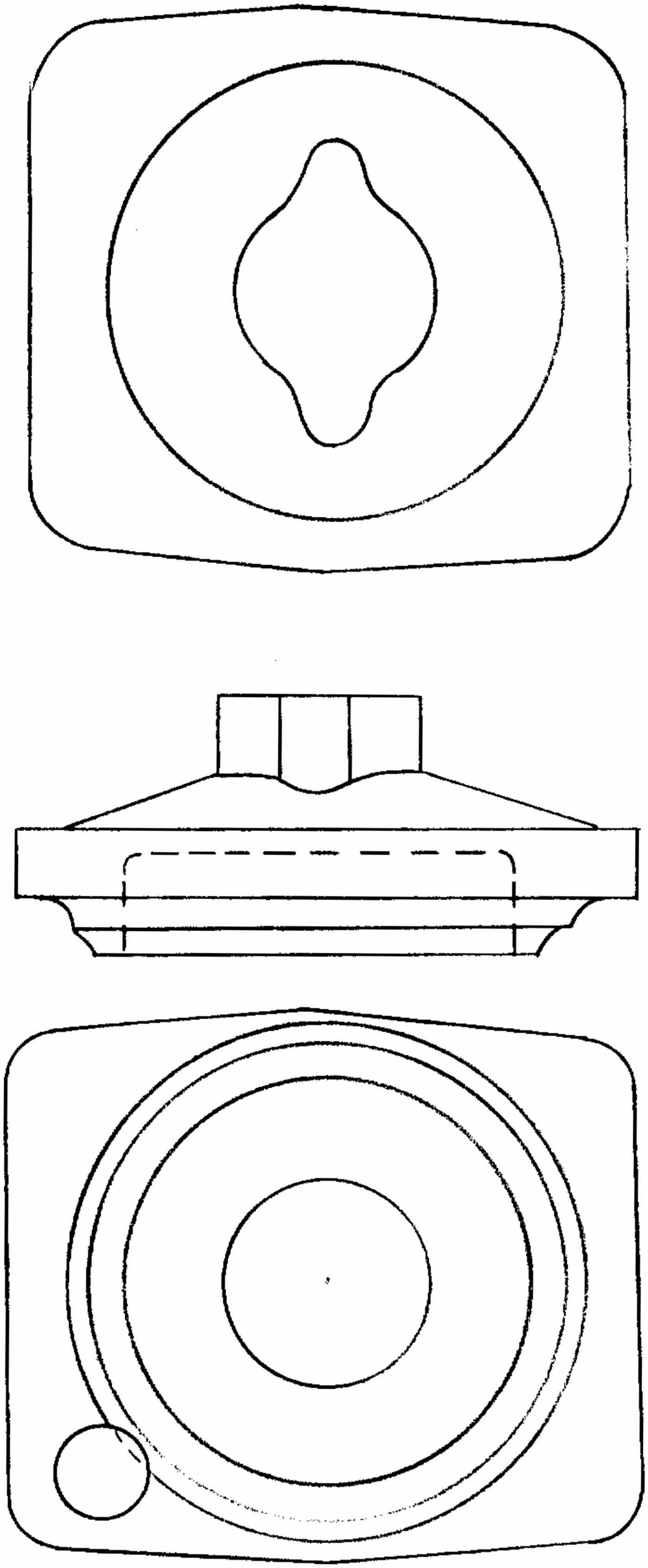


Figure 13 - Schematic of Test Casting - Scale 1:1

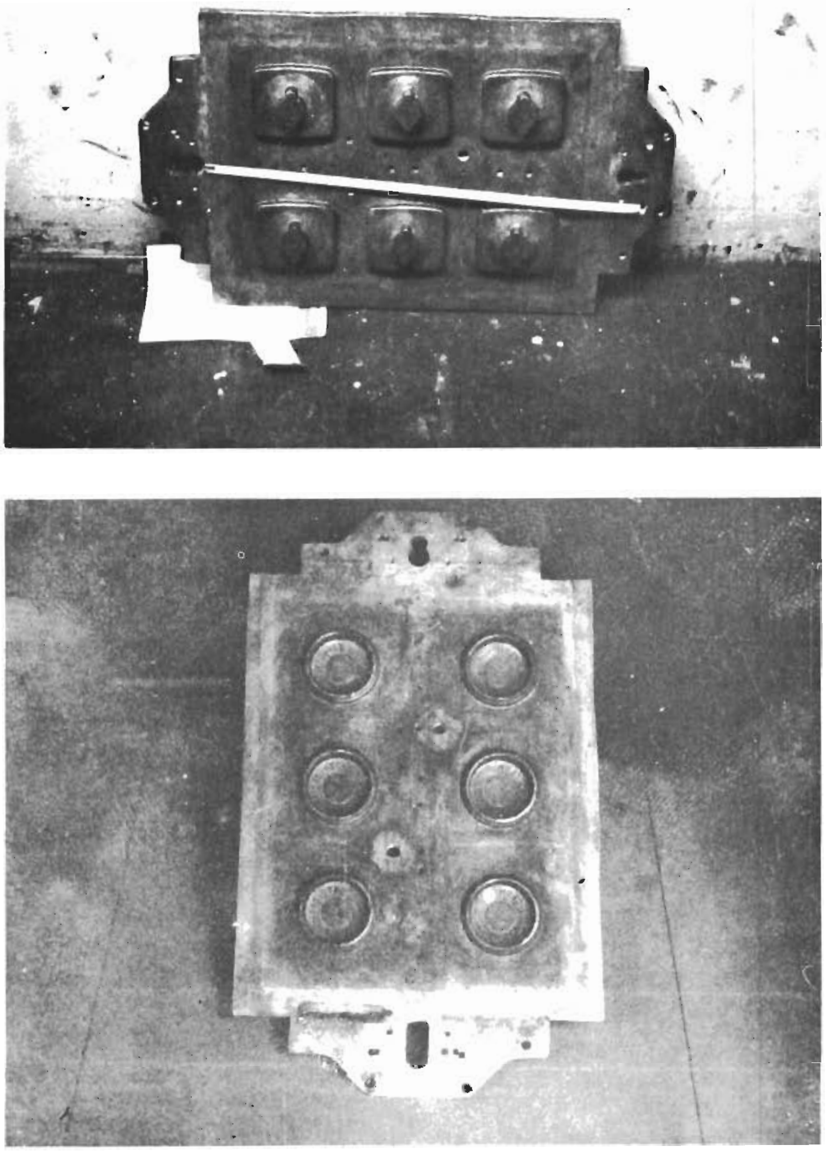


Figure 14 - Cope and Drag Sections of Test Mold Scale 1:8

The mold ingredients were as follows:

a) Great Lakes 1012-41 Graphite
b) Pacific Black Pitch
c) Niagara Laundry Starch
d) C-3 Carbonaceous Cement (Electrode Joint Cement)
e) Water

The processing procedure was as follows:

a) Mix dry ingredients (graphite, pitch, starch)
b) Add water
c) Ram into patterns lightly coated with parting agent (Stevens Liquid Parting Agent)
d) Remove from pattern
e) Air dry at room temperature for 8 hours
f) Oven dry at 250° F, 8 hours
g) Pack Molds in container and cover with graphite
h) Fire at 1550° F, 12 hours

Two molds were prepared in the above manner. These molds are schematically depicted in Figure 15. Mold B was to be used to evaluate glazed flux surfaces. Three coating thicknesses were applied prior to glazing: sections 1 and 2 were flux coated approximately 0.005 inches thick, sections 3 and 4 approximately 0.01 inches thick, sections 5 and 6 approximately 0.015 - 0.020 inches thick. Mold A was to be used to evaluate spray coated flux surfaces. Sections designed L had a 0.005 inch flux coating, H had a 0.015 inch flux coating, and X were uncoated.

In addition, two large complex impeller cores were spray coated. It was planned to glaze one prior to pouring and to let the other remain as-coated. All mold coating was done by using alcohol as a flux carrier and compressed air as the spray medium. The design of the impeller is proprietary and cannot be shown in this report. It was, however, approximately six inches in diameter and of sufficient complexity to introduce casting difficulties not encountered in the test molds. For example, the blades of the impeller were very thin and were attached to much larger sections, thus providing adjacent areas with sharply varying rates of solidification. Equipment difficulties encountered during the glazing operation resulted in total degradation of one impeller mold and partial degradation of test mold B.

When the source of these problems was recognized, it was decided to scrap the degraded impeller mold and glaze the other. This was successfully accomplished as no degradation of the core resulted. Mold B was used even though it was partially degraded. It should be emphasized that the glazing operation may be accomplished rather easily and the problems encountered during these tests were a result of equipment malfunction. In summary, three molds were prepared for casting of high purity CP titanium:

a) Glazed impeller mold.
b) Glazed partially degraded test mold (6 castings).
c) Coated test mold (4 coated, 2 uncoated).

All test molds were centrifugally cast as part of a production heat together with other production items. The molds were set on a rotating table. A schematic sketch of the gating system for one test mold is shown in Figure 16.

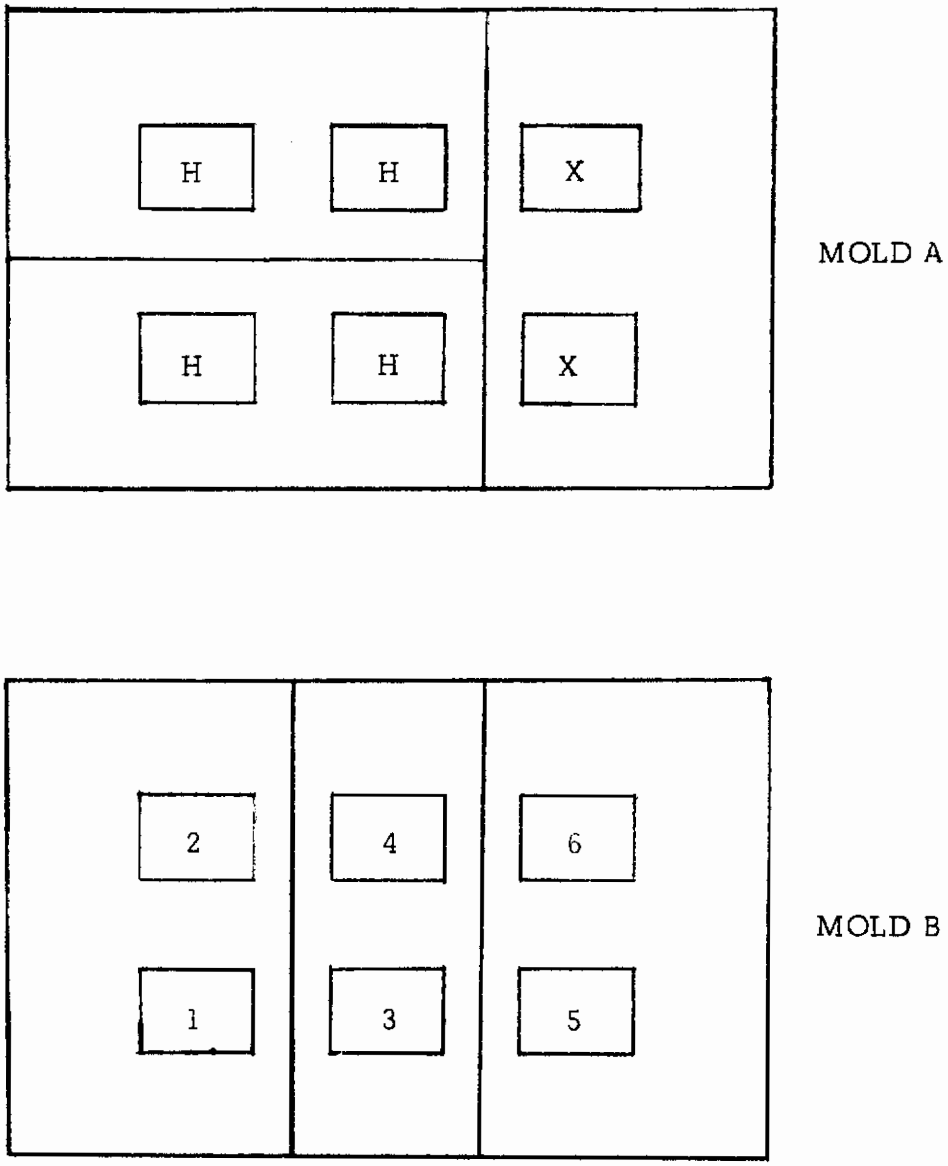


Figure 15 - Casting Locations in Test Molds

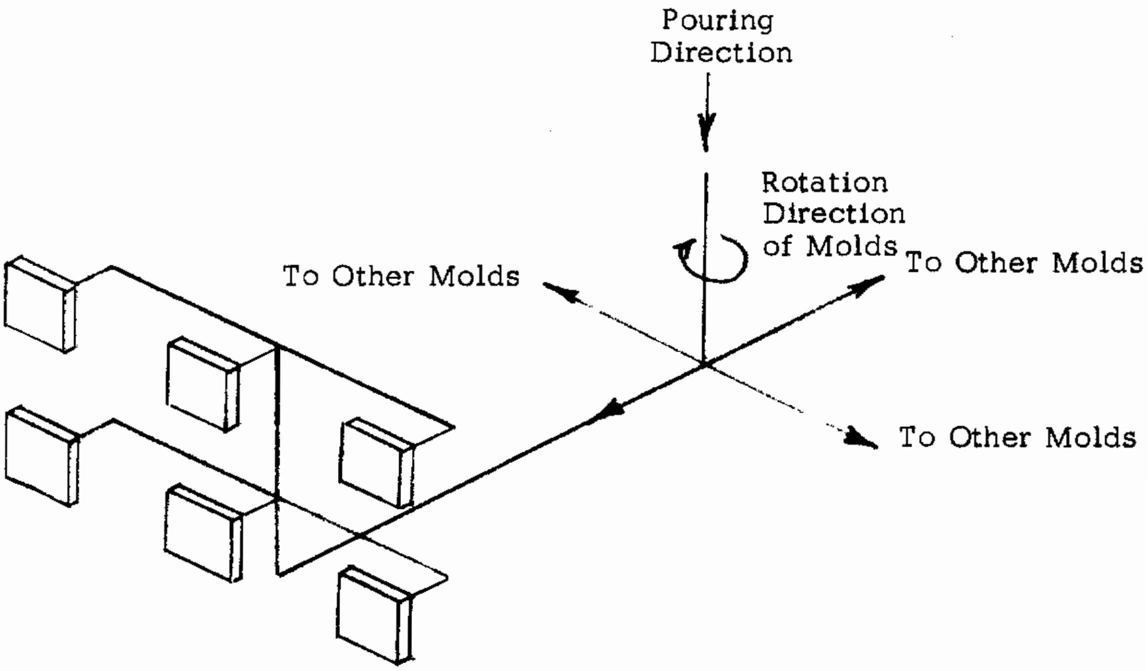


Figure 16 - Schematic of Gating System Employed for Test Castings poured at Oremet

The other test molds were similarly gated. Commercially pure titanium was consumable electrode melted and centrifugally cast. Centrifugal casting procedures were employed to assist filling and reduce surface imperfections such as cold shut.

Since the glazed mold was degraded during processing, an exact comparison between castings from it and from the coated mold cannot be made. All observations made ignored effects of mold degradation except where noted.

The color exhibited on the surfaces of the castings was equivalent except for the two castings designated H. All exhibited some discoloration, felt to be from water traces in the molds. Castings H, however, were substantially discolored. It was found that this color was from water vapor picked up by the flux coating prior to casting and was eliminated by mold storage after coating in an oven at 250° F. Shot blasting was sufficient to clean up all casting surfaces. A semi-quantitative comparison of times required to clean the castings interestingly indicated that those from either coated or glazed molds required approximately one half the time to clean contrasted to castings from uncoated molds.

The surfaces of the two castings designated X, taken from mold A, and those designated 2, 4 and 6 taken from mold B exhibited equivalent smoothness, again disregarding effects from the degraded molds. Flux coatings thicker than 0.005 inches do not appear suitable as the resultant castings exhibited substantial irregularities on the surface. This results from irregular melting of the flux in these heavier coatings and apparently cannot be eliminated.

Burn-in, that is, molten metal penetration of the mold is observable to some degree on all castings as seen in Figure 17 and Figure 18. The effect is substantial on the castings from the glazed molds but this can be attributed to mold degradation. Castings X, L and H, also exhibit this effect but to a far less degree. Related experiments discussed in other sections of this report indicate that flux additions as either glazed coatings or as high temperature binders have the effect of increasing surface hardness which would decrease the tendency for burn-in.

Quite sharp contrasts in retention of mold surface detail of the castings are evident. Two general modes of surface detail are present in the castings. One is dimensional in nature while the other is the fine detail of the pattern number. Comparing castings X, L and H, dimensional retention is about equivalent. Sharp detail, however, is reduced with the addition of the flux coating and with increased coating thickness. It appears that the coating procedure and technique results in filling in or covering fine detail in the mold. The castings from glazed molds all exhibited good dimensional retention and sharp detail in areas not subjected to burn-in where the degraded mold broke down. These are indications that detail retention and smoothness are enhanced by flux glazing. This can be attributed to filling of the voids between the graphite particles through glazing.

Microhardness surveys at various locations in representative castings were made. Results indicate that a general pattern exists in all castings. Casting surfaces in all cases are harder than the areas away from the surface. Further, this layer appears to be 0.005 to 0.015 inch in thickness. There are also indications that flux glazed surfaces, but not flux coated surfaces reduce the thickness of this layer. Figure 19 schematically depicts the regions surveyed.

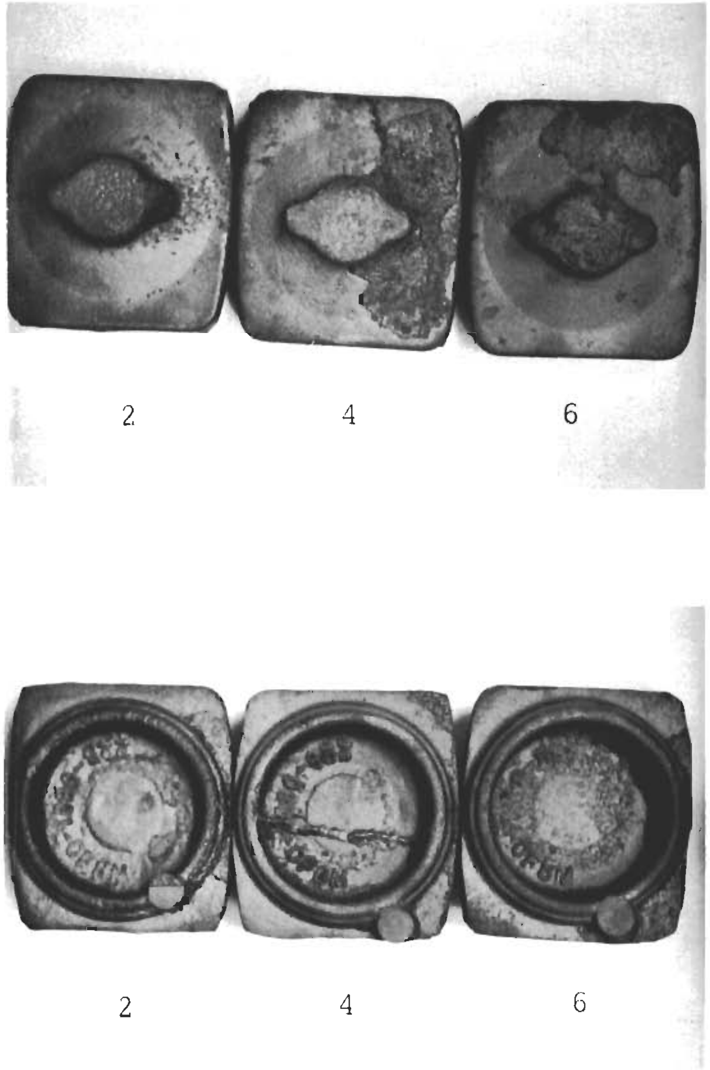


Figure 17 - Top and Bottom of Three Representative Castings from Glazed Mold

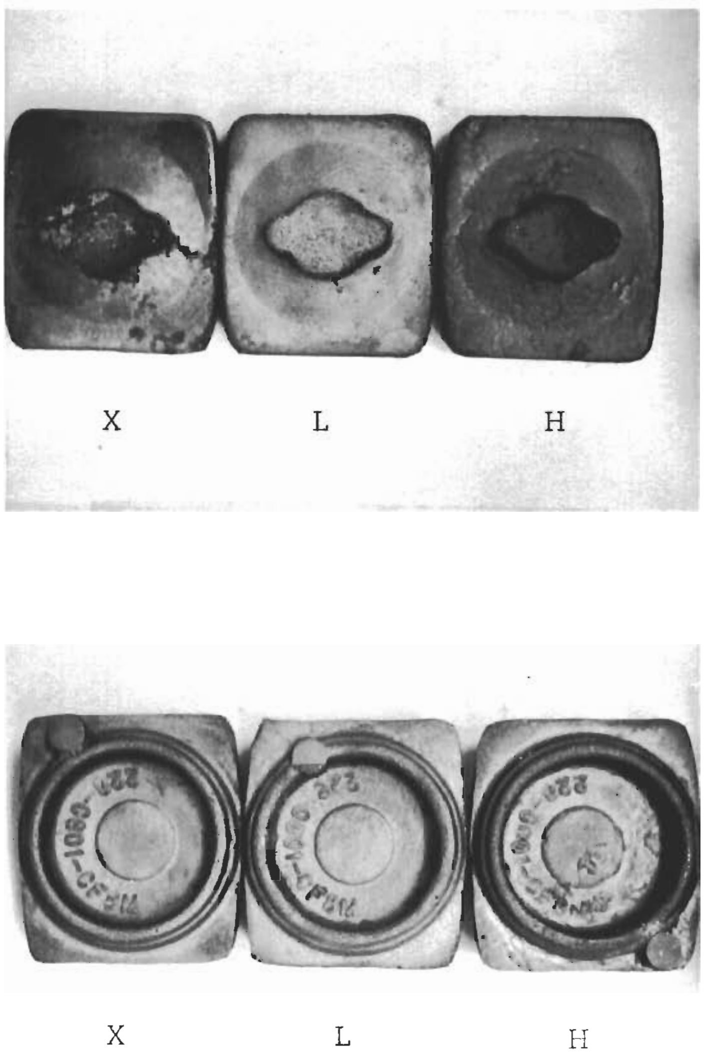
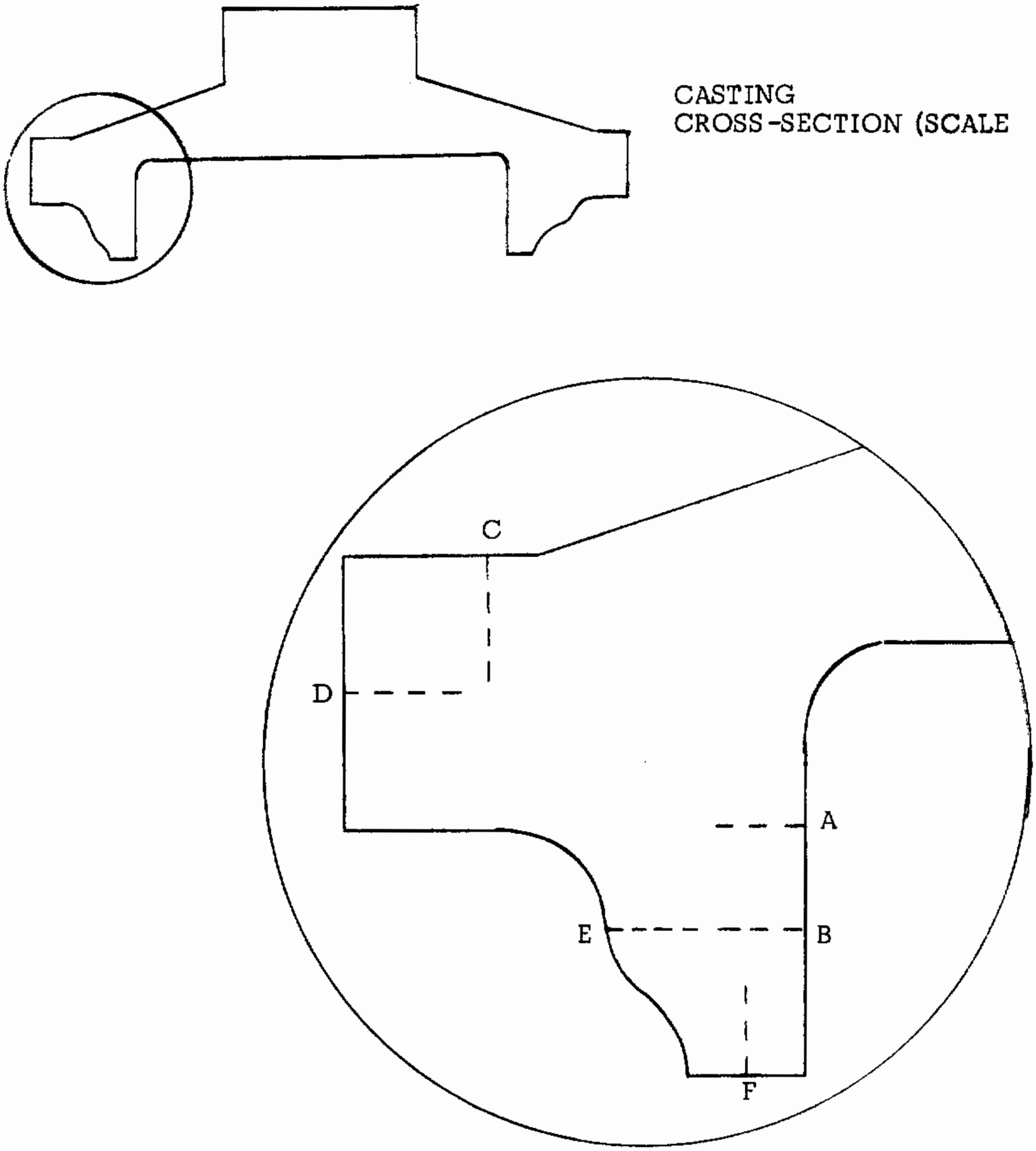


Figure 18 - Top and Bottom of Three Representative Castings from Coated Mold (one from uncoated section)



CASTING
CROSS-SECTION (SCALE 1:1)

Figure 19 - Location of Hardness Surveys

The results of these surveys are plotted in Figure 20.

A series of chemical analyses were also performed to determine carbon content as a function of distance from the surface of the casting. The location chosen is shown in Figure 21. It was chosen because there was intimate contact between the graphite mold and the castings which was caused by shrinkage of the casting during cooling. Further, this area allowed for the precise machining required to obtain samples for the carbon analyses. Seven layers 0.005 inch deep were successively machined from the castings on a lathe and the shavings were carefully collected and segregated to represent a given layer. Each group of shavings was analyzed separately. A casting from an uncoated mold, a glazed mold, and a lightly coated mold were all treated in this manner. The results of the analyses are shown in Figure 22.

Though some scatter in the data is present, there is a definite indication that incorporation of the flux into the mold reduces carbon pickup and diffusion into the casting. The most striking reduction appears in the casting from the flux coated mold.

Metallographic analysis was also performed on these specimens. Figures 23, 24, and 25 exhibit the microstructure of these specimens near point E (Figure 19). The microstructures are essentially equivalent. No correlatable trends or anomalies are observable.

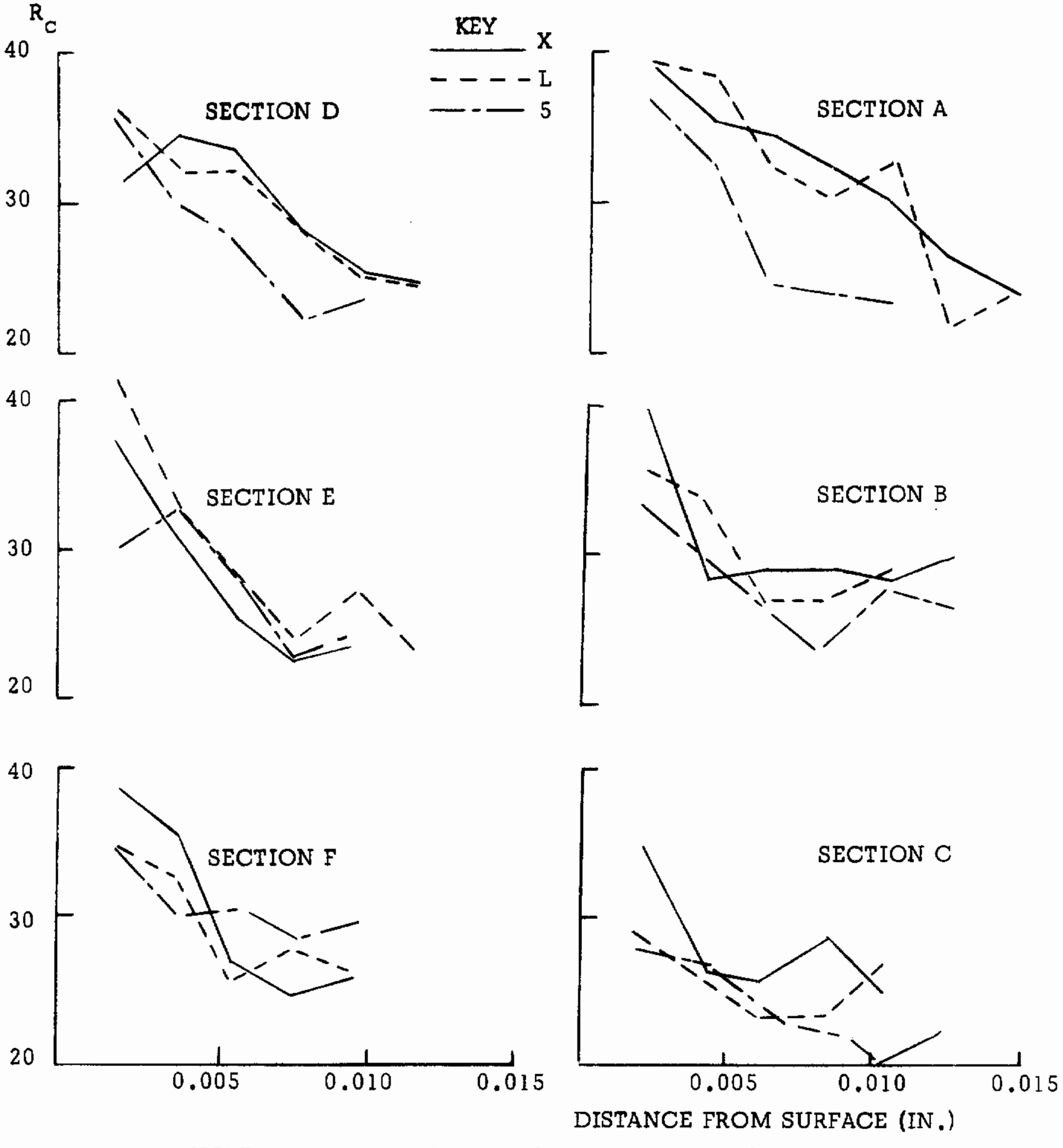
Basically, there were four aspects of titanium foundry practice which required improvement in order to accommodate the presence of the flux in rammed graphite mold mixes. These were:

a) Improvement of casting surface detail
b) Reduction of mold-metal reactions
c) Reduction of complexity of mold processing times and temperatures
d) Reduction of time required for casting removal from molds and core removal from finished castings

Improvement of surface detail and the reduction of mold metal reaction were shown to be achieved through mold coatings as evidence in these directions was observed during the initial portion of this study. It was felt that employment of the flux as a high temperature binder for rammed graphite molds would substantially accomplish all of these objectives eliminating the requirement for a mold coating step in the mold processing cycle. An extensive effort was undertaken to develop this theory further.

Mold Composition

Numerous mold compositions were rammed and processed during this phase of the study. These are tabulated in Table 2. These mold mixes were initially evaluated primarily by the physical properties of the mold, specifically abrasive resistance of the surface and general mold strength. Based on the result of the experimental compositions one through eleven, three molds were prepared for actual titanium casting. The casting designated 15A was made in a mold of composition 11 while castings 15B and 15C were of mold composition 4.



NOTE: X - Uncoated, L- Light Coating, 5 - Glazed

Figure 20 - Hardness Surveys

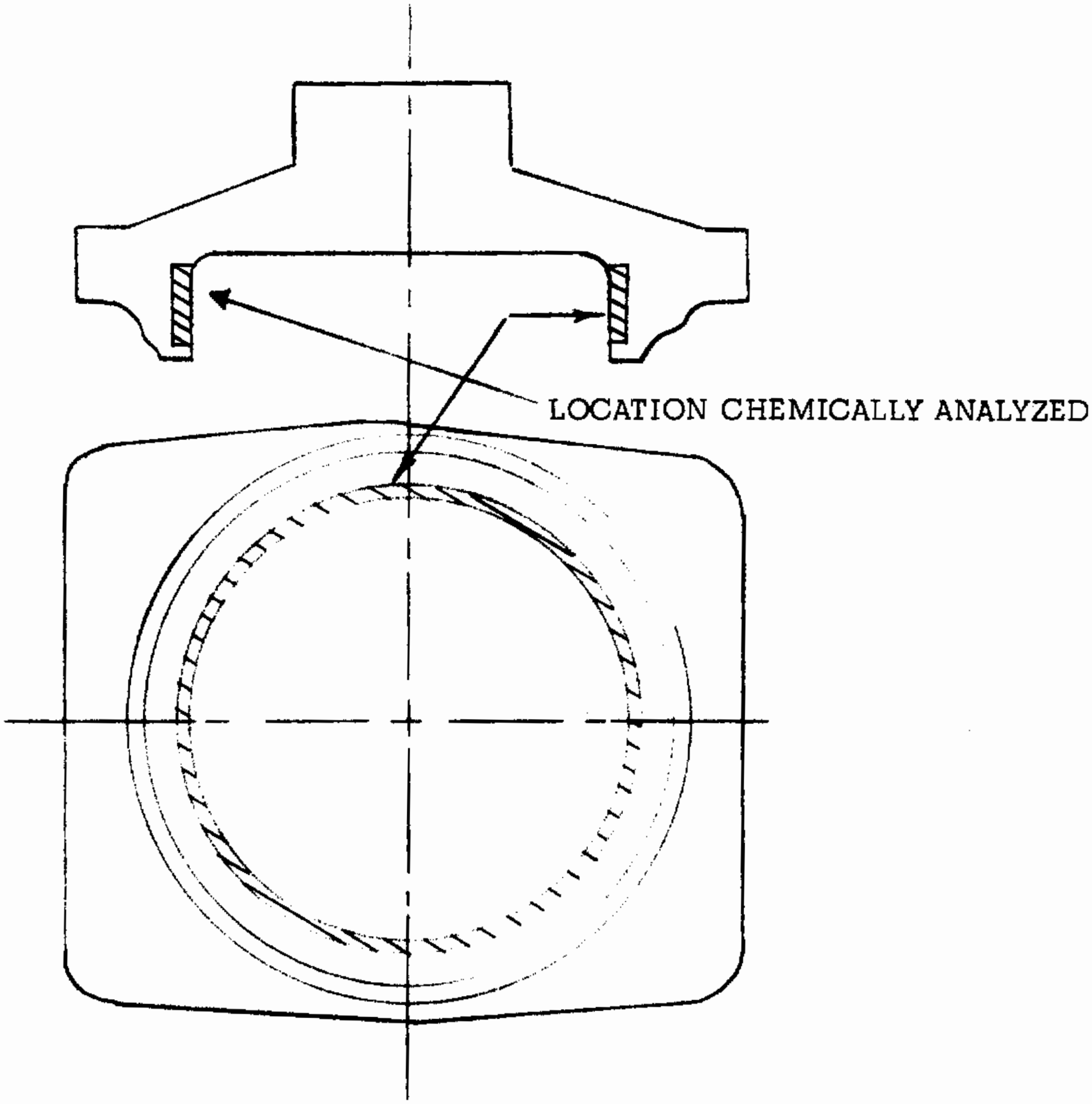


Figure 21 - Location of Area of Casting Chemically Analyzed for Carbon

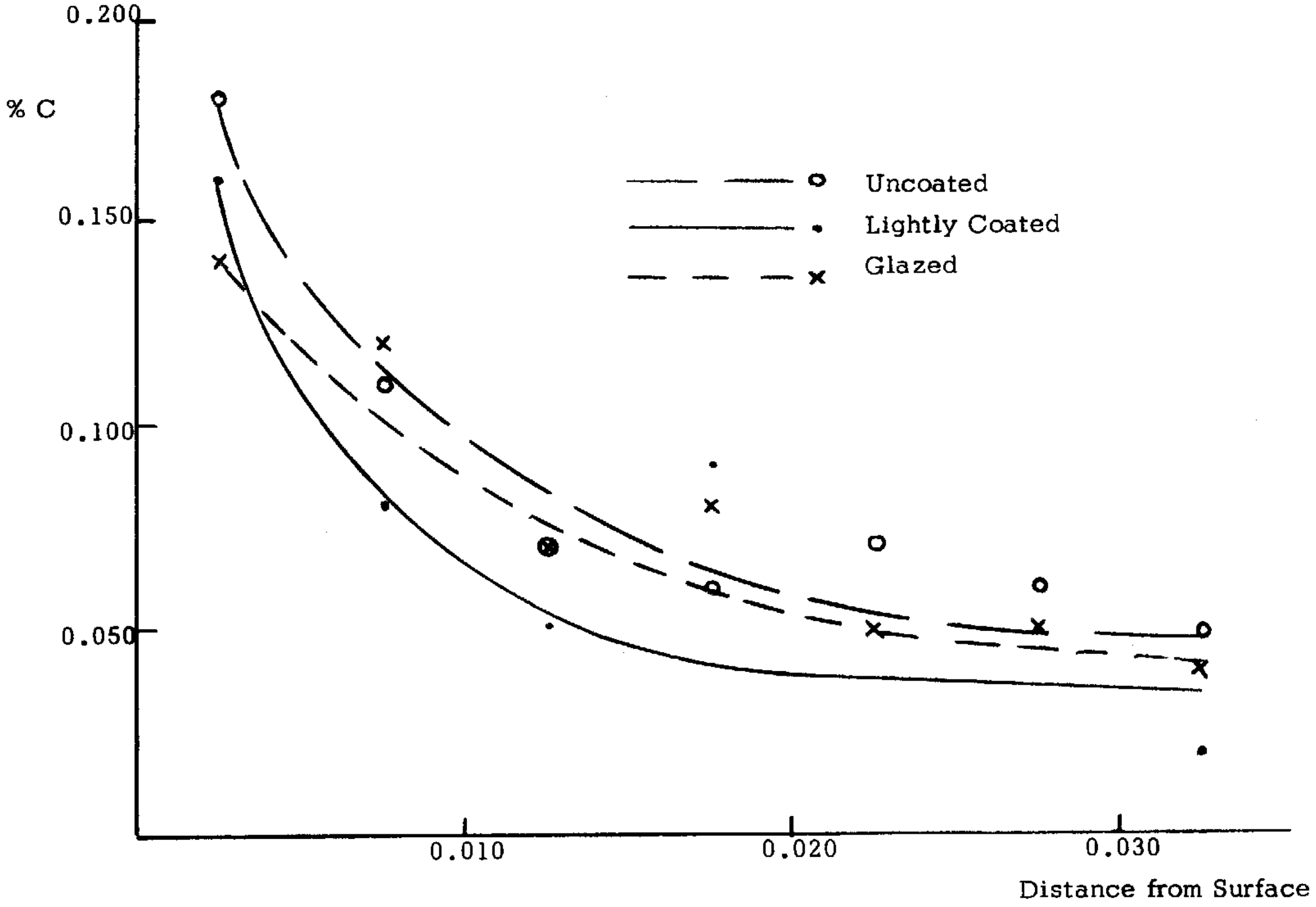


Figure 22 - Carbon Content as a Function of Distance from Surface

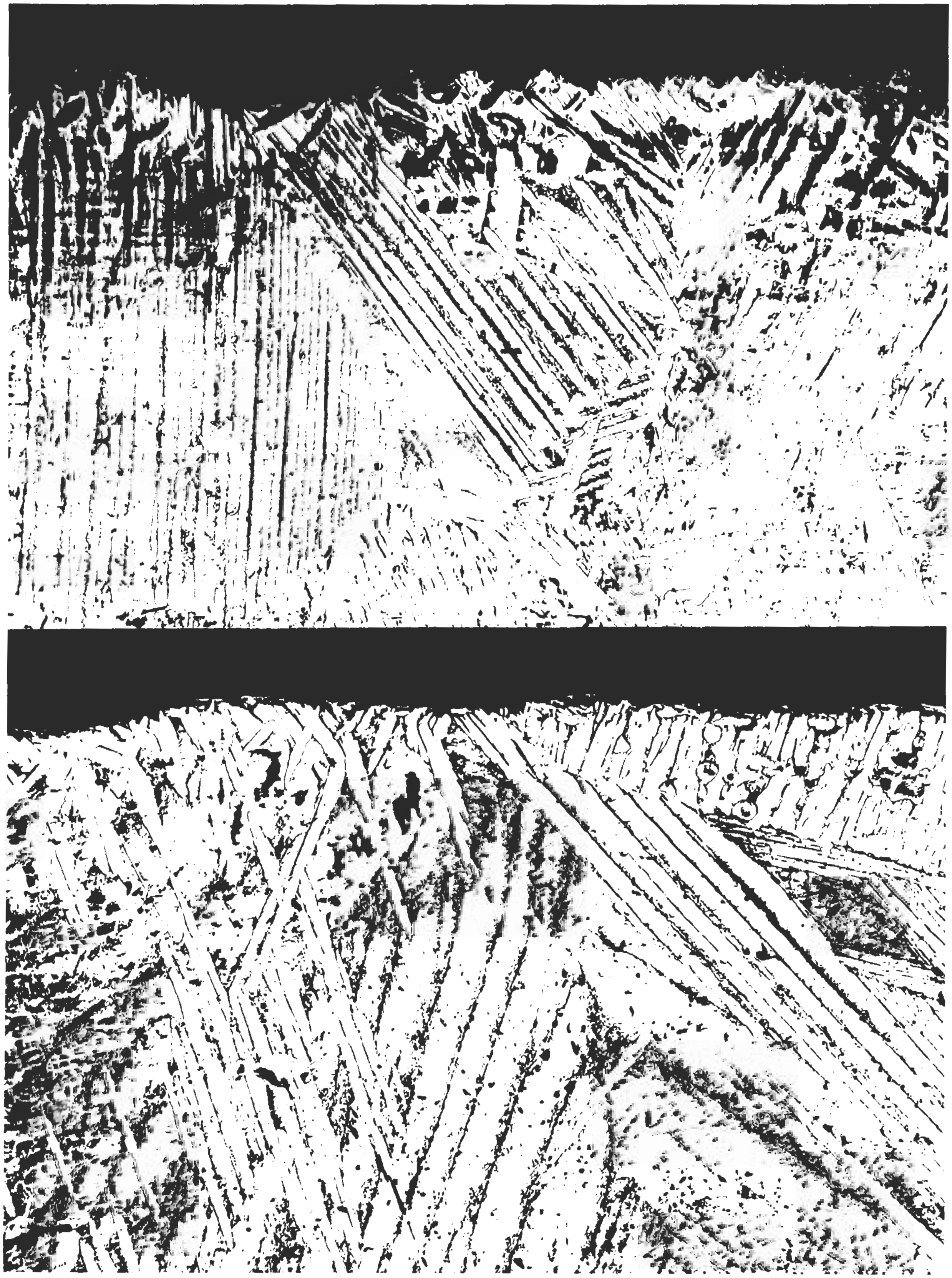


Figure 23 - Microstructure of Castings 2 and 4 at Surface

Modified Kroll's Etch 200X

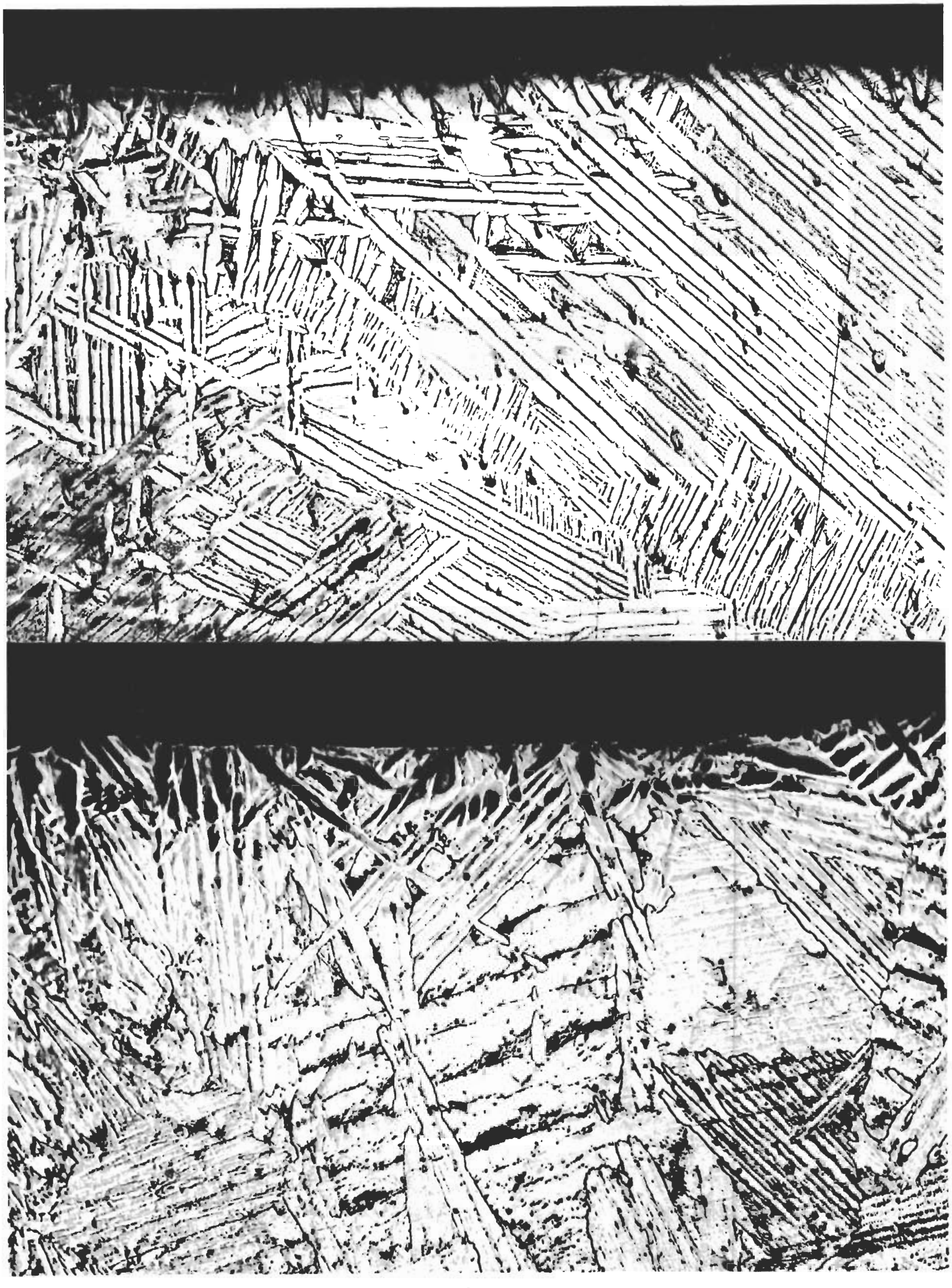


Figure 24 - Microstructure of Castings 6 and X at Surface

Modified Kroll' s Etch 200X

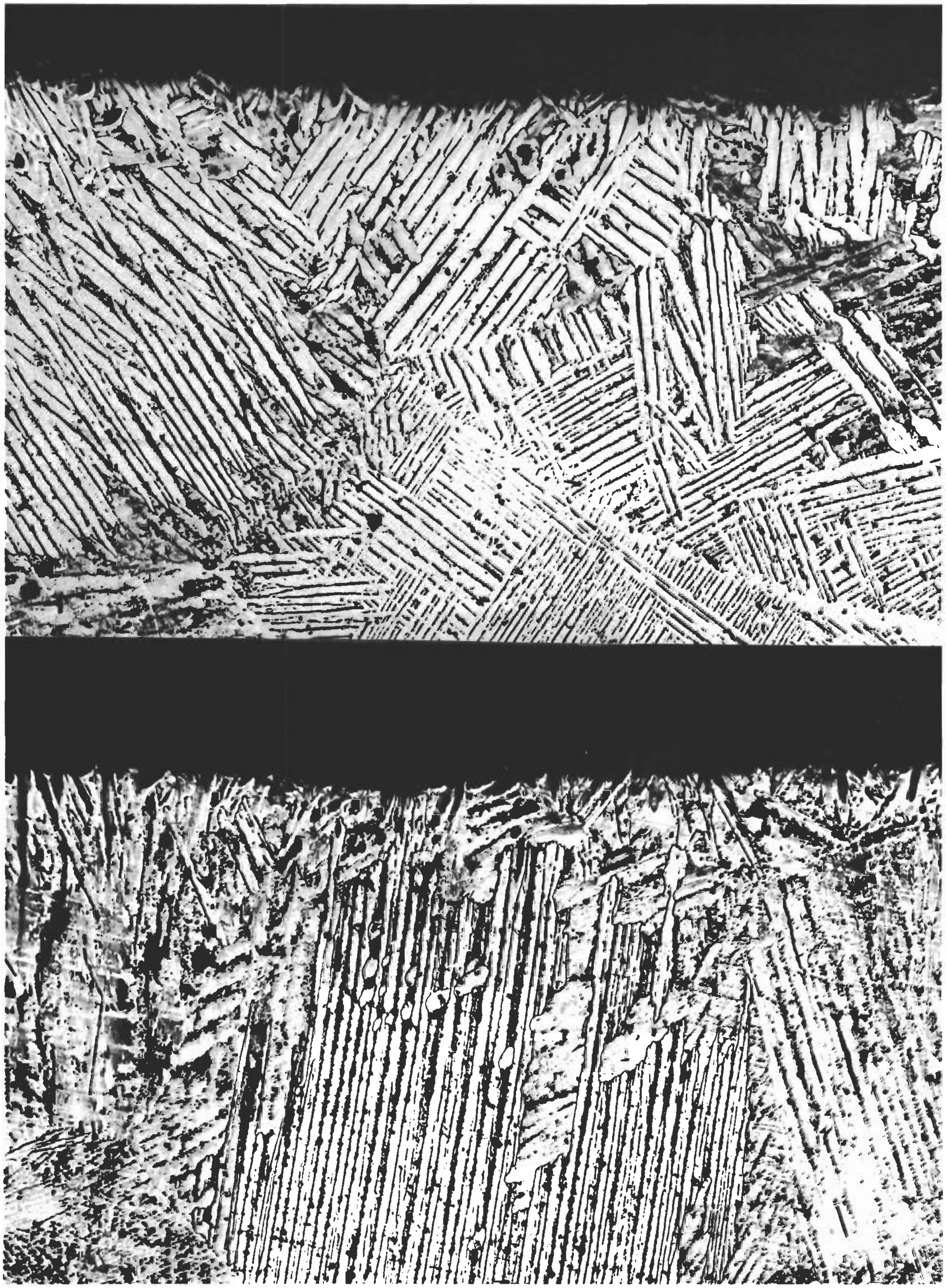


Figure 25 - Microstructure of Castings L and H at Surface

Modified Kroll's Etch 200X

TABLE 2 - COMPOSITION PROCESSING AND PROPERTIES OF EXPERIMENTAL RAMMED GRAPHITE MOLD MIXTURES

Exp #	Graphite	Flux	Water	Starch	Western Bentonite	Pitch	Sodium Silicate	Carbonaceous Cement
1	100	5	10.7					
2	100	10	10.1					
3	100	15	10.7					
4	100	20	10.7					
5	100	10	10.7*					
6	100	10	15.5					
7	100	15	15.5					
8	100	20	15.5					
9	100	5	10					
10	100	15	8					
11	100	20	8					
12	100	50	8					
13	100	21	10	7				7
14	100	21	10	7				21
15	100	30	28				14	
16	100	14					20	
17	100	10	28				14	
18	100		14				14	
19	100	14	14	7		14		
20	100	14	14	7		3		
21	100	14	14	7		7		
22	100	28	21	7		14		
23	100	20	18	6				
24	100	20	20	10				
25	100	20	18	6				
26	100	40	18	6				
27	100	40	16					
28	100	25	6					
29	100	25	12					
30	100	25	17					
31	100	25	25					
32	100		10		10			
33	100		8		5		4	
34	100		20		20			
35	100		5		10		10	

Exp #	Graphite	Flux	Water	Starch	Western Bentonite	Pitch	Sodium Silicate	Alundum Cement
36	100	10	15		5		5	
37	100		5		15		10	
38	100		15		10			
39	100	15	20					
40	100	10	16		14			
41	100	11.5	12.3	4.6				
42	100	11.5	12.3	2.3				
43	100		15	6				
44	100	13	15	1				
45	100	15	15	1				
46	100		15	1				
47	100		15	3				
48	100	15	15	3				
49	100	5	15	1				
50	100	10	15	1				
51	100	15	15	1				
52	100	15	15	1	8			
53	100	15	15	1	10			
54	100	15	15	1	12			
55	100	25	15	1	10			
56	100	15	15	3	8			
57	100	15	20	1	12			
58	100	25	15					25
59	100	10	15					15
60	100	20	15	7				
61	100	20	10	0				14**
62	100	20	0	0				20**
63	100	15	15	0			15	
64	100	15	15	0			10	
65	100	15	15	0			5	
66	100	15	15	3				1
67	100	15	15	3				3
68	100	15	15	3				5
69	100	15	15	3				10
70	100	25	15	3				

Exp #	Graphite	Flux	Water	Starch	Western Bentonite	Pitch	Sodium Silicate
71	100	25	15	3			
72	100	25	15	3			
73	100	20	15	5			
74	100	20	15	5			
75	100	20	15	5			
76	100	20	15	0			
77	100***	20	15	0			10
78	100***	20	15	3			0
79	100***	20	10	2			0
80	100***	20	10	0			5

* alcohol ** linseed oil ***reclaimed graphite

Exp #	Baking	Firing	Remarks Pertaining to Mold Properties
1	3 hrs -300°F	1500°F	Physical properties of test samples formed from mixtures and baked as indicated were more favorable with the increased percentages of flux. With 5% addition of flux, a very weak rammed specimen is obtained after baking. With as much as 50% addition of flux an extremely hard (uniform throughout) core briquette is obtained after baking. A study of baking times and temperatures would not improve strength values with low percentages of flux as a binder.
2	"	"	
3	"	"	
4	"	"	
5	"	"	
6	6 hrs -300°F		
7	"		
8	"		
9	"		
10	2 hrs. -350°F		
11	"		
12	"		
13	2 hrs -400°F		Extremely hard baked surface - Not water soluble
14	"		Extremely hard baked surface - Not water soluble
15	"		Centers of core briquettes sandy - Not water soluble
16	"		Centers of core briquettes sandy - Not water soluble
17	"		Centers of core briquettes sandy - Not water soluble
18	"		Centers of core briquettes sandy - Not water soluble
19	"	1300°F	Hard core - Not water soluble
20	"	"	Water soluble - Not enough retained strength after firing
21	"	"	Fairly hard core - Only slightly water soluble
22	"	1600°F	Hard Core throughout - Not water soluble
23	"	"	Good surface hardness - center sandy - water soluble
24	"	"	Not sufficient fired strength
25	"	"	Hard surface - center sandy - water soluble
26	"	"	Hard core throughout - water soluble
27	2 hrs -300°F	1500°F	Hard core throughout - water soluble
28	5 hrs -300°F	"	Insufficient green strength - insufficient baked strength
29	"		Insufficient green strength - insufficient baked strength
30	"		Good green strength - good baked strength
31	5 hrs -300°F		Good green strength - slightly inferior to #30
32	2 hrs -300°F		Good green strength - slightly inferior to #30
33	"		Low green strength - low baked strength
34	2 hrs -300°F		Too gummy
35	"		Fair green strength - good baked strength
36	"		Low green strength - Sandy after drying
37	"		Good green strength - fair dry strength

Exp #	Baking	Firing	Remarks Pertaining to Mold Properties
38	2 hrs - 300° F		Fair green strength - fair dry strength
39	"		Good green strength - good baked strength
40	"		Good green strength - fair baked strength
41	24 hrs - 250° F		Sticky mix - mold hard throughout after processing
42			Only fair green strength but less sticky - good after processing
43	250° F		Water soluble - fair strength
44	1 hr - 250° F		Good strength after baking
45	1 hr - 250° F		Good strength and surface scratch resistance
46	"		No strength after baking
47	"		Inferior to 45
48	"		Inferior to 45 but better than 47
49	1-1/2 hrs - 350° F	1400°	Fair fired strength
50	"	1400° F	Fairly good fired strength
51	"	1400° F	Good fired strength
52	"		Not adequate
53	"		Not adequate
54	"		Not adequate
55	"		Good strength, good surface hardness, best of series 52-57
56	3 hrs - 700° F		Not sufficient strength
57	"		Fairly good
58	1-1/2 hrs - 350° F		Good green strength, good processed strength
59	"		Inferior to alundum
60	8 hrs - 250° F	1400° F	1/2 hr. 1400° F increases scratch hardness water solubility decreased - stronger but not adequate
61	4 hrs - 400° F		Flux migrates to surface - hard but sandy center
62	"		Poor green strength - extremely hard - not water soluble
63	5 min. - 500° F		Extremely hard - not water soluble
64	"		Extremely hard - only slightly water soluble
65	"		Hard surface - sandy center - slightly water soluble
66	1 hr - 600° F		Water soluble, strength increases with measured amounts of Alundum cement, but still not completely adequate, center is sandy
67	"		
68	"		
69	"		
70	16 hrs - 150° F		Fair to good baked strength
71	"	1 hr - 800° F	Center becomes sandy with increased temp. baking
72	"	1400° F	
73	5-1/2 hrs - 800° F		4" x 4" sample - poor scratch hardness - scratch decreases as baking time increases

Exp#	Baking	Firing	Remarks Pertaining to Mold Properties
74	5-1/2 hrs - 400° F		4" x 4" high scratch resistance - hard center water soluble, however, starch not burned out
75		1400° F	4" x 4" samples - good scratch hardness - center sandy
76	6 hrs - 400° F		Extremely hard - not as soluble in water as starch systems
77	3 hrs - 600° F		Molds ruptured during baking - the reclaimed graphite contains more fines and the decreased permeability would not permit the steam to vent from the mold
78	"		
79	8 hrs - 250° F		Baking followed by torch heating faces to remove the volitiles but not glazing the surfaces, excellent scratch and mold hardness with 80 better than 79.
80	"		

The following mold processing techniques were employed:

15A - baked at 300° F for 1 hour and then fired at 1450° F until mold reached that temperature
15B - baked at 300° F for 3 hours
15C - baked at 400° F for 3 hours

Mold 15C was also lightly spray coated with flux. All molds retained dimensions during baking and/or firing. A hard, abrasion resistant surface layer formed, though below this layer the mold was sandy and easily abraded. Overall, these molds were slightly inferior in appearance and strength to standard rammed graphite molds.

The resultant castings are exhibited in Figure 26. In general, all castings have smooth surfaces, though some pinholes are evident. In general, all have good dimensional retention and good surface smoothness. Also, the molds readily dissolved in water facilitating casting "shake-out".

It was noted that improvement of mold strength and reduction of the sandy condition at the mold centers would be necessary to insure good casting quality. Experiments 12 through 26 evaluated mold compositions with additions of starch, pitch, carbonaceous cement and sodium silicate. Observations indicated:

1. Increasing flux content of the molds increased mold abrasion resistance and strength substantially, although high temperature strength was poor.
2. Large additions of sodium silicate were not satisfactory as the resultant molds were no longer water soluble and strength was not improved.
3. Additions of 10 percent pitch were unsatisfactory as molds again were not water soluble and reduced amounts of pitch additions did not improve strength significantly.
4. The composition of graphite, flux, water, and starch resulted in water soluble molds (though less soluble than those not containing starch) and improved mold strength at all flux levels.
5. Western bentonite additions improved green strength of molds.

Sandy, weak mold centers were thought to be caused by the water carrying the flux to the mold surface during oven drying of the molds. This effect was reduced substantially by processing modifications and slight variations of the composition of the mold.

Primarily, the ratios of flux, water and starch were varied as in experiments 27 through 51. Earlier experimentation indicated that this was the most satisfactory general mold system. Processing variables were investigated by baking at various temperatures up to the firing temperature and also firing at 1400° F for various periods of time.

From all considerations, mold composition number 51 is the most appealing composition evaluated for the mold system: graphite-flux-water-starch. Green strength is adequate for handling. The mold strength after baking and/or firing is satisfactory. The surface scratch hardness has a value of about 80, and the complete water solubility of the mold affords rapid shakeout after casting. Though the strength of the mold is adequate after firing and/or baking for normal handling, even higher strength levels were desired to minimize the

Figure 26 - Castings 15A, 15B, 15C with Risers Attached

mold scrap rate as a great deal of handling and working are performed on rammed graphite molds because of the individual nature of each pouring setup. An extremely tough, machinable mold is, therefore, necessary for use in conjunction with centrifugal casting. While composition 51 results in good strength levels, higher strength levels are desirable for this application. Therefore, it was decided to use this composition for experimental test molds and cores while varying mold processing techniques in an attempt to further improve mold strength. To facilitate this evaluation, a cored valve body weighing about 3 lbs. was chosen as the casting shape to be used for evaluating molds and cores under actual casting conditions.

Figure 27 shows the cope and drag sections of the rammed graphite test mold for cored valve bodies with the core in place. The mold is uncoated as shown.

The mold processing techniques used for this evaluation are tabulated in Table 3. Note that except where indicated, cores and castings were identically processed and made of the same compositions. Castings taken from molds 19A, 19B and 19C all exhibited some cold shut on external surfaces and all did not completely fill, indicating that there was insufficient superheat of the molten metal. Casting 19A exhibited the least cold shut on the external surfaces and none on the internal surfaces adjacent to the core. The internal dimensions of the casting matched the core dimensions quite satisfactorily. Casting 19A is shown in Figure 27. Some flash at the mold parting line is evident. This is a result of slight mold mismatch and is not due to mold breakdown. Castings 19B and 19C both exhibited more cold shut than 19A though casting 19B was superior to 19C.

Molds 20A and 20C were of composition 48 while Mold 20B was of composition 56 which contained 8 parts Western Bentonite. Western Bentonite was added in an attempt to increase mold strength. Mold and core 20C were lightly spray coated with flux.

Numerous cold shuts were present in casting 20A, but the core remained intact. 20B and 20C exhibited little cold shut but the cores broke down. Also 20B exhibited some surface porosity. Casting 20C exhibited least cold shut and had good retention of surface detail and dimensions.

Molds 21A and 21C were of composition 51. Mold 21B was of composition 57 incorporating Western Bentonite. Several of the compositions studied in this series of experiments included Western Bentonite as earlier results indicated increased mold strength resulted from its addition. Composition 57 offered the best mold properties of the molds containing Western Bentonite. All molds were lightly flux coated. All cores were of composition 51 and were placed into a furnace at 1000° F and brought to 1400° F in 20 minutes and fired at that temperature for approximately five minutes. All were quite hard and scratch resistant. In fact, this processing technique initially developed for core processing resulted in such strong cores that firing of experimental molds was evaluated. The resultant cores were also extremely water soluble.

Direct firing of molds does improve mold strength but not to the degree expected after observing results of direct firing of the cores. In all cases, the surfaces were quite hard. The hardening mechanism of direct firing is caused by

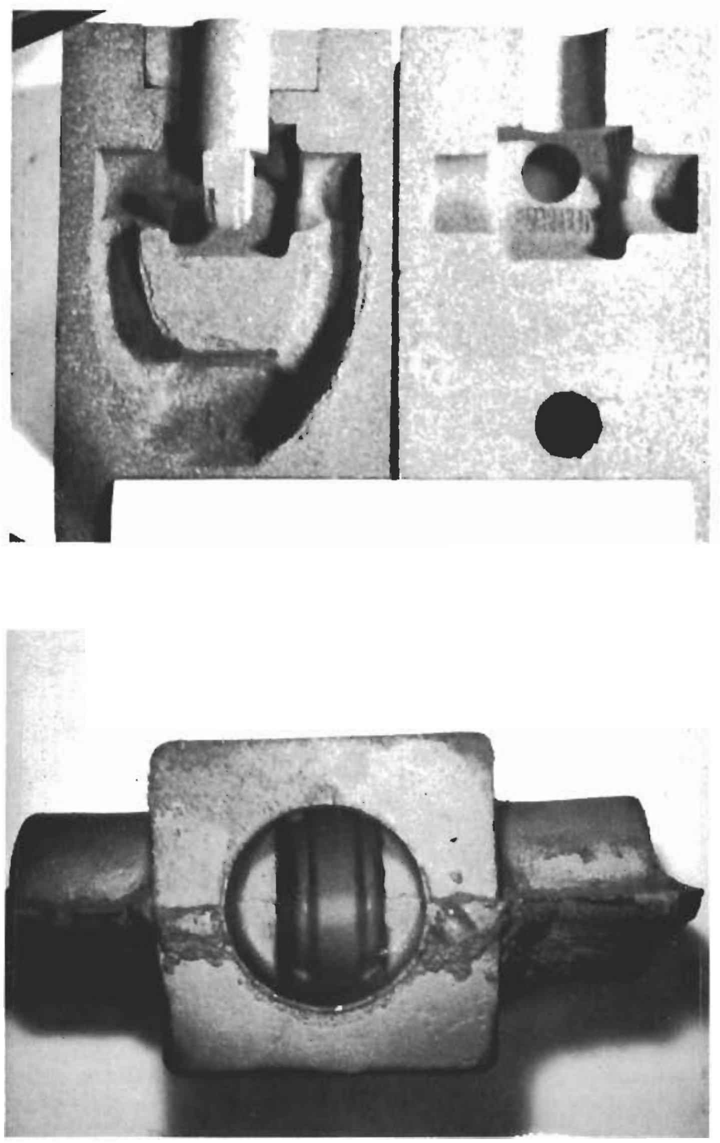


Figure 27 - Cope and Drag Sections of Rammed Graphite Test Mold with Core in Place and Resultant Casting 19A

TABLE 3

MOLD PROCESSING FOR RAMMED GRAPHITE TEST MOLDS

Mold No.	Baking	Firing	Stored
19A	600°F - 1 hour	until reached 1400°F	300°F
19B	600°F - 1 hour	900 - 1 1/2 hrs	300°F
19C	600°F - 1 hour	-	300°F
20A	700°F - 4 hours	-	300°F
20B	700°F - 4 hours		300°F
20C *	700°F - 4 hours	until reached 1300°F	300°F
21A*	700°F - 2 hours	until reached 1350°F	400°F
21B*	700°F - 3 hours	-	400°F
21C*	700°F - 3 hours	-	400°F
23A	300°F - overnight	-	300°F
23B	300°F - overnight	-	300°F
24A	-	1400°F-1 hr	400°F
24B*	-	1400°F-1 hr	400°F
24C	900°F - 3 hours		400°F
25A	-	1400°F-1 hr	300°F
25B	-	1400°F-1 hr	300°F
25C	300°F - hour	1400°F-1 hr	300°F
26A	300°F - 3 hours		300°F
26B *	300°F - 3 hours		300°F

---

* Spray flux coated

transport of the flux by the water in the liquid phase from the center of the mold to the edge during baking and/or firing. Firing appears to reduce the amount of flux carried, but does not totally eliminate the transport. However, the mold becomes progressively weaker away from the surface. Hence, direct firing is more effective for cores than molds, as core sizes are small compared to molds.

All castings from heat 21 exhibited some cold shut though 21C exhibited the most (probably resulting from being poured last from the same heat). All cores remained intact and the internal surfaces of the casting adjacent to the cores was excellent exhibiting no cold shut and good dimensional retention. Casting 21B exhibited some external surface porosity.

Castings 24A, 24B and 24C were of composition 55. They were also cored valve bodies as previously described. Mold 24A was fired at 1400° F. Mold 24B was lightly spray coated with flux using water as a carrier and then fired. Mold 24C was similarly coated but was baked for three hours at 900°F. All resulting casting surfaces were rough and exhibited surface porosity. Firing of the molds appears to reduce this tendency but does not eliminate it. The porosity is probably a result of retained moisture in the Western Bentonite.

Though the addition of Western Bentonite improved mold quality and strength, the unacceptable surface porosity exhibited in castings from molds containing Western Bentonite resulted in the elimination of this clay from consideration as a mold constituent.

Alundum cement was another mold additive evaluated as a mold strengthener. Composition 58 results in good rammability, good green strength and a hard, strong mold after firing.

Mold 25C was of composition 58. Molds 25A and 25B were of composition 51 though 25B included 10 extra parts flux. The processing of these molds is described in Table 3. Fine surface porosity was observed on the three castings poured, though 25B and 25C exhibited somewhat more than 25A.

Mold 26A was of composition 59 while 26B was of 51. 26B was lightly flux coated. The mold surfaces were heated with a torch until glazed. The cores were of composition 51. Detail of mold 26A was superior to 26B. However, some pinholing was evident on the cope side of casting 26A though no severe reaction was observed. Traces of pinholing on 26B were observed.

Linseed oil was evaluated as a mold strengthener in experiments 61 and 62. In the latter, no water was used. The results indicated that this addition was not suitable. The resulting mold properties were poor.

Experiments 63 through 65 evaluated sodium silicate additions without Western Bentonite as earlier experiments (35-37) evaluated the combination. Additions over 5 pbw of sodium silicate substantially reduced the water solubility of the mold. However, the addition of 5 pbw substantially increased mold strength.

Low temperature baking was investigated in experiments 70-72 in an attempt to improve the interior strength of molds using MITRON flux as a binder. Table 4 is a tabulation of the various mold processing techniques attempted. Baking at 200° F for 16 hours produced molds with excellent properties. Surface

TABLE 4
VARIATIONS OF MOLD PROCESSING

Composition				Processing	Remarks
Graphite	Flux	Starch	Water		
100	15	3	15	1 hour at 600°F - 2 samples processed, 1 packed in graphite	no difference in strength center slightly sandy for both techniques
100	15	3	15	3 samples processed A) 16 hours at 150°F B) 16 hours at 150°F, 1 hr, 800°F C) 1/2 hour at 1400°F	sample A was best of group, but center was easily abraded
100	25	3	15	2 samples processed A) 16 hours at 150°F	A) 3/4 inch hard surface layer, center moist
				B) 16 hours at 200°F*	B) hard throughout
				sample B was then packed in graphite, 1400°F for 1/2 hour	degraded badly
100	25	0	15	16 hours at 200°F	1/8 inch hard surface layer center sandy but not moist

*best properties obtained

scratch hardness was excellent and the molds were uniformly hard throughout. In order to evaluate the low temperature processing technique, three one inch gate valve castings were poured into molds of the following compositions.

	Composition					Processing
Exp	Graphite	Flux	Starch	Water	Alundum Cement	
70	100	25	3	15		64 hours at 200° F
71	100	25	3	16	10	16 hours at 200° F
72	100	25	0	15		16 hours at 200° F

Castings taken from these molds had extremely porous, rough surfaces. This indicated that the low temperature processing technique did not remove or burn off a sufficient quantity of the mold ingredients which are reactive with titanium.

The addition of alundum cement to rammed graphite molds of the system flux-graphite-water substantially increases mold strength and hardness. However, the presence of alundum cement in large quantities caused porosity in castings. Later experimentation (compositions 66-69) indicated that lower quantities of alundum cement did not appreciably strengthen the mold though the problem of pinholing was eliminated. Note that all the molds containing alundum cement were water soluble. However, results obtained indicated further effort was not warranted.

The results of the laboratory tests indicated that:

1. Composition 51 appears to be the most satisfactory mold composition of those evaluated in terms of molding properties, resultant casting quality, and mold solubility.
2. Immediate firing after mold or core ramming rather than after baking improves mold and core strength.
3. Western Bentonite additions improve mold properties but cause surface porosity in the resultant castings. It has been concluded that Western Bentonite is not a suitable flux-rammed graphite mold constituent for titanium castings because retained moisture causes unacceptable surface porosity in the resulting castings.
4. Large additions of alundum cement result in hard, strong, water soluble flux-rammed graphite molds. The large additions caused porosity in titanium castings and small additions do not produce acceptable quality molds.

In order to evaluate flux mold coatings and mold composition 51 for molds and cores under commercial titanium casting conditions, a second heat was made at Oregon Metallurgical Corporation. The following castings were poured into molds treated by MITRON personnel:

1. Two inch gate valve - Commercial mold mix lightly flux coated. Core made with MITRON composition. Approximate casting weight was 10 pounds.
2. Cylinder - 4 inch diameter by 5 inches in length. Commercial mold mix lightly flux coated. Approximate casting weight was 10 pounds.
3. Wafer - 6 inch diameter by 3/4 inch thick - slight taper toward outer edge. MITRON mold composition 51. Approximate casting weight was 4 pounds.

Two castings of each type noted were poured. The light flux coating was used because previous experiments indicated a light coating would be beneficial with respect to reducing carbon pickup from the mold.

The chemical analysis of the CP titanium heat was as follows:

C	0.036%	N	0.023%
H	0.006%	Fe	0.110%
O	0.23%	Ti	remainder

The primary reason for the use of the two inch gate valve was to evaluate the MITRON mix as a core. Initial results indicated this mix could be used to obtain commercially produced cored castings of excellent quality. The mold half and cores are shown in Figure 28. Core detail was excellent as shown in Figure 29. It required but a matter of seconds to remove the core by washing it out with a stream of water contrasting to approximately 1/2 hour required for typical core knockout. A slight amount of graphite adhered to the surface of the cored section but this material was rubbed off with no difficulty. Sand blasting produced very clean core surfaces exhibiting excellent detail.

The flanges and the bonnet of this casting were machined, a normal operation to complete a cast valve body. The machined surfaces exhibited no porosity. In addition, no cold shut was observed on the surfaces in the as-cast condition both on the external portions of the valve and on those surfaces adjacent to the core.

The second valve body was evaluated by destructive techniques at both Oremet and MITRON with the following results:

1. No evidence of excessive carbon pickup or carbide formation anywhere on the casting was found during the evaluation at Oremet.

2. After cutting the casting in half and X-ray evaluation, there was no evidence of any deleterious porosity.

3. There is very slight roughness of the surface in some areas probably due to slight removal of the flux binder. In no way, however, can this be construed as deleterious.

4. The casting is acceptable as a commercial valve body which could be supplied to a customer.

The wafer castings taken from molds made with the MITRON mix did not exhibit adequate surface quality because the molds were not fired properly. This resulted in the mold washing into the molten metal. No conclusive results could be obtained from the surface of these castings.

Carbon analysis as a function of distance from casting surface was performed on the cylinder casting. The results are tabulated and graphically presented in Figure 30. Specimens for analyses were taken at 0.003 inch intervals of depth from the surface. A total of twelve specimens were taken. In some instances, the representative specimen weight allowed two determinations to be made. The linear portions of the curve were extrapolated and thus indicated

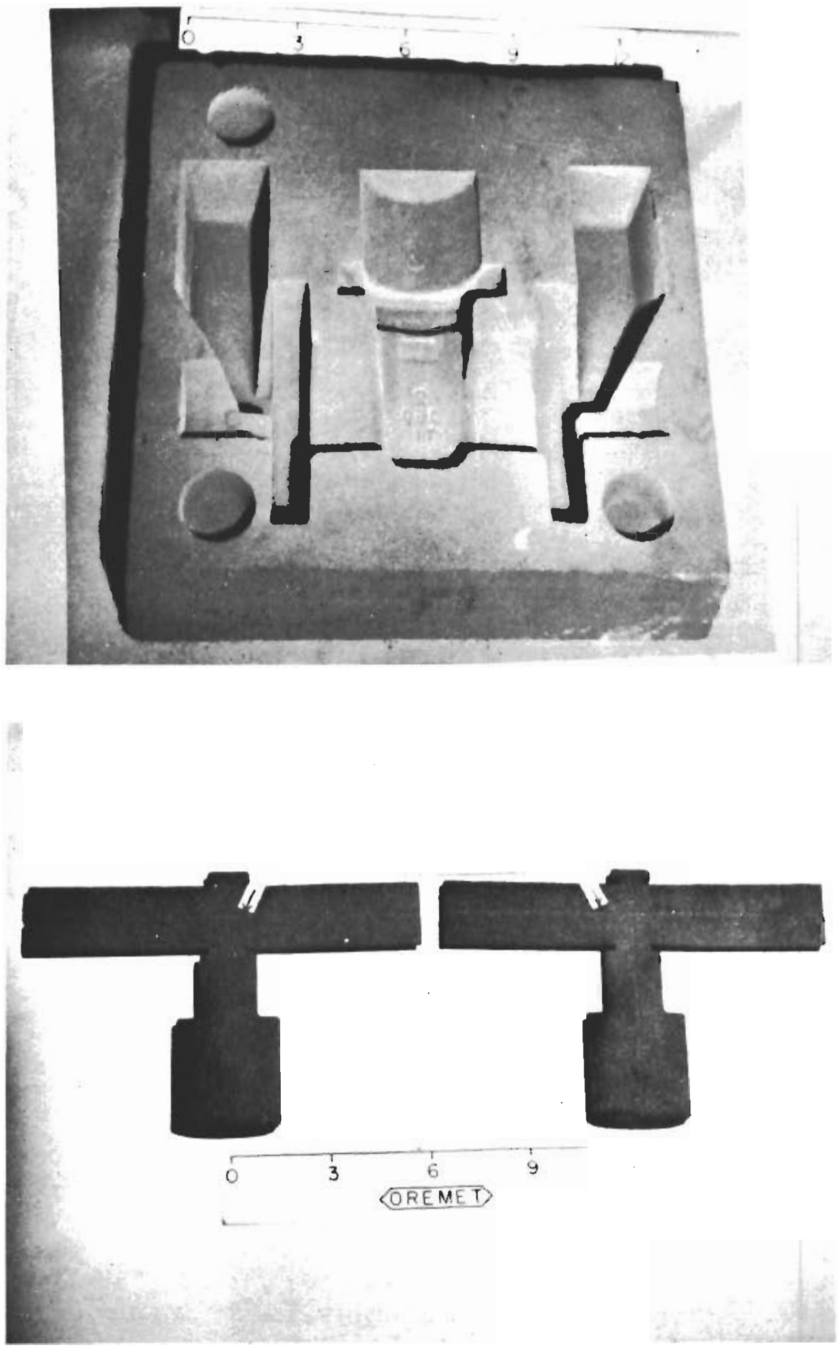
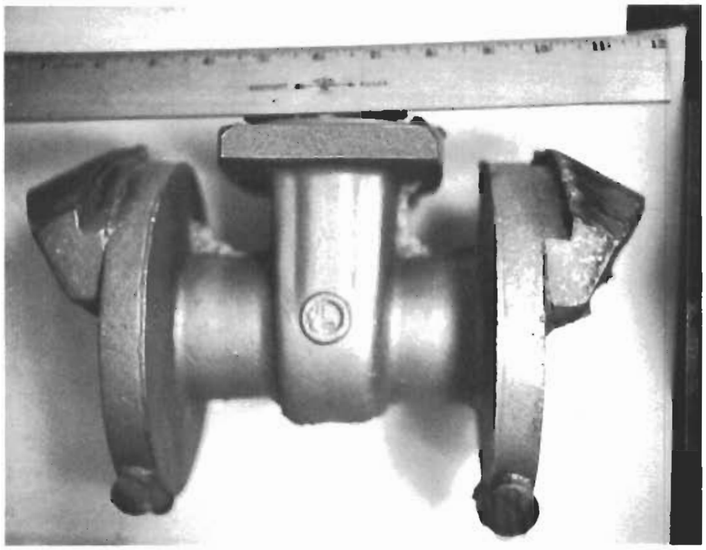


Figure 28 - Mold Half and Core Halves for Two Inch Gate Valve Casting



Gate Valve Casting Obtained at Oremet

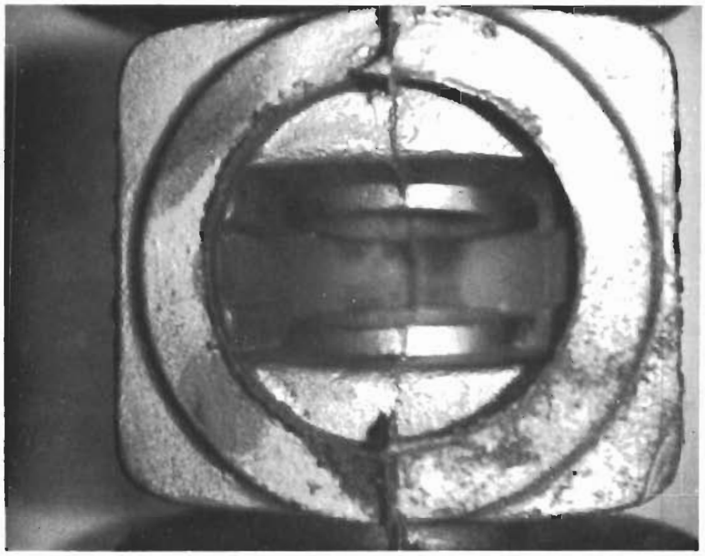
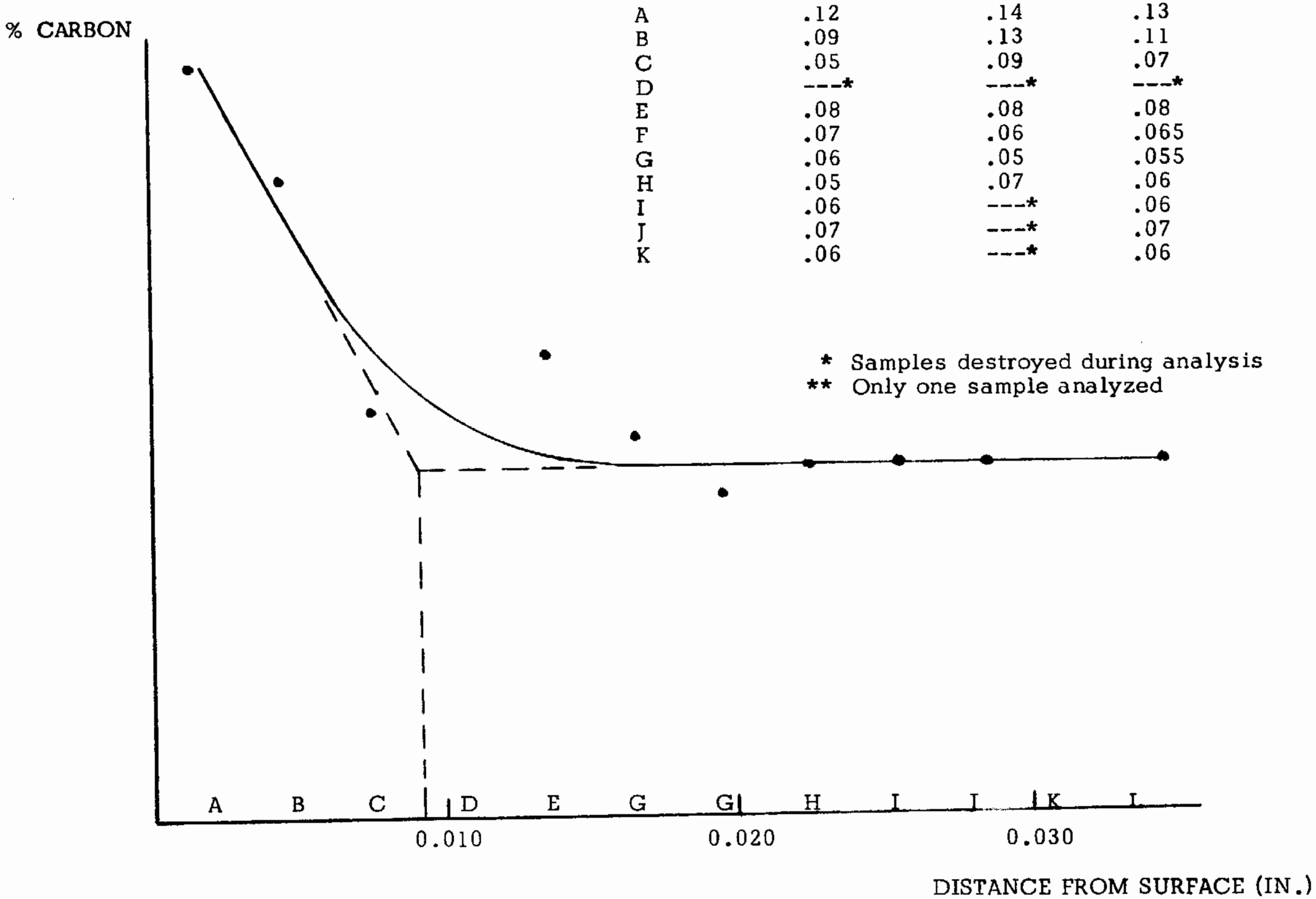


Figure 29 - Cored Section of Two Inch Gate Valve Obtained at Oremet



Sample	Sample 1	Sample 2	Average
A	.12	.14	.13
B	.09	.13	.11
C	.05	.09	.07
D	---*	---*	---*
E	.08	.08	.08
F	.07	.06	.065
G	.06	.05	.055
H	.05	.07	.06
I	.06	---*	.06
J	.07	---*	.07
K	.06	---*	.06

* Samples destroyed during analysis
** Only one sample analyzed

Figure 30 - Carbon Content as a Function of Distance from Surface from Cylinder Casting

that carbon penetrated no deeper than approximately 0.009 inch. Note that samples closer to the surface have higher carbon content, but even near the surface, the total carbon present is not high.

Tensile specimens were machined from the cast cylinder and the 6 inch diameter wafer casting. These results are tabulated in Table 5. These tensile properties differ somewhat from those discussed later as these castings are somewhat larger resulting in slower solidification rates and hence larger grain size. Some porosity was observed at the fracture surfaces of Sample A; this caused the reduced elongation and reduction in area obtained. It should be emphasized that a completely acceptable cored valve body casting was obtained with a core which did not have the most desirable green strength and center hardness.

A third heat was made at Oremet with the following objectives:

1. To further evaluate MITRON rammed graphite molds and cores under commercial foundry conditions.

2. To evaluate coated zircon shell and graphite shell molds containing flux under commercial foundry conditions.

3. To obtain test bars for a quantitative comparison of various mold processing variables.

In order to achieve these objectives, the castings tabulated in Table 6 were processed. Figure 31 is a schematic of the mold locations and the gating system used to obtain the desired castings.

The composition used in all molds and cores employing MITRON flux as a binder was:

Graphite	100 parts by weight
Flux	20 parts by weight
Starch	1 part by weight
Water	15 parts by weight

The slight increase of flux content over composition 51 compensates for the higher percentage of fines in the reclaimed graphite used by Oremet. The MITRON flux was used as a binder for all but two of the castings poured. Mold 10, a one inch gate valve, was made with the commercial molding technique, but the core was made with the MITRON flux binder. Mold 11, tensile plugs, was made with the commercial mix and used as a standard.

For this heat, every feature of mold and core making worked in an excellent manner and extremely good mold detail was obtained. No major problems occurred until the molds were assembled. The flux-rammed graphite mold after baking has a 1/16 inch thick hard surface. The commercial mold is uniformly hard throughout. Therefore, the molds lacked sufficient baked strength throughout to satisfy the requirements of the present gating technique at Oremet. Presently, gates are cut into the backs of the molds. When the metal is poured through the areas cut into the MITRON mold, the loose graphite particles errode and in some cases are found as inclusions on the cast metal surfaces. An attempt to bond these loose graphite particles was made by

TABLE 5

TENSILE DATA FROM CYLINDER AND WAFER CASTINGS

Sample	Castings	YS	UTS	%E	%RA
A	Wafer	66KSI	85.5KSI	6	11.8
B	Wafer	68.5	87	14	18.5
C	Cylinder	66.5	86	13	18.5
D	Cylinder	73	85	15	15.5

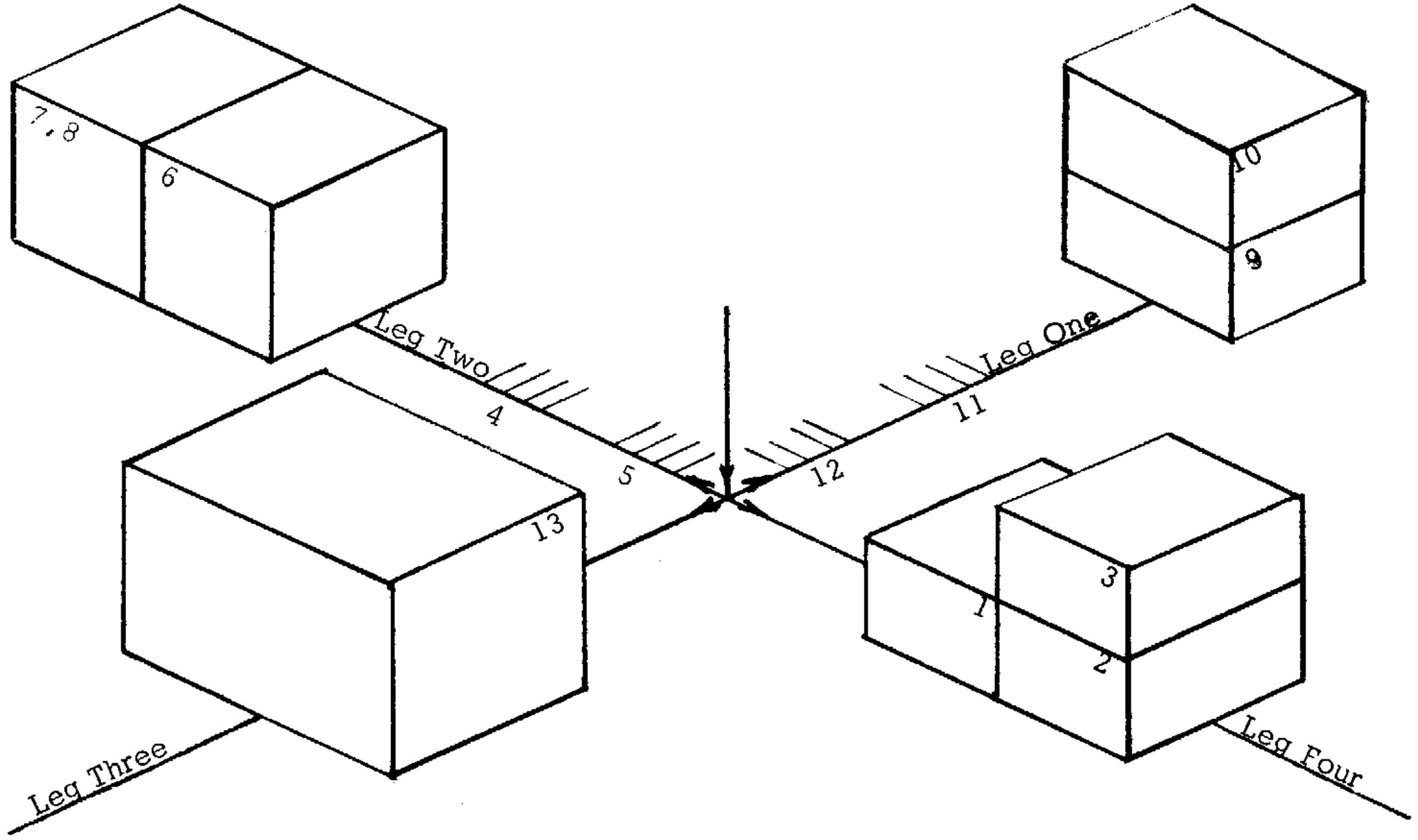


Figure 31 - Schematic of Mold Locations and Gating System

TABLE 6

CASTINGS PROCESSED DURING SECOND HEAT

Mold	Mold Type	Dimensions	Mold	Binder	Coating	Processing
1.	cylinder	4" dia. x 5" long	Rammed Graphite	MITRON	light flux	fired at 1400°F (oven), 15 min.
2.	cylinder	4" dia. x 5" long	Rammed Graphite	MITRON	light flux	looked at 600°F, 1 hour
3.	cylinder	4" dia. x 5" long	Rammed Graphite	MITRON	light flux	fired at approx. 1400°F (torch)
4.	tensile plugs	4" long	Rammed Graphite	MITRON	-	fired at 1400°F (oven), 6 min.
5.	tensile plugs	4" long	Rammed Graphite	MITRON	-	baked at 600°F, 1 hour
6.	cored valve body	1" gate	Rammed Graphite	MITRON	light flux	fired at approx. 1400°F (torch)
7.	cylindrical step		Zircon Shell	7% flux 3% phenolic	-	standard shell processing
8.	cylindrical step		Graphite Shell	15% flux 12% phenolic	-	standard shell processing
9.	cored valve body	1" gate	Rammed Graphite	MITRON	light flux	baked at 600°F, 2 hours
10.	cored valve body	1" gate	Rammed Graphite	Commercial	light flux	standard Commercial Processing
11.	tensile plugs	4" long	Rammed Graphite	Commercial	-	standard Commercial Processing
12.	tensile plugs	4" long	Rammed Graphite	MITRON	-	fired at approx. 1400°F (torch)
13.	impeller core	10" dia.	Rammed Graphite	MITRON	-	baked at 600°F

painting and spraying the machined gate areas with a mixture of flux and water and then baking. This technique did harden the areas but it was impossible to reach all of the machined surfaces and so errosion did occur.

Another problem associated with mold assembly is the strapping of the mold halves to the pouring table. A mold that does not have sufficient strength throughout tends to break and the edges crumble into the mold cavity prior to pouring. These pieces of mold produce defects in the castings. Some difficulty was experienced with the MITRON molds because the pressure of the bands tended to crush the edges of the mold cavity.

After the molds were attached to the pouring table, the entire assembly was baked at 250° F to remove any moisture which was picked up during the assembly. Commercial purity titanium was consumable electrode melted and centrifugally cast. The resulting castings are shown in Figure 32 after removal of the mold materials. In general, the results of the castings indicated no gross reaction between titanium and the mold areas. The cored sections were also excellent with the only imperfections resulting in areas where the core broke down and sections of the mold were penetrated by the molten metal. Figure 33 illustrates the mold and core. The thin sections of the core were weak resulting in mold breakdown.

Three cylinder castings were made with various mold processing cycles. No significant differences in surface finish were noted for the three techniques attempted. Cylinder casting 3 is shown in Figure 34. The three cylinders were analyzed to determine the depth of carbon penetration. The results plotted in Figures 35, 36, and 37 indicate the depth of carbon penetration into castings taken from rammed graphite molds containing flux is essentially less or, at most, equivalent to the depth of carbon penetration into castings taken from standard rammed graphite molds. This can be shown by comparing these results to Figure 30, carbon analysis of a casting from a lightly flux coated commercial mold. Further, it is generally stated that carbon contamination penetrates 0.010 inches per inch of casting thickness for castings from machined graphite molds and even more rapidly for castings from expendable graphite molds. As these cyclinders are four inches in diameter, the carbon penetration is substantially less than would be expected from a casting this size.

Quantitatively, the carbon content data is questionable. The difference in apparent carbon content between that shown by these specimens and that obtained by the previous carbon determination of the cylindrical castings described previously results from sampling difficulties which of necessity introduce some surface material into each sample,because it was impossible to center the cylinder in the lathe. This, of course, would affect the carbon content of each sample. The results, however, indicate that this effect is quite constant from sample to sample, and hence does not affect the determination of depth of carbon penetration as this determination is not a function of quantitative accuracy of the analyses, but rather is determined from a qualitative comparison of the individual chemical analyses datum.

Tensile specimens and Charpy impact specimens were also machined from the three cylinder castings. The results are tabulated in Table 7.

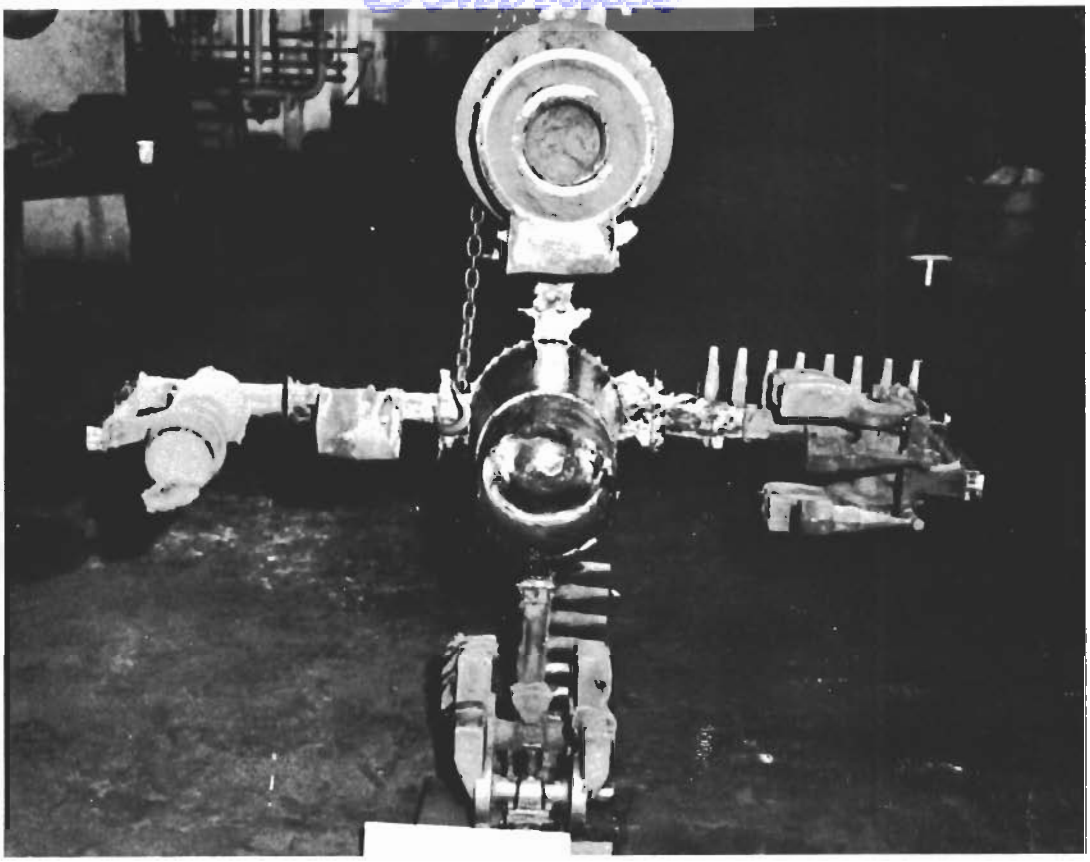


Figure 32 - Castings Poured on Heat 3 after Removal of Mold Material

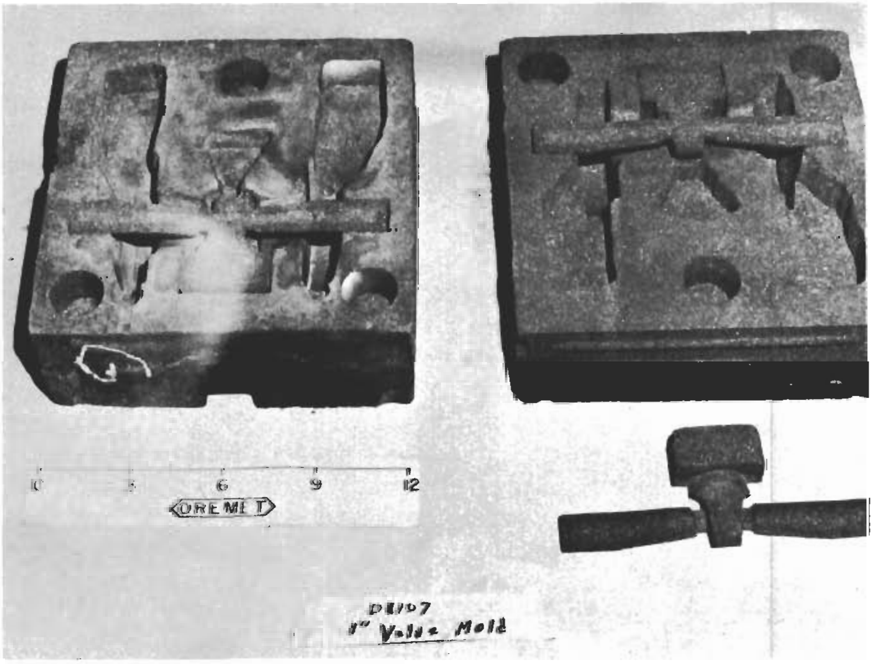


Figure 33 - One Inch Valve Body Halves with Cores in Place

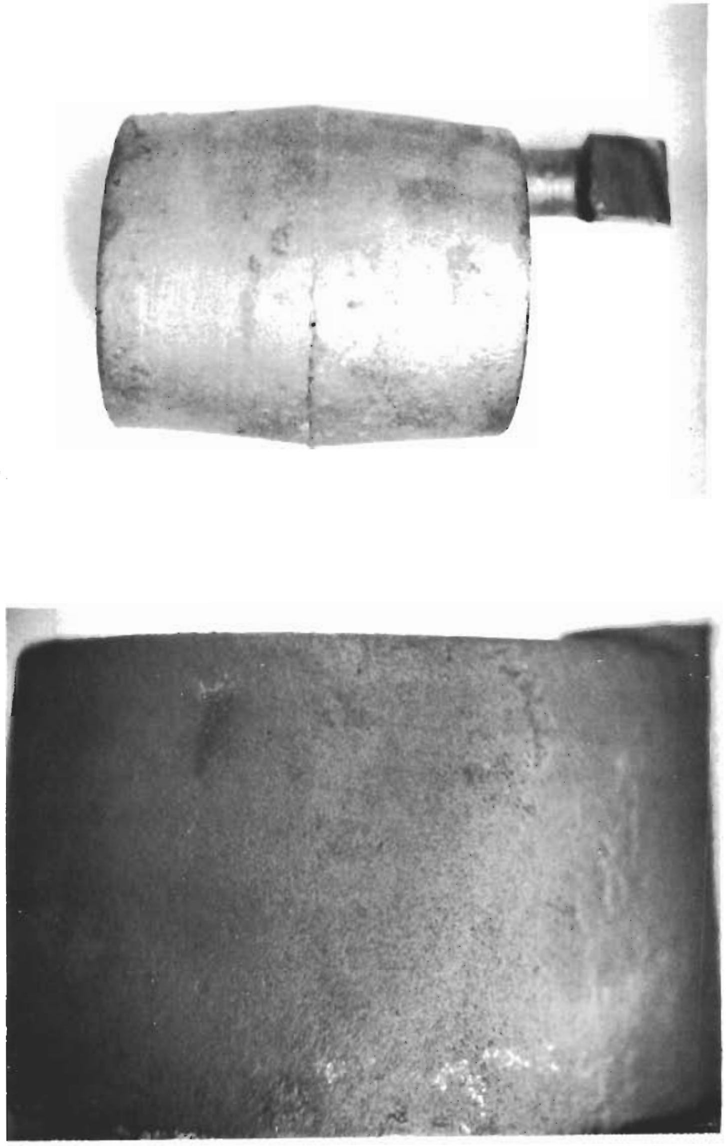
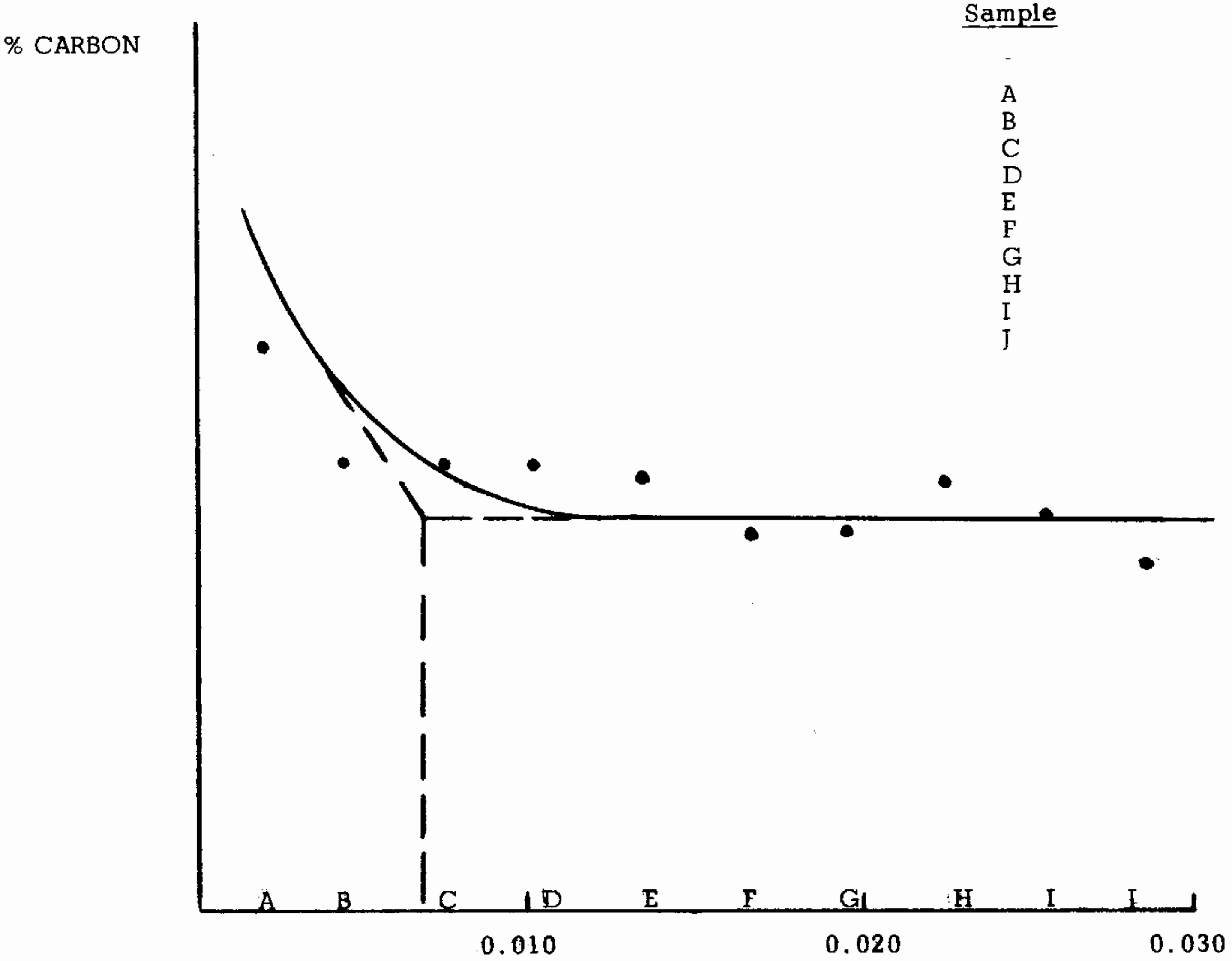
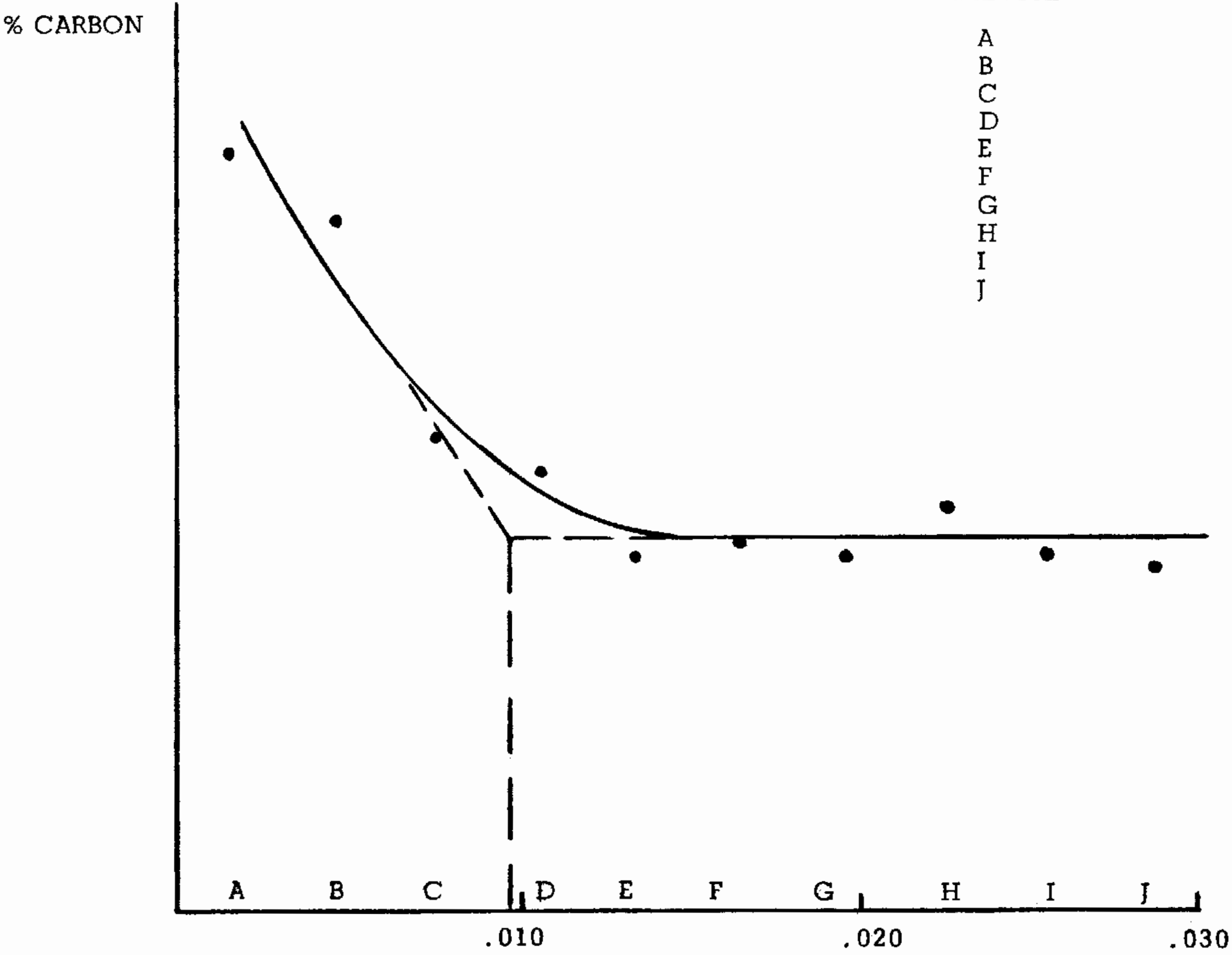


Figure 34 - Cylinder Casting 3, Representative Surface Area



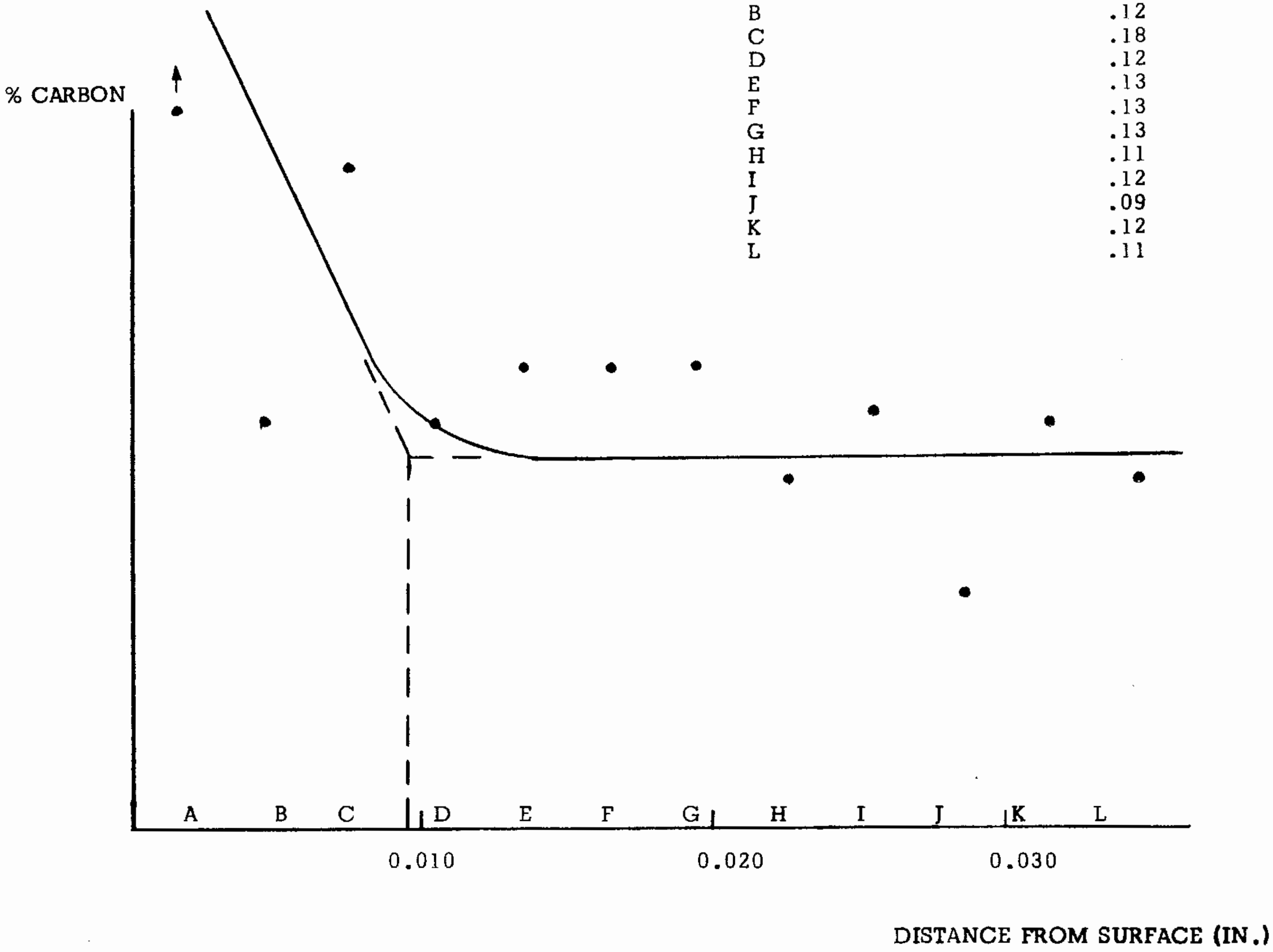
Sample	Carbon
A	0.24%
B	.17
C	.17
D	.17
E	.16
F	.13
G	.13
H	.16
I	.14
J	.11

Figure 35 - Carbon Content as a Function of Distance from Surface from Cylinder Casting 1



Sample	Carbon
A	0.45 %
B	.41
C	.28
D	.26
E	.21
F	.22
G	.21
H	.24
I	.21
J	.20

Figure 36 - Carbon Content as a Function of Distance from Surface from Cylinder Casting 2



Sample	Carbon
A	0.31%
B	.12
C	.18
D	.12
E	.13
F	.13
G	.13
H	.11
I	.12
J	.09
K	.12
L	.11

Figure 37 - Carbon Content as a Function of Distance from Surface in Cylinder Casting 3

TABLE 7

TENSILE AND IMPACT PROPERTIES OF CYLINDER CASTINGS 1, 2, and 3*

Tensile Properties

Casting	Specimen	YS	UTS	%E	%RA
1	A	75 ksi	87.5 ksi	7.1%	17.4%
1	B	85	89	9.6	6.7
2	A	85	98.5	9.2	7.5
2	B	83	97	8.9	10.4
3	A	76.4	88.4	9.6	10.3
3	B	82	90.5	9.6	14.5

Charpy Impact Strength

Casting	Specimen	Impact Strength
1	A	14 ft lbs.
1	B	12
2	A	8
2	B	8
3	A	12
3	B	13

* All molds were rammed graphite with MITRON flux as the binder.

All mold cavities were lightly flux coated.

1 - oven glazed at 1400°F for 15 min.
2 - baked at 600°F for 1 hour
3 - torch glazed at approx. 1400°F

The samples taken from castings 1, 2, and 3 exhibit equivalent tensile properties while the Charpy samples taken from castings 2 exhibit lower impact strength than those taken from castings 1 and 3. Examination of the specimen fracture surfaces indicated a relatively fine grain structure in samples from casting 2 compared to castings 1 and 3. The test samples from casting 2 were taken closer to the casting surface and this would account for the difference in properties.

Tensile specimens were machined from the tensile plugs; the location of the specimens in each plug is schematically shown in Figure 38. Four sets of tensile plugs, each containing four samples, were cast. Tensile plugs designated 11 are the controls. The mold was made of the standard commercial mix. The others employed MITRON flux as a binder. Mold 4 was oven glazed. Mold 5 was oven baked. Mold 12 was torch glazed.

These tensile specimens have been tested in the as-cast condition and the results are tabulated in Table 8. Note that as all specimens are from similar castings; the results are directly comparable as chemical composition and solidification rates, hence grain size are approximately the same for each specimen. All molds and processing techniques appear comparable after consideration of the data. The tensile properties of test bars from molds containing MITRON flux are equivalent to the tensile properties of test bars obtained from molds using standard rammed graphite binders.

The impeller casting attempted was completely filled, but the surfaces were extremely rough. This part is extremely complex and the strength of the MITRON core was not sufficient to produce a good quality casting with a smooth surface for this highly complex shape.

The fourth heat at Oregon Metallurgical Corp., Albany, Oregon, was used to evaluate the applicability of molds containing flux for large castings poured under static conditions. Two compositions and three processing techniques using both high and low temperature baking were studied and compared to standard Oremet molds. Table 9 summarizes the molds and cores processed. Two molds containing alundum cement were included to verify under actual commercial conditions the laboratory conclusion that the alundum addition was not acceptable. This was done because the mold properties with the alundum additive were extremely attractive.

No problems occurred during all phases of mold and core processing. Ramming characteristics and green strength of flux containing molds were essentially equivalent to molds made with the commercial composition. Similarly, mold handling was no problem. Mold surface hardness was adequate after processing. Scratch hardness tests yielded valves of 70 to 80 for the MITRON molds, while the commercial molds generally register from 90 to 95.

The resultant castings were not satisfactory. A great deal of porosity was present, especially in the tensile plugs. In addition, all castings from molds with the flux binder had exterior surfaces which appeared to be associated with a reaction of titanium with a residual volatile, either water or starch, both of which would be associated with insufficient processing. The interior casting surfaces adjacent to the cores were quite smooth and free of porosity compared to the external surfaces. This is attributed to the less

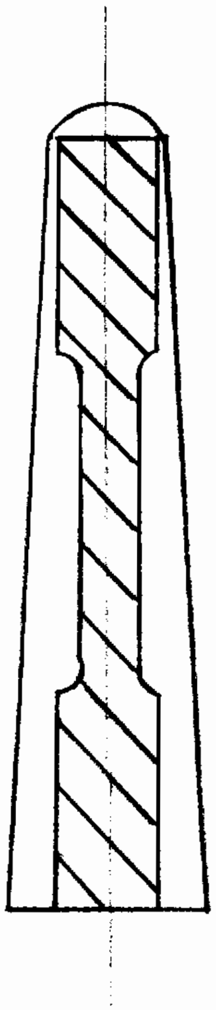


Figure 38 - Schematic of Tensile Specimen Location in Tensile Plugs.

TABLE 8

TENSILE DATA FROM TENSILE PLUGS

Specimen	YS	UTS	%E	%RA
11 A	76 KSI	97 KSI	18	25
11 B	76	104	17	28
11 C	74.5	96.5	19	25
11 D	75	99	16	24
Average Properties Commercial Binder: Control	75.4	99.1	17.5	25.5
4 A	74.5	95	17	18.5
4 B	74	96.5	16	22
4 C	82.5	96	16	24
4 D	76	95	15	17
Average Properties MITRON Binder Oven Glazed	76.7	95.6	16.0	20.4
5 A	75	97	21	22.5
5 B	77	98	16	21
5 C	75	97	18	25
5 D	75	104	17	23.5
Average Properties MITRON Binder Oven Baked	75.5	99.0	18.0	23.0

TABLE 8 (Continued)

	Specimen	YS	UTS	%E	%RA
	12 A	76	98.5	17	22.5
	12 B	73	97	14	18.5
	12 C	77	97.5	19	24
	12 D	73	98.5	17	25
Average Properties MITRON Binder Torch Glazed		74.8	97.8	16.8	22.5

TABLE 9
MOLDS AND CORES PROCESSED DURING FOURTH HEAT

	TYPE	COMPOSITION	PROCESSING
I.	3 inch gate valve mold	2	D
	associated core	2	B
II.	Allison mold	1	A
	associated core	2	B
	mold inserts	1	A
III.	Bracket Molds		
	a)	2	B
	b)	2	C
	c)	3	B
	d)	1	A
IV.	Tensile Molds		
	a)	2	B
	b)	2	C
	c)	3	B
	d)	1	A

Mold Compositions:

1) Standard Commercial

2) 100 graphite pbw
   20 flux
   3 starch
   15 water

3) 100 graphite
   20 flux
   3 starch
   15 water
   10 alundum cement

Mold Processing:

A) Standard Commercial

B) 800°F-1 hr. bake; 225°F overnight

C) 225°F drying overnight

D) 800°F, 1 1/2 hr. bake; 225°F overnight massive nature of the cores compared to the molds; this would afford more complete removal of volatiles in the same processing time. No differentiation of casting appearance could be correlated to molds containing alundum cement.

To specifically determine the origin of the surface reaction observed, several laboratory tests (73-76) were performed. In order to determine the effects of time and temperature on mold processing 4 inch cubes of the same composition were used for experiments 73 to 75.

The weight of each ingredient was carefully controlled and weight loss as a function of baking time was determined. The results are plotted in Figure 39. At a baking temperature of 225° F, eight hours are required for the complete removal of water. At 400° F, two hours are required for the complete removal of water. At both temperatures, no starch is removed. At a baking temperature of 800° F, two hours are required for the removal of both starch and water. One half hour at 1400° F (firing temp.) is required for the complete removal of starch and water.

A comparison of the processing time and temperatures used at Oremet for the fourth heat and the results obtained with the laboratory samples indicated that the molds were processed for a sufficient length of time to remove the water but not the starch. Baking overnight at 225° F was more than sufficient for the removal of water.

Based upon the results of the laboratory samples, two additional heats were poured at Oremet using a slightly modified flux rammed graphite processing technique. Because of the problems previously encountered with the changing fines content of the graphite aggregate used at Oremet, six formulations were mixed and rammed into bracket molds for evaluation. This mold is shown in Figure 40. The following compositions were selected for actual pouring.

	Mix 70	Mix 80
Graphite	100 pbw	100 pbw
Flux	25	20
Starch	3	0
Sodium Silicate	0	10
Water	15	15

These mixtures were determined experimentally to be the most suitable for use with the reclaimed graphite used at Oremet. The major portion of MITRON's laboratory work was performed with graphite which had not been reprocessed. A decrease in water content from 15% to 10% was necessary because the decreased permeability resulting from the increased fines content of the reclaimed graphite did not allow the steam to vent from the center of the molds during baking. This caused the mold surfaces to rupture during heating. It was found that by reducing the moisture content to 10%, satisfactory molds were produced.

Two bracket molds made of composition 79 and 80 were baked at 250° F for eight hours followed by heating but not glazing the mold cavities with a torch. The object of this treatment was to retain the interior mold strength which can be produced with a low temperature bake and then remove the

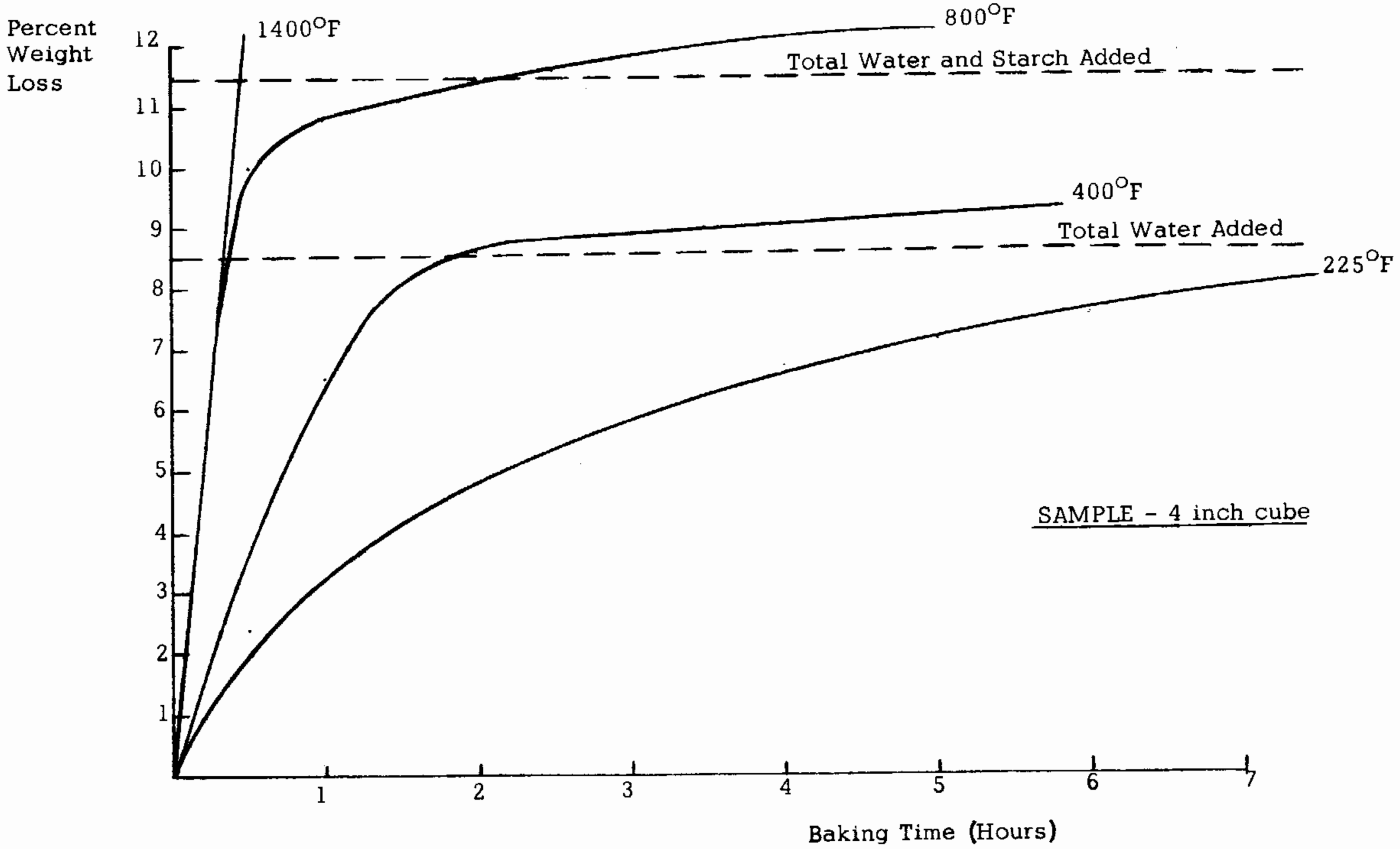


Figure 39 - Effect of Time and Temperature on Water and Starch Content of Molds.

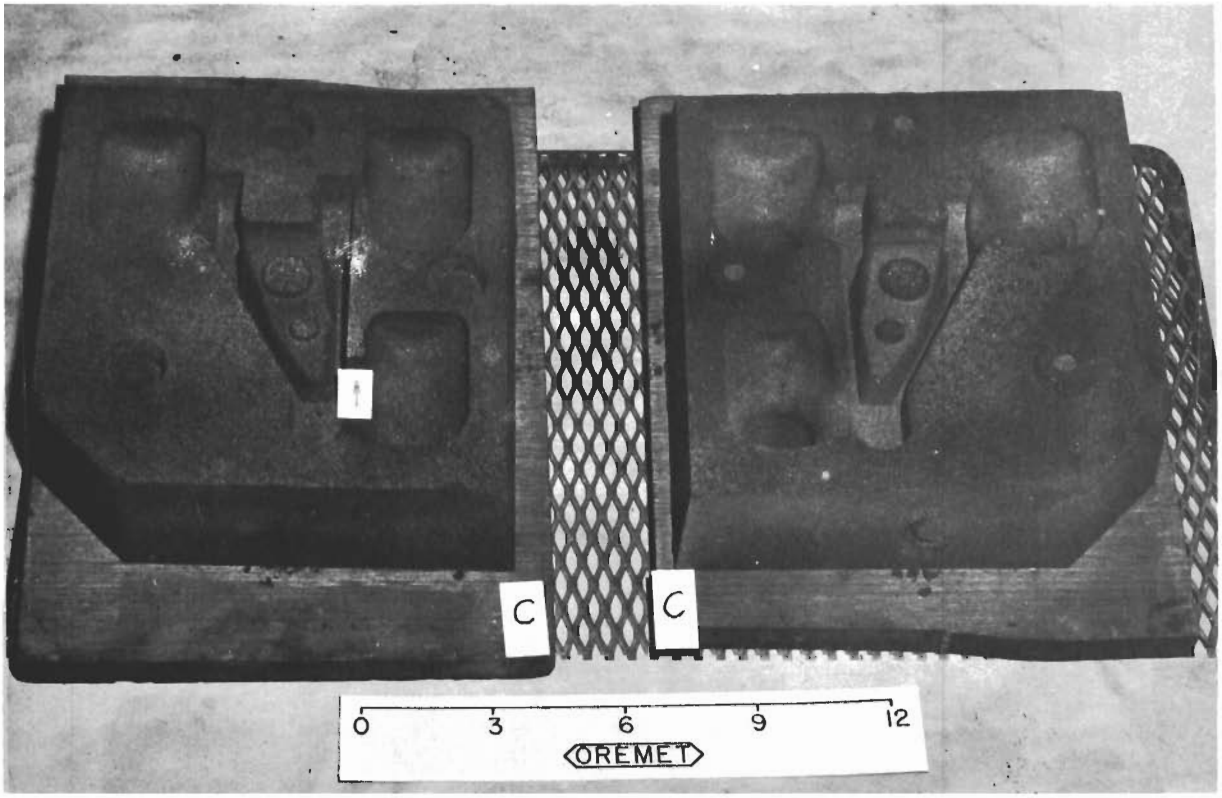


Figure 40 - Experimental Bracket Mold

volatiles (starch) from the surface of the mold cavity by heating the surface to a temperature above 800° F. The graphite on the surface of the mold cavity is protected from oxidation by the flux.

CP titanium was centrifugally cast into these molds using standard techniques and the resulting castings were excellent. Figure 41 is the bracket casting made with Mix 79 after riser removal. Figure 42 exhibits the bracket casting made with composition 80 prior to riser removal and final cleanup. There is obviously no reaction of the titanium with the mold materials. In many areas, the cast surface is equivalent to that which would be would be expected from a shell mold. Many of the surface defects commonly caused by graphite molds are not present. Radiography of this casting showed that it was sound. The casting taken from mold Mix 80 was also excellent.

In order to further evaluate mold Mixes 79 and 80, two Allison molds (Figures 43, 44, 45, 46) were rammed and processed using the procedures outlined for the bracket molds. A core made with the standard commercial composition was used with the mold made with MITRON Mix 79. Both core and mold for the second casting were made with MITRON Mix 80. Figure 47 exhibits two views of the casting taken from mold Mix 80 and again the results were excellent. The finish on this casting was almost equivalent to that obtained on the bracket. It required approximately 10 minutes to completely wash the core from the casting.

Tensile plugs were obtained on the sixth heat representing MITRON' s compositions 79 and 80. Control plugs from the standard commercial mix were also obtained and labeled #6. Tensile plugs were also obtained from the fifth heat using the commercial mixture. These were labeled #5. The results of the tensile tests are listed in Table 10. The properties of the tensile plugs made with the MITRON composition are essentially equivalent to the properties obtained with the standard commercial mix.

A series of chemical analyses was performed to determine the depth of carbon penetration into the bracket casting using mold Mix #80. The data is plotted in Figure 48. The surfaces of the casting were set up parallel to the cutting cool and successive layers were milled off and the chips collected. The first layer was 0.004 inch and the subsequent layers were 0.003 inches. The results obtained indicate that the depth of carbon penetration is essentially equivalent to that obtained on other castings made using the MITRON flux as a binder, that is, approximately 0.010 inch.

Figure 49 is the Allison casting made with Mix 79. This casting was made with a core of the standard commercial composition,e.g.,not containing MITRON flux. No attempt was made to remove the core since it is quite hard and is not water soluble. The exterior surfaces of this casting are excellent though no direct evaluation of this casting can be made other than surface condition as two different systems were used.

In general, the results of this heat indicated that the mold composition incorporating MITRON flux and the processing techniques developed produce excellent quality titanium castings under commercial conditions.

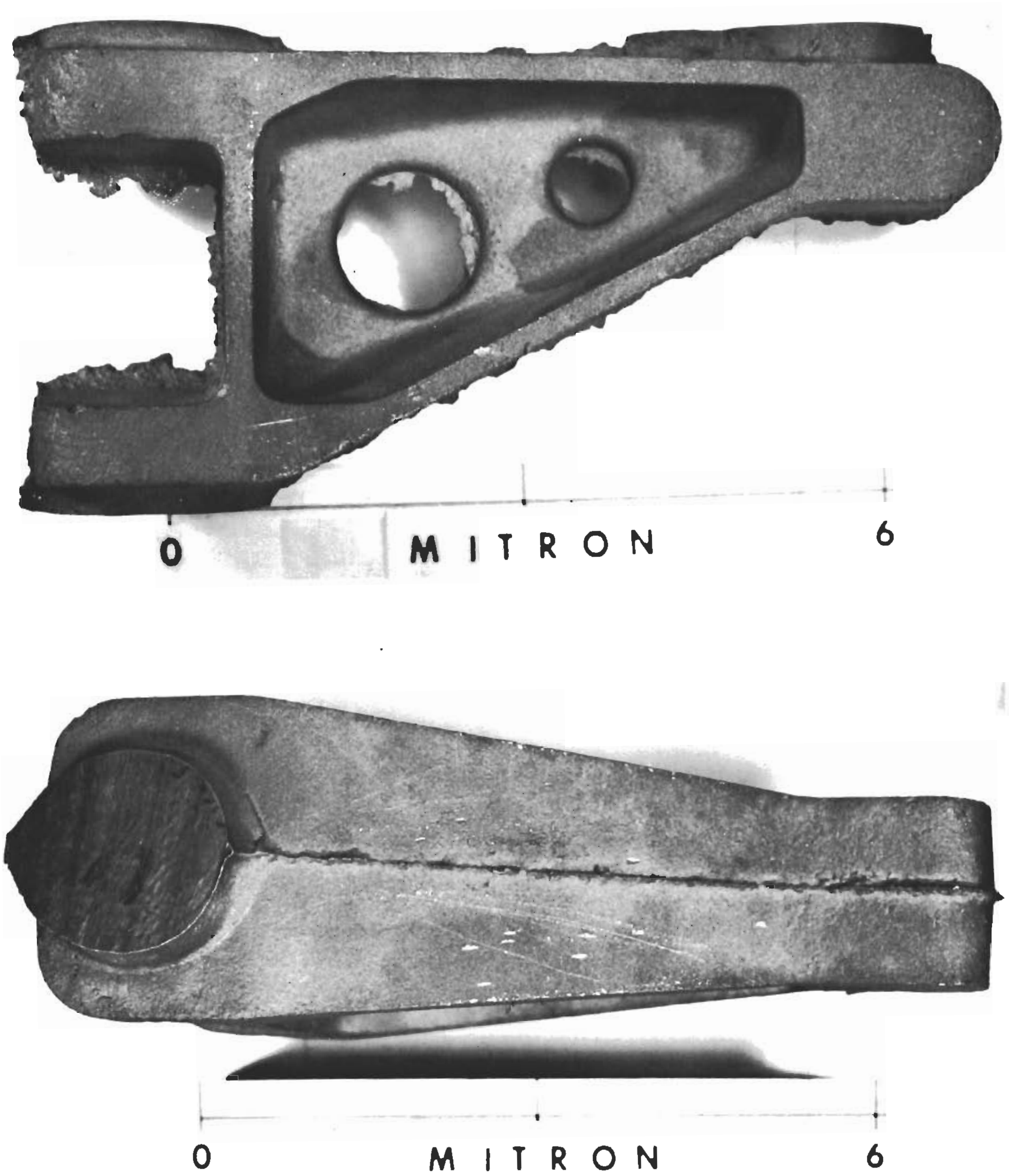


Figure 41 - Experimental Bracket Casting - Mold Mix 79

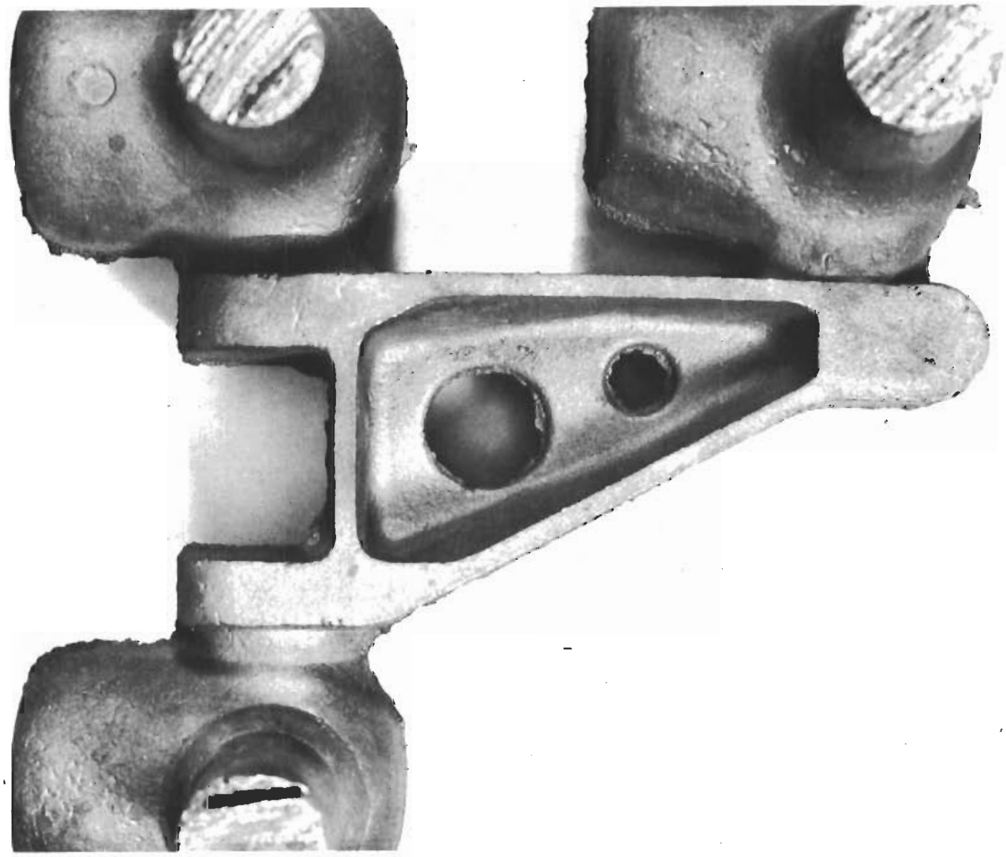


Figure 42 - Experimental Bracket Casting - Mold Mix 80

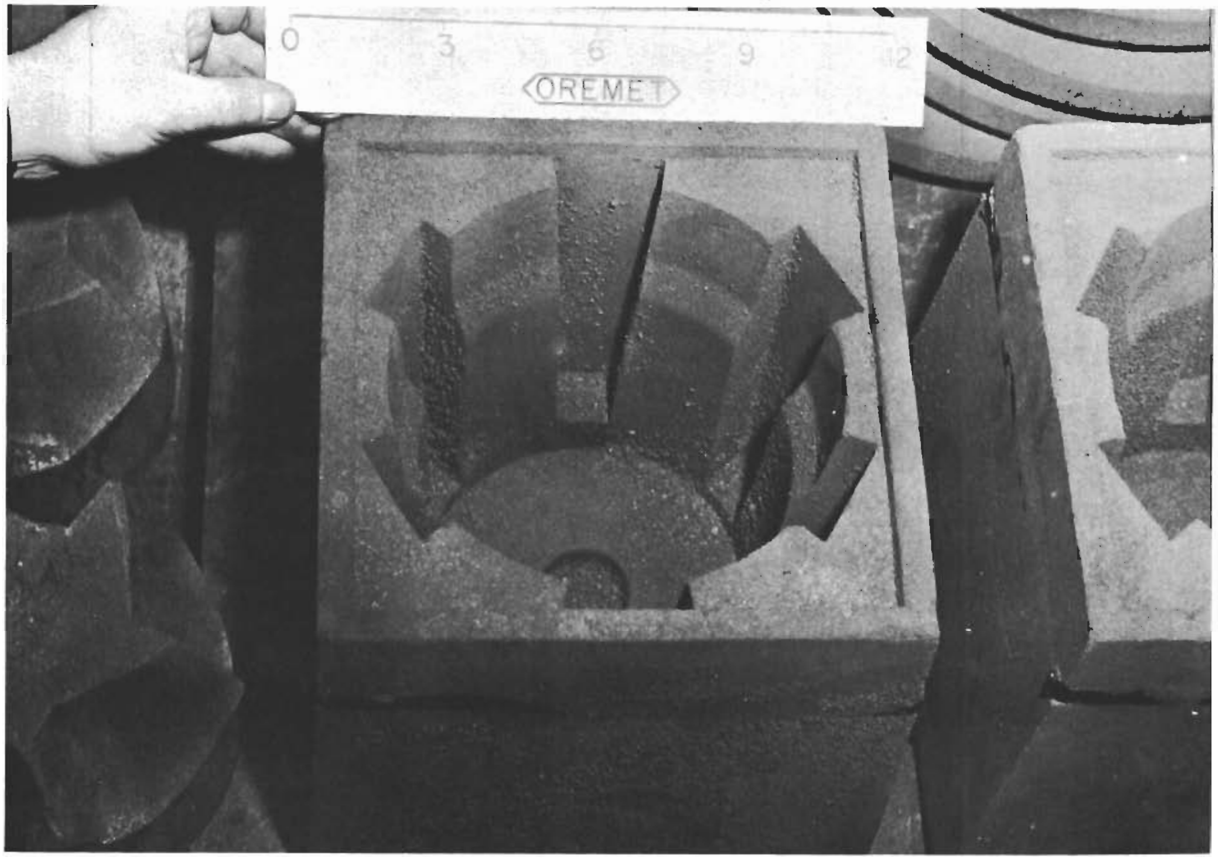


Figure 43 - Allison Aerospace Mold Without Inserts

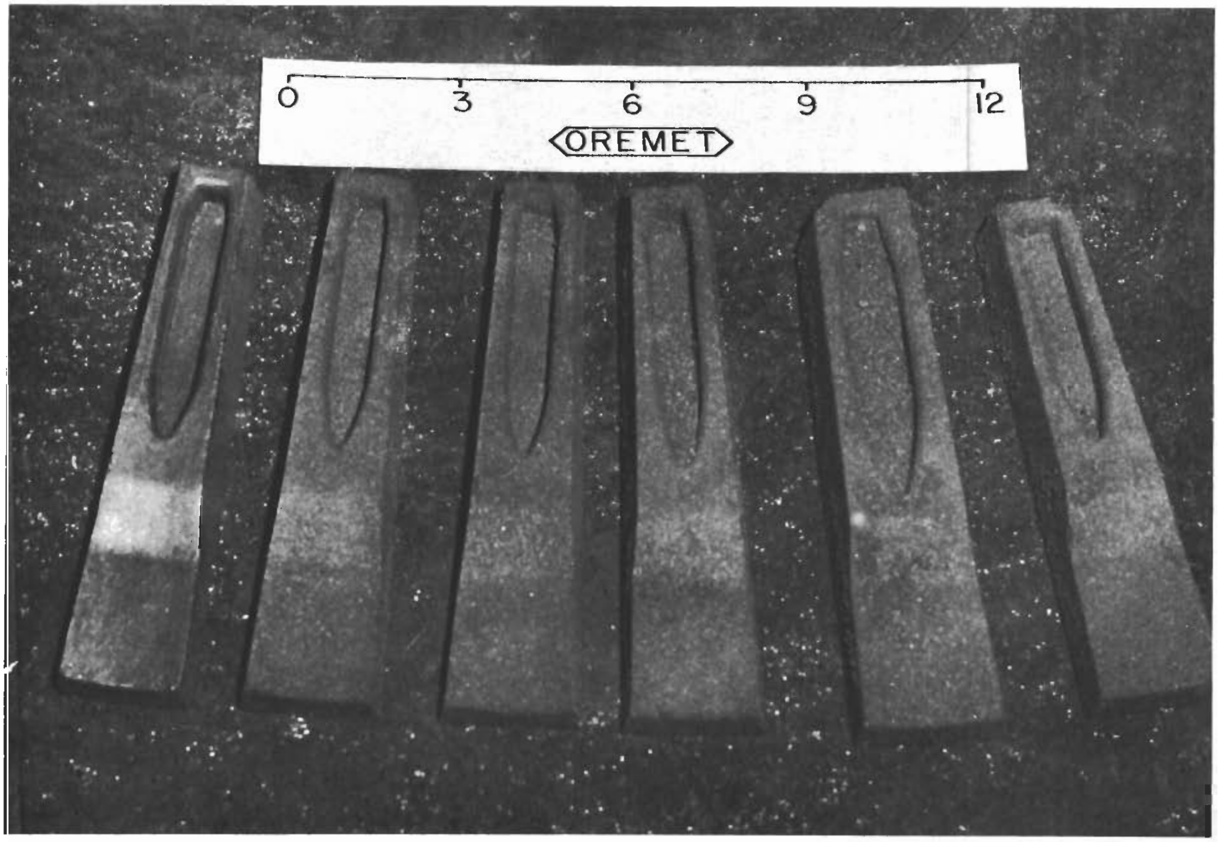


Figure 44 - Inserts for Allison Aerospace Mold

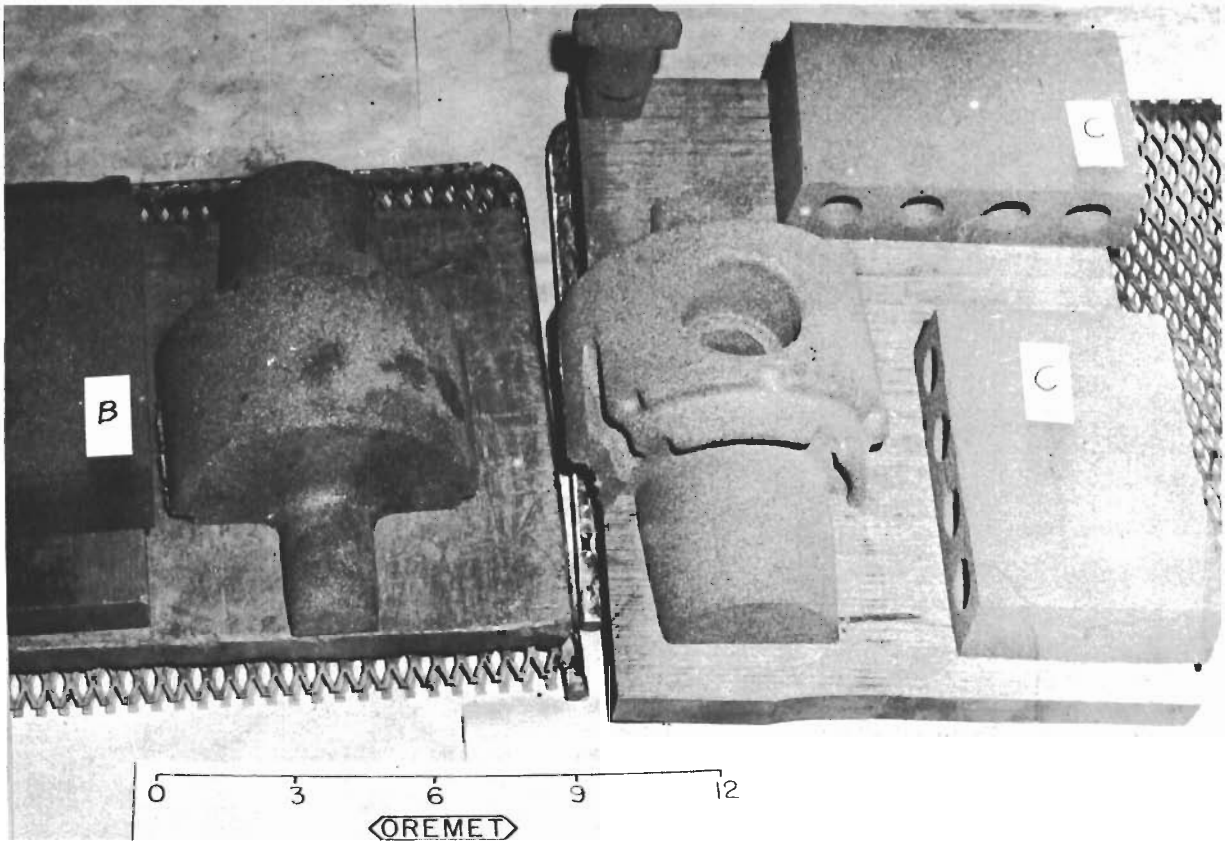


Figure 45 - Core for Allison Aerospace Mold B & C - Tensile Plugs

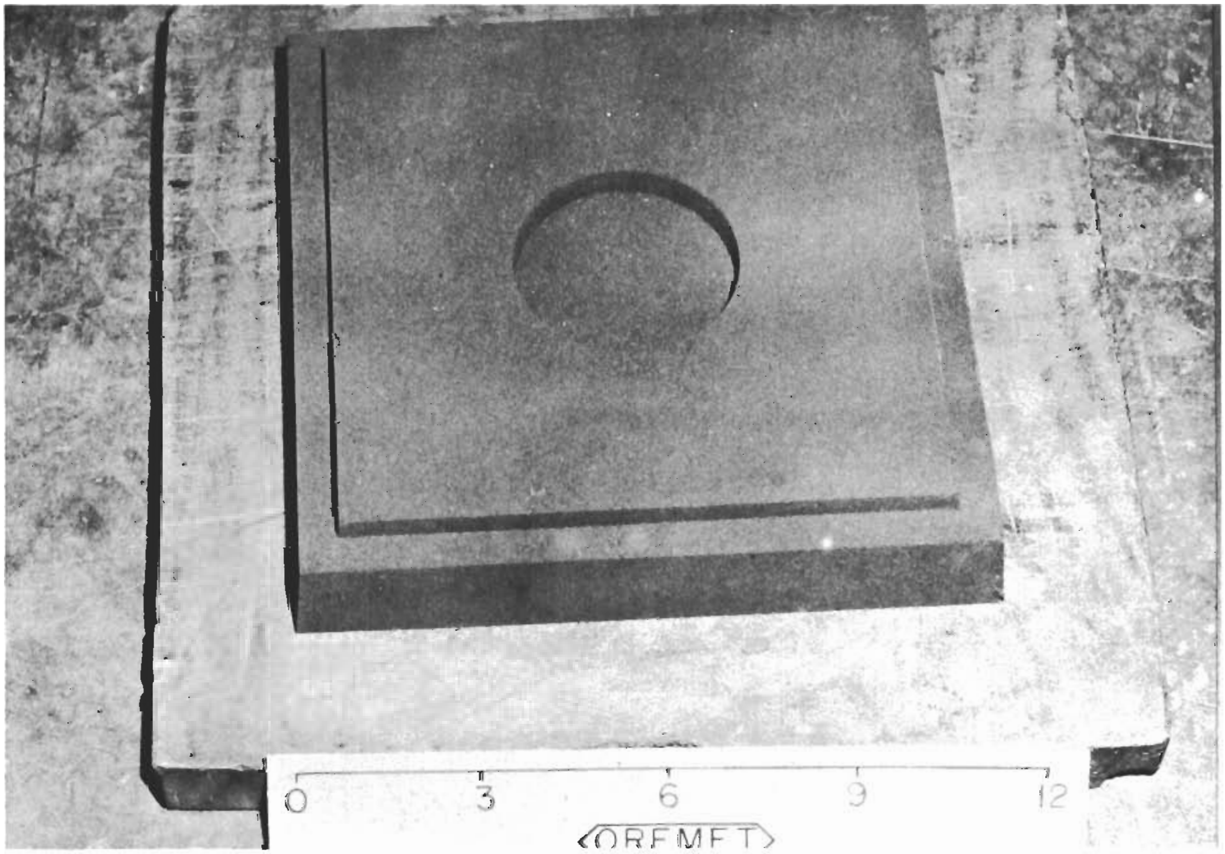


Figure 46 - Top for Allison Aerospace Mold

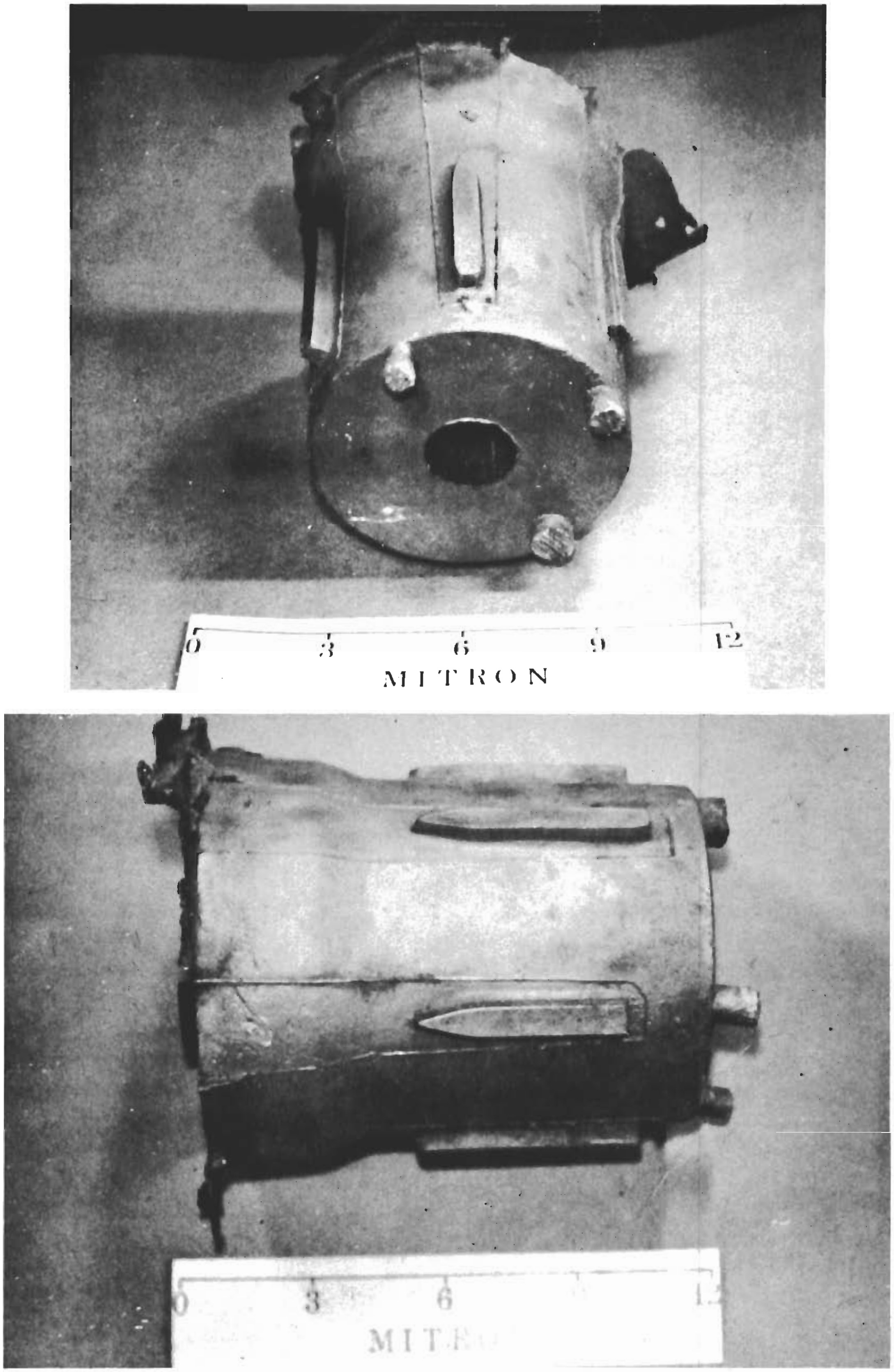


Figure 47 - Experimental Allison Casting - Mold Mix 80

TABLE 10

TENSILE PROPERTIES OF CAST TEST SPECIMENS

Samples	YS	UTS	%E	%RA
79A	83200 psi	98800 psi	20	26
79B	83600	98200	19	26
79C	82800	97400	22	27
79D	83800	98000	20	27
80A	84000	98000	19	21
80B	85400	97800	18	20
80C	84400	98400	19	21
80D	85800	99000	18	23
5A	81400	98400	17	18
5B	83600	98000	17	24
6A	83800	98400	19	30
6B	83800	100200	18	29

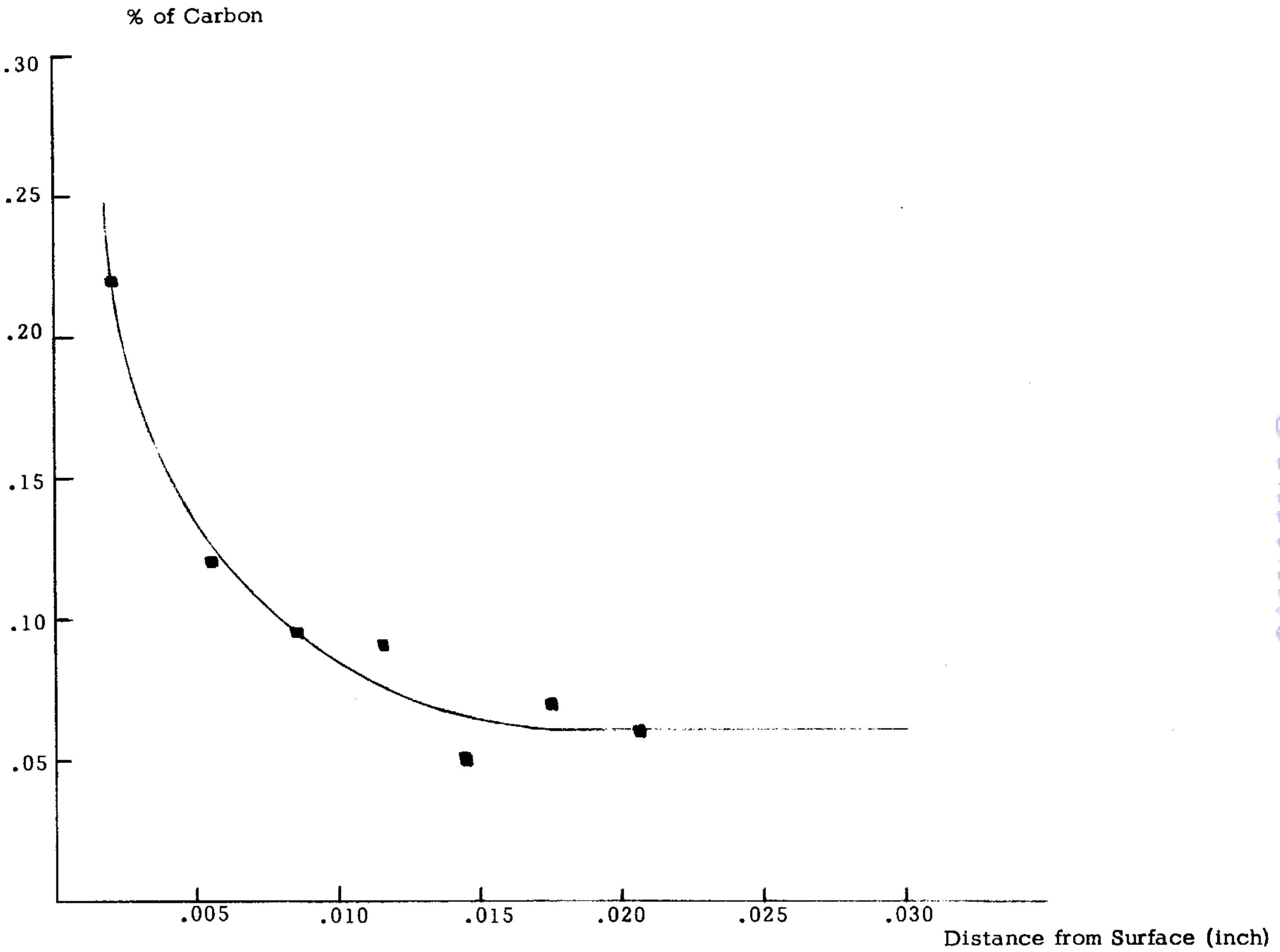


Figure 48 - Carbon Content as a Function of Distance from Surface of Bracket Casting Made With Mix #80

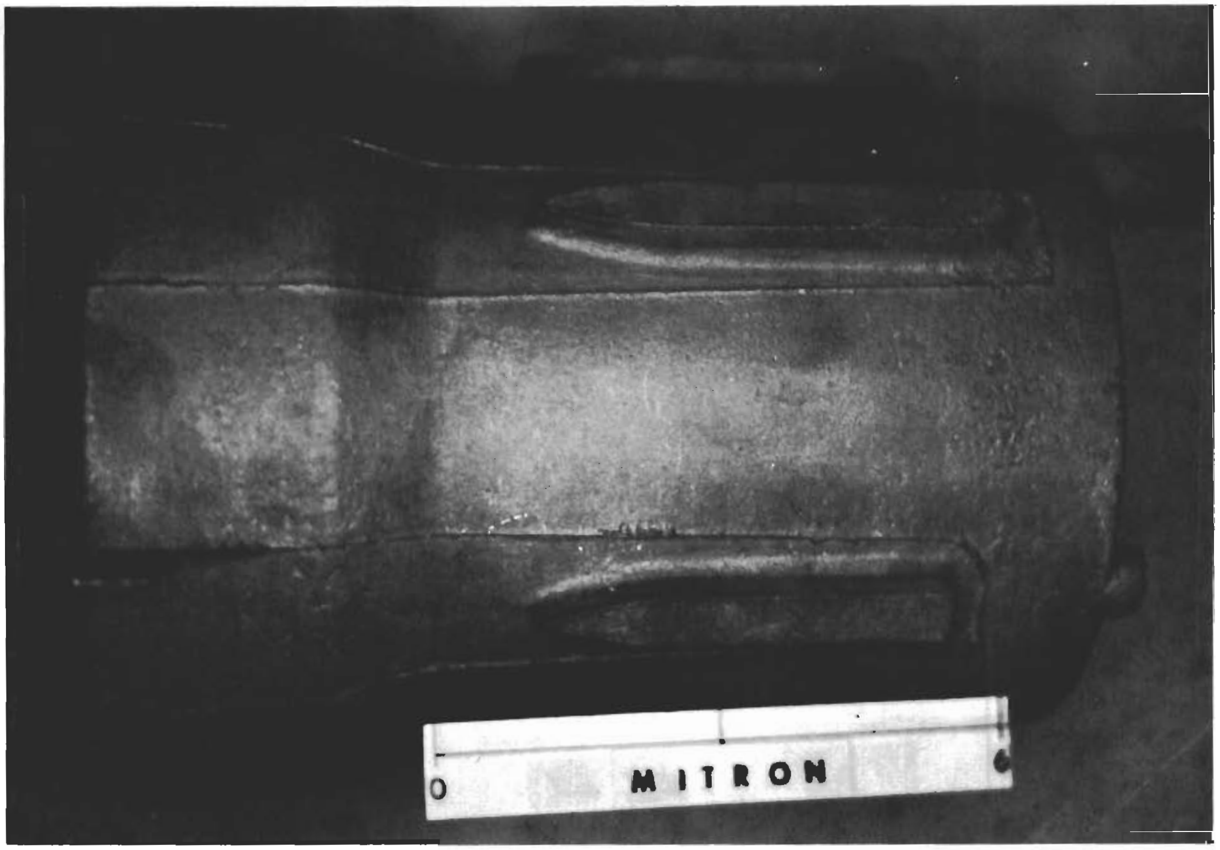


Figure 49 - Allison Casting Made with Mold Mix 79
Core Made with Commercial Mix

During the seventh and eighth heats under commercial conditions, additional castings were poured under standard foundry conditions to further demonstrate the applicability of the developed mold composition and processing technique and also to determine the effect of using reclaimed graphite so as to more fully simulate actual practice. Two bracket castings were poured on MITRON's seventh heat at Oremet. Mold compositions 79 and 80 were used. Mold processing consisted of baking for 8 hours at 250° F, followed by heating, but not glazing the mold cavities with a torch.

The graphite particle size and screen distribution of the mold aggregate was considerably different from the previous heat at Oremet, primarily because the reclaimed graphite does not have a consistent particle size distribution. This resulted in some processing modifications as difficulties were encountered. One half of a bracket mold made with Mix 79 was badly degraded when the mold cavity was heated with a torch. This half was then sprayed with a mixture of flux and water and rebaked. The remaining bracket mold halves were torch heated until the walnut dust mold parting agent was apparently burned off. This required less time than was used for the degraded mold. After examining the castings, it was obvious from the slight surface imperfections and gas holes that, with one exception, the parting agent was not completely removed. The mold half which degraded and was then flux coated a second time yielded excellent results. This half of the casting had no surface imperfections. The processing difficulties encountered were caused by the graphite particle size distribution. The graphite used for these molds had a much lower fines content. The molds could not withstand the temperatures required to completely burn off all the walnut dust parting agent. A more detailed discussion of the effect of particle size on mold properties and processing is discussed in a subsequent section.

Two Allison castings were poured on MITRON's eighth heat at Oremet. The mold compositions and processing are essentially the same as those reported for the previous heat. Unfortunately, due to scheduling, the inserts for the Allison mold made with Mix #79 were made prior to pouring the bracket castings and walnut dust was used as a parting agent. No walnut dust was used for the second Allison casting and, as a result, the Allison casting made with Mix #80 is superior to the casting from Mix #79. The casting surfaces were excellent and equivalent to those reported for the previous heats. These results were obtained in spite of the fact that the fines content of the graphite aggregate was not high enough to produce molds with the best possible properties.

Tensile plugs were cast with both heats and the results are listed in Table 11. Samples listed as 79, 80, and C are from heat 7 with 79 and 80 indicating the MITRON mix used. The control samples, C, were made with the standard commercial composition. Samples numbers 79A, 80A, CA are from the eighth heat. The data indicates that test specimens from the MITRON molds yielded properties essentially equivalent to those obtained with the standard commercial composition.

TABLE 11

TENSILE PROPERTIES OF CAST TEST SPECIMENS

Samples	YS	UTS	%E	%RA
79A	83900 psi	92400 psi	16	19.7
	83000	90700	16	18.5
	82500	91300	16	19.7
	83800	92600	16	22.1
80A	83400	92200	20	23.4
	83700	92300	13	25.1
	84500	92600	18	26.8
	83700	92100	16	22.1
C	84200	92900	21	27.4
	83600	91900	20	27.9
79A	80000	88400	19	28
	80300	88700	18	25
	80800	89300	18	24.2
	80200	88800	18	25.9
80A	80200	89100	19	20.3
	79100	88000	18	21.4
	80200	88400	18	21.5
	80100	88400	17	24.6
Ca	79700	88700	20	30.3
	81400	90700	21	28.8

Mold Properties

As a result of the observation of the differences in grain size distribution, screen analyses were performed on the BB-5 graphite used by MITRON and the reclaimed graphite used for the fifth and sixth heats at Oremet. The aggregates were sampled with a splitter set and the screen analyses are listed in Table 12. Both aggregates have essentially a 4 screen distribution. The major portion of the material is trapped on the 40, 50, 70 and 100 screens. The major difference is found in the amount of fines or the material trapped on the 140, 200, and 270 screens and the pan. The fines content of the BB-5 is 1.91 g., and the reclaimed graphite 9.64g. This has a significant effect on mold properties as increasing the fines content definitely increases mold strength.

Table 13 illustrates the differences in mold properties which can result from the aggregate distribution. The mold scratch hardness and tensile strength tests were performed using standard American Foundry Society methods. The tensile properties were determined using "dog-bone" briquettes and a Universal Strength Machine. Mold ingredients were carefully controlled and the processing cycle for both systems was identical. The results definitely establish that the reclaimed graphite has superior scratch hardness and tensile strength when compared to the BB-5 graphite. The results indicate that a fines content of 10% in the graphite aggregate will produce molds with optimum properties.

Mold shrink was also determined for 1 x 1 x 12 inch samples. The samples were processed using the standard technique and there was no measurable mold shrinkage.

TABLE 12

SCREEN ANALYSIS - BB-5 GRAPHITE

U.S. Series Equivalent Number	Amount of Sample Retained on Sieve		Multiplier	Product
	(grams)	Per cent		
30	0.28	0.29	20	5.8
40	27.39	28.24	30	848
50	31.91	32.92	40	1315
70	22.00	22.65	50	1133
100	13.55	13.92	70	975
140	1.27	1.31	100	131
200	0.27	0.28	140	39
270	0.05	0.05	200	10
Pan	0.32	0.33	300	99
	97.04	100.00		4556

SCREEN ANALYSIS - RECLAIMED GRAPHITE

30	0.93	0.87	20	1.74
40	22.28	21.20	30	636.00
50	35.15	32.30	40	1280.00
70	22.79	21.58	50	1075.00
100	15.41	14.59	70	1020.00
140	5.03	4.82	100	482.00
200	2.39	2.55	140	357.00
270	0.68	0.64	200	128.00
Pan	1.54	1.45	300	435.00
	106.20	100.00		5414.74

BB-5 Graphite - AFS Grain Fineness Number = $\frac{4556}{100}$ = 45.6

Reclaimed Graphite - AFS Grain Fineness Number = $\frac{5414.74}{100}$ = 54.2

TABLE 13

SCRATCH HARDNESS AND TENSILE STRENGTH OF RECLAIMED AND BB-5 AGGREGATES

		RECLAIMED GRAPHITE				BB-5 GRAPHITE			
Processing		Bake 8 hours at 250° F		Bake & Torch		Bake 8 hours at 250° F		Bake & Torch	
FORMULATION		Scratch	Tensile	Scratch	Tensile	Scratch	Tensile	Scratch	Tensile
graphite	100	95	140 x	92	70	93	55	75	45
flux	20	90	145	92	65	89	80	78	40
starch	2	92	155	90	90	91	60	82	45
water	10	94	130	91	95	91	85	78	45
graphite	100	95	125	93	110	94	75	90	75
flux	20	94	120	92	100	95	80	89	80
sodium silicate	5	95	145	92	105	94	85	90	75
water	10	96	110	93	90	94	75	90	80

Shell Molding

For many applications, it would be advantageous to apply shell molding procedures to titanium casting. However, the reactivity of titanium with conventional materials used in shell molding prohibits the current application of this technique.

Generally speaking, the shell mold process for the production of foundry molds is a departure from the conventional sand molding method in that only dry sands are used to obtain pattern reproductions. The molds are permeable shells having an overall thickness of 1/8 to 3/8 inch. This process is far more economical than the machined graphite mold process and is probably less expensive than the rammed graphite mold process.

Three shell mold formulations were tested. These are tabulated in Table 14. Two shell molds of formulation 1 were made using the following procedure. The mix was dry blended in a Hobart mixer for 12 minutes. The cast iron shell mold pattern shown in Figure 12 was prepared with a light coating of silicone grease to facilitate removal of the shell mold from the heated pattern after curing. The pattern was preheated to 475° F, the sand-resin mix was invested on the hot pattern for 12 seconds using the dump box technique and cured for 3 minutes at 570° F, then ejected from the pattern.

The cope and drag sections were glued together using the same powdered thermosetting resin placed on the cold mold half. The second half was then placed on the cold mold half immediately after curing. Pressure was then applied to obtain a completed shell mold. The completed mold was then placed in a steel box and backed with copper shot prior to pouring as shown in Figure 50. Flux coatings were applied to the mold cavities of each mold half prior to gluing the mold halves together.

Mold 13A was uncoated while mold 13C was spray coated with flux. The resultant castings are shown in Figure 51. The protection afforded the titanium by the flux coating is clearly evident though not complete. There is a substantial reduction of mold-metal reaction as evidenced by the closer dimensional retention and improved surface smoothness.

Molds 14A and 14B were prepared from graphite (formulation 2), with 14A uncoated and 14B flux coated. Mold 14C was prepared from formulation 3. Molds 14A and 14B were prepared using normal procedure, then packed in graphite and fired at 1600° F until all volatiles were removed. Mold 14C was fired at 1500° F for 15 minutes. The phenolic resin completely burned out and the flux acted as the binder.

The resultant castings are exhibited in Figure 52. All exhibited smooth surfaces and excellent dimensional retention. This indicated that flux may be applicable as a binder for graphite shell molds, thus simplifying mold processing and casting removal. Mold 14C, however, was not as abrasion resistant as desired.

Based upon these results, two shell molds were evaluted under commercial conditions during heat 3 at Oremet. These are designated 7 and 8 in Table 5.

TABLE 14

SHELL MOLD FORMULATIONS

Formulation	Graphite	Pitch	Flux	Zircon Sand	Phenolic Resin	Investment Time
1				100	3	12 sec.
2	80	8			12	40 sec.
3	80		15		12	40 sec.

Figure 50 - Shell Mold Backed with Copper Shot Prior to Pouring

Figure 51 - Cylindrical Step Castings from Shell Mold

Numbers 13A and 13C

Figure 52 - Cylindrical Step Castings from Shell Mold Numbers 14A, 14B, 14C

The composition of the shell molds used is as follows:

Zircon Shell		Graphite Shell	
Zircon sand	100 parts by weight	Graphite	80 parts by weight
Phenolic resin	3 parts by weight	Phenolic resin	12 parts by weight
Flux	7 parts by weight	Flux	15 parts by weight

A graphite mold was formed around the two shell molds to facilitate pouring. A front view and a top view of the shells are exhibited in Figure 53. The zircon shell mold is on the right. The front view also shows the ingates at the bottom of the molds. Figure 54 exhibits the casting taken from the zircon shell mold and Figure 55 shows the casting from the graphite shell mold. Close up views of the top portion of the casting and also the ingate are shown. Gross reaction between titanium and the zircon shell mold was not observed. Reaction between the titanium and this shell mold appears to have been inhibited by the flux as only a slight amount of pinholing is observable on the casting surface. The molten metal was not rejected from the mold cavity during solidification, indicating there was no violent mold/metal reaction. No burn through was noted and the casting exhibited good dimensional retention. Note that the thin section near the ingate exhibits no porosity and is quite smooth.

Similar results were noted with the casting taken from the graphite shell mold. In general, the surface is somewhat rougher primarily due to the mold being porous. No pressure was applied during the formation of the shell. The casting exhibits some flash at the mold parting line, a result of slight mold mismatch. Again the thinner sections of the casting exhibit smooth surfaces compared to the heaviest top sections. In both cases, the pinholing is related to the phenolic resin binder, and particularly for the graphite shell which has substantially more phenolic resin. Modifications of shell mold fabrication techniques to minimize or eliminate the phenolic resin would greatly improve the surface quality of shell cast titanium.

Microstructural examination of the sectioned castings indicates that no gross surface reactions occurred. There is, however, a definite difference between the microstructures of the two castings, particularly at the surface. This difference is illustrated by the photomicrographs in Figures 56, 57, 58, and 59.

Figures 56 and 57 represent areas of the casting taken from the zircon shell mold which was flux coated, and Figures 58 and 59, the casting from the graphite shell mold which was flux coated. Both are cylindrical step castings with 3/4 inch diameter bases and 2 inch diameter tops. Figures 56 and 58 represent equivalent areas through the 2 inch section. There is obviously no apparent gross reaction of the titanium with the flux coated zircon shell mold. The broad acicular alpha structure extends out to the casting surface with no reaction zone.

In the case of the flux coated graphite shell mold, there is a definite transition from a fine acicular structure at the surface, to the characteristic broad acicular cast structure at the interior of the casting. This is probably due to the rapid chilling of the molten titanium in contact with the graphite.

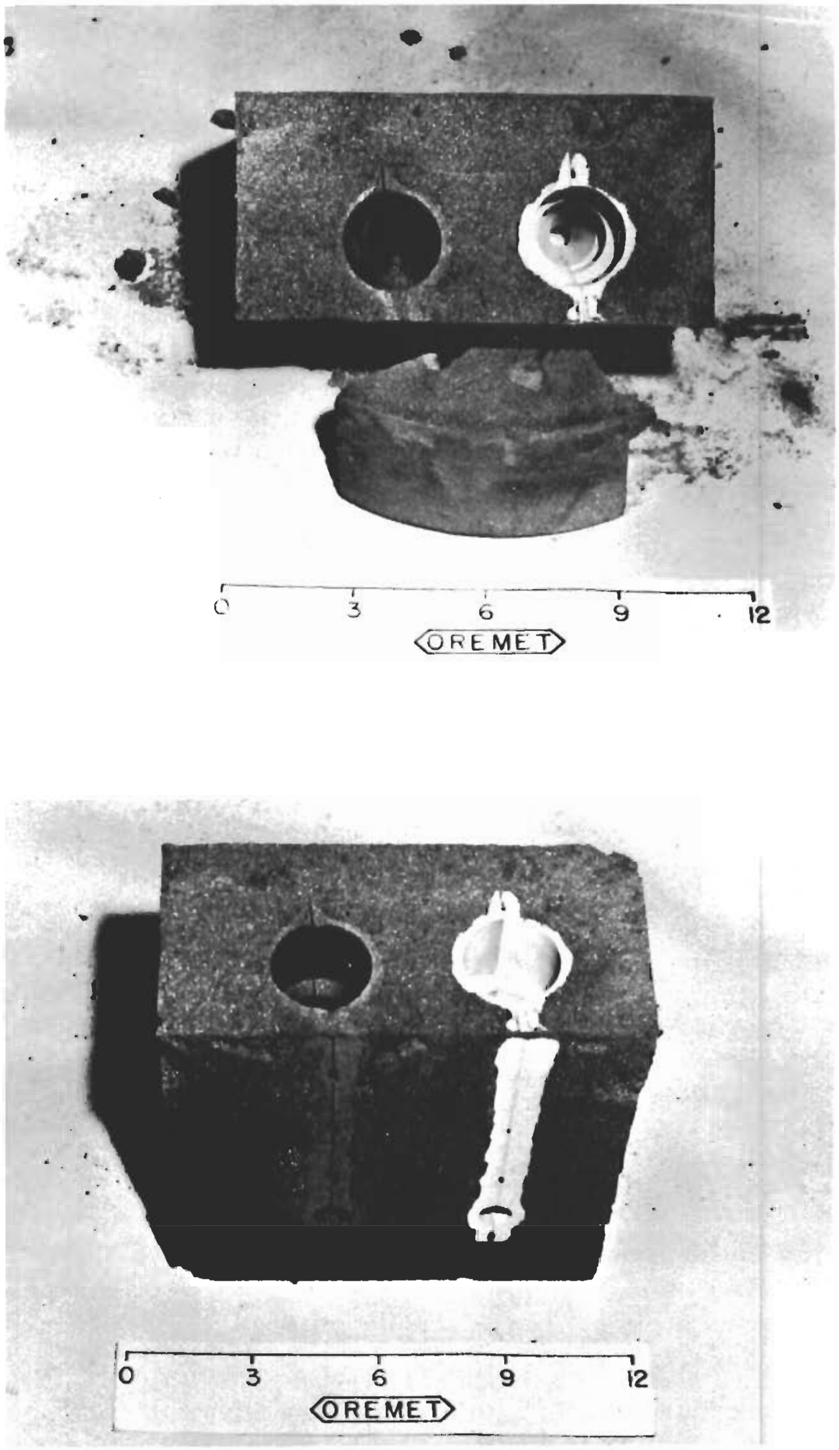


Figure 53 - Shell Molds Packed in Graphite Prior to Casting

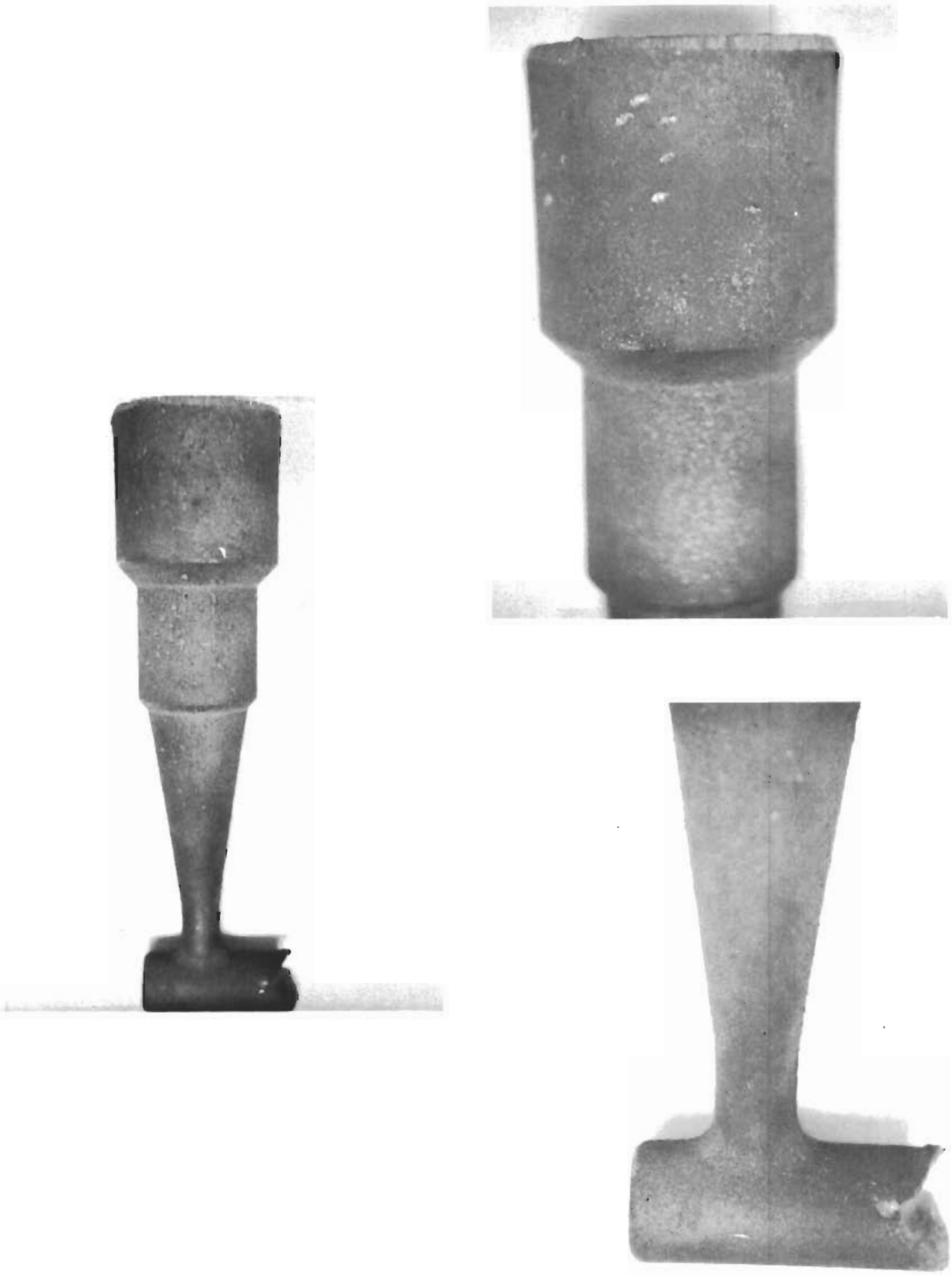


Figure 54 - Casting from Zircon Shell Mold with Risers Attached

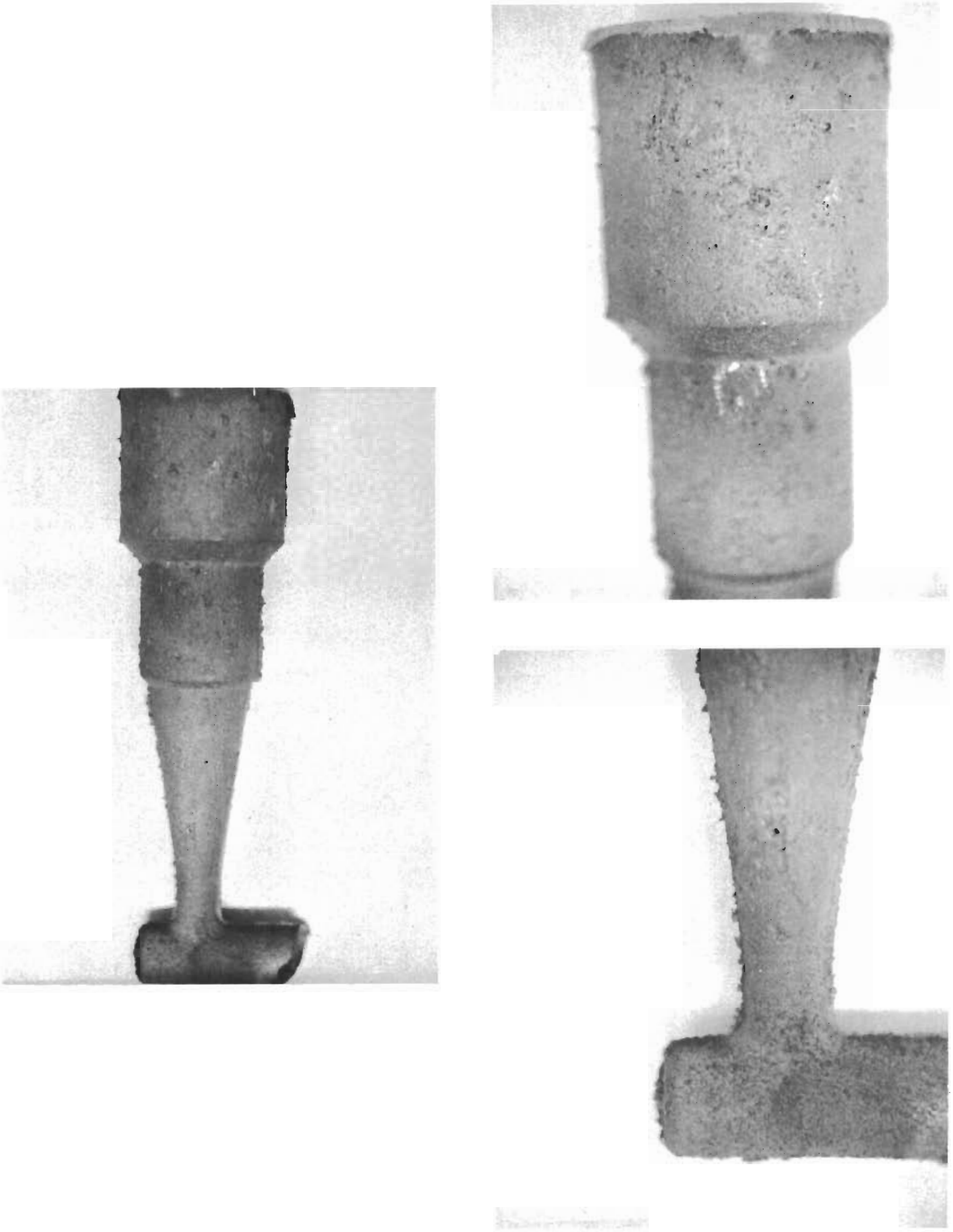


Figure 55 - Casting from Graphite Shell Mold

with Risers Attached

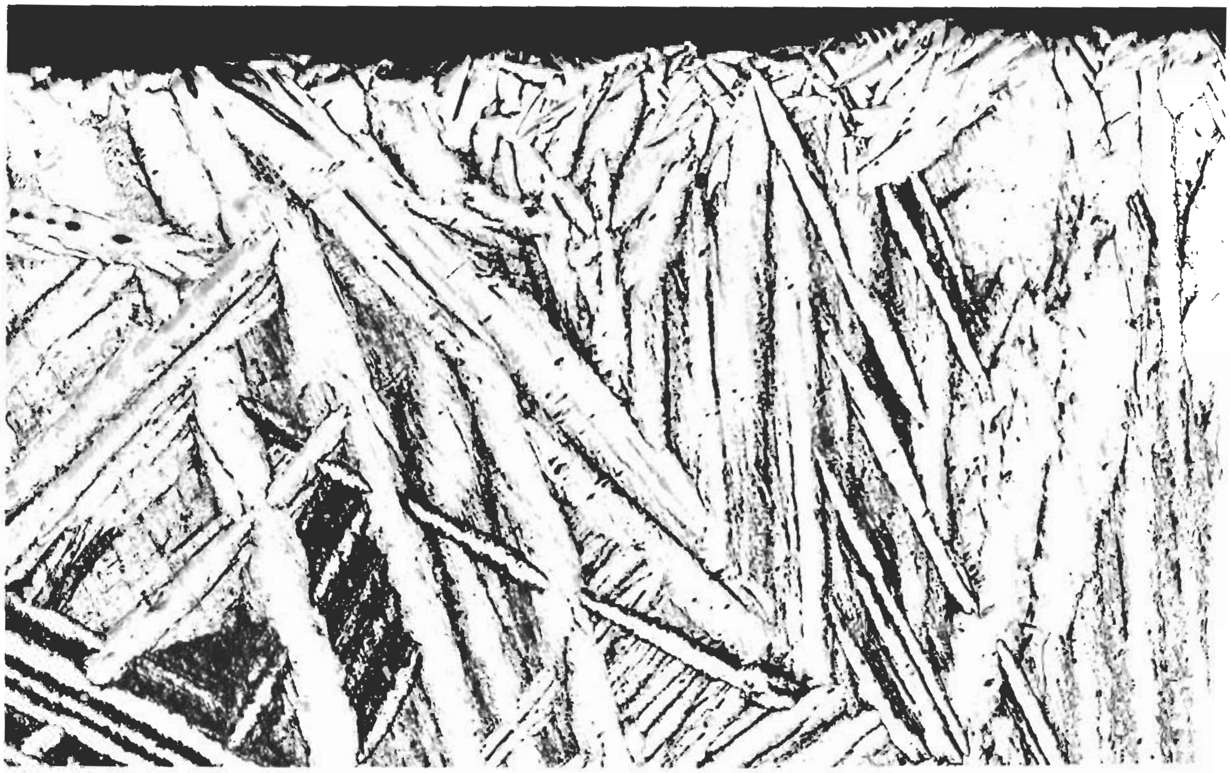


Figure 56 - Surface of Casting from Zircon Shell Mold
Sectioned through 3/4 inch Diameter Base
Modified Kroll's Etch 75X

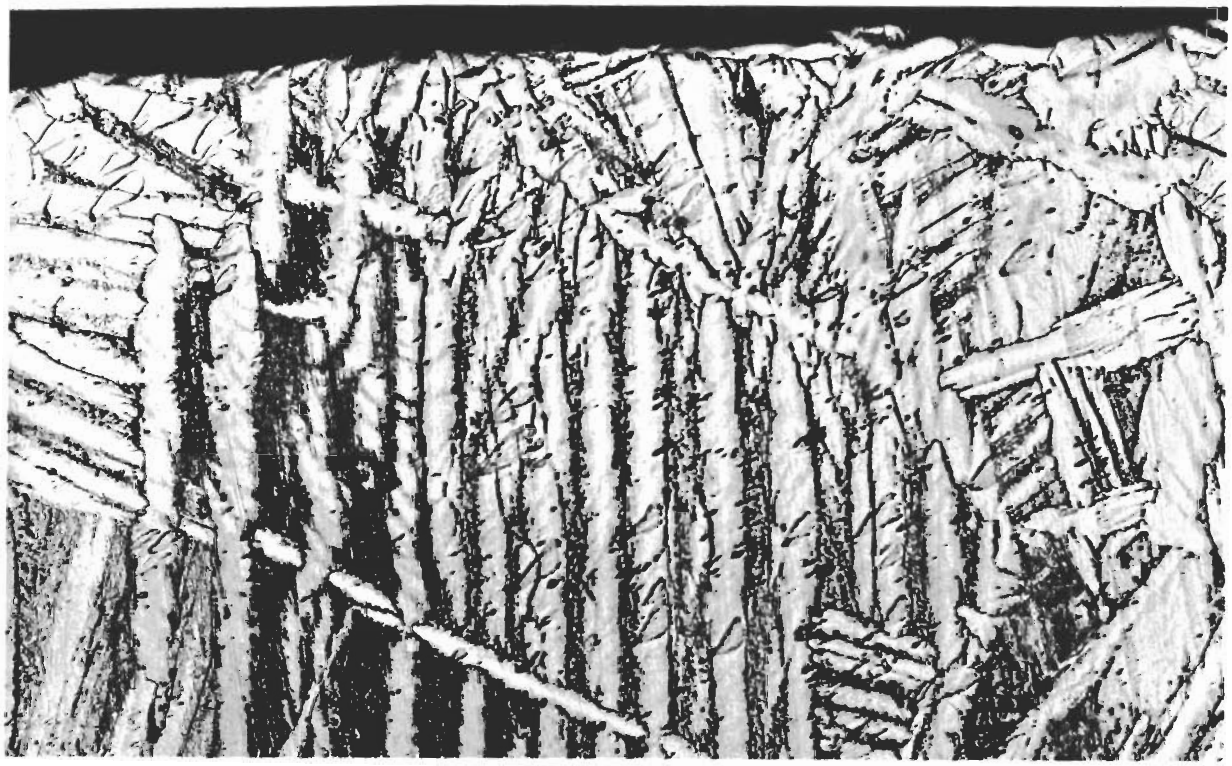


Figure 57 - Surface of Casting from Zircon Shell Mold
Sectioned through 2 inch Diameter Top
Modified Kroll's Etch 75X

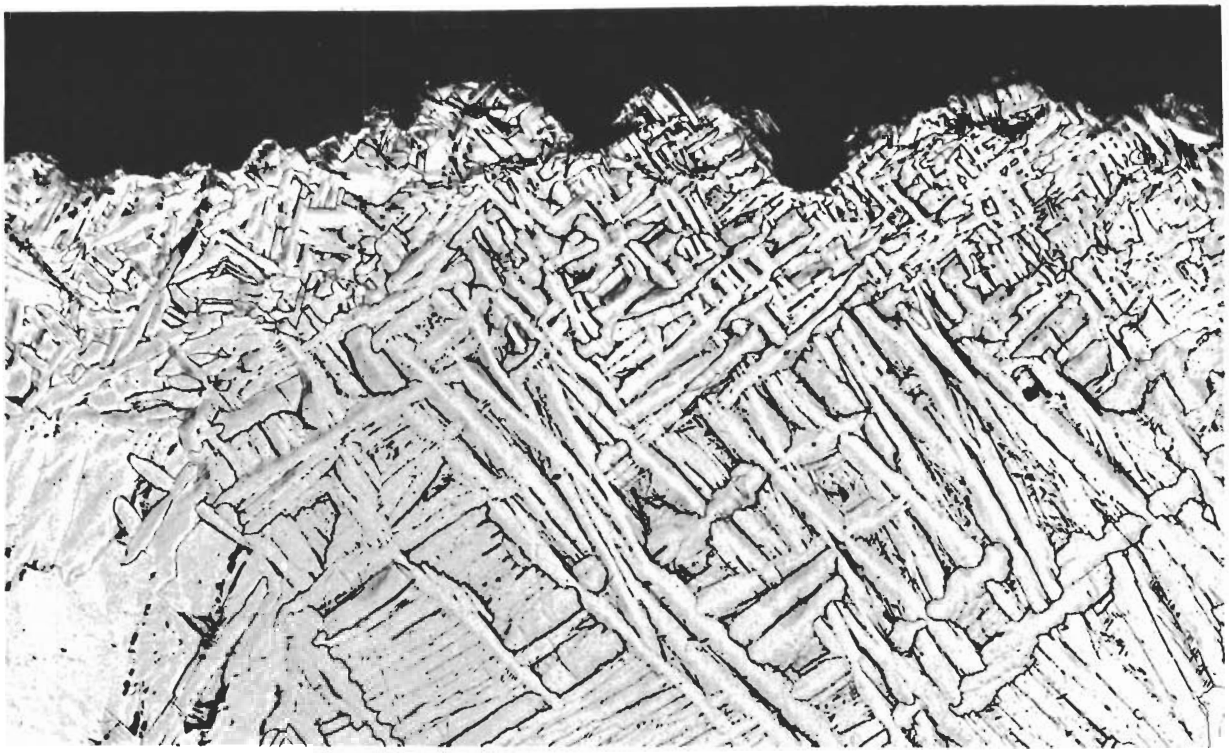


Figure 58 - Surface of Casting from Graphite Shell Mold
Sectioned through 3/4 inch Diameter Base
Modified Kroll's Etch 75X

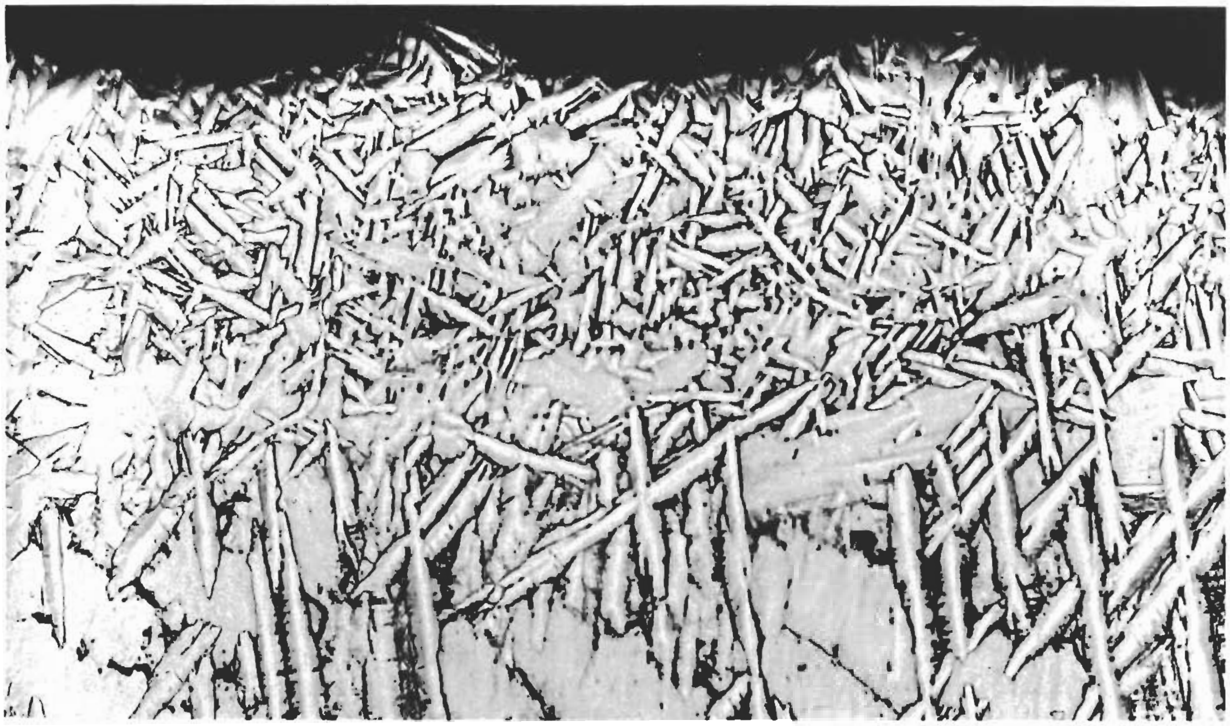


Figure 59 - Surface of Casting from Graphite Shell Mold
Sectioned through 2 inch Diameter Top
Modified Kroll's Etch 75X

It is also interesting to note the much smoother surface on the casting taken from the zircon shell mold. These results indicate the feasibility of applying standard shell molding procedures, modified by flux incorporation, to titanium foundry practices.

Mold and Core Washes

A brief study of mold and core washes was undertaken with the primary emphasis being placed on their applicability to flux-rammed graphite molds and cores. The purpose of a mold wash is to produce smooth mold surfaces which result in castings exhibiting smoother surfaces and better detail. At present, mold wash techniques are rarely applied in titanium casting procedures. This is primarily a result of the inability of present casting procedures to produce highly complex casting shapes requiring close dimensional tolerances. As titanium casting procedures are refined, more complex castings of titanium will be required and hence will result in increased usage of mold washes. The mold washes currently employed are based primarily on graphite and carbonaceous cement using alcohol as a carrier for application.

The system initially employed for this mold wash study was based upon flux, lampblack, and alcohol. Lampblack was used because it is a very fine form of carbon, hence it produces very smooth mold washes. Two mold wash compositions were evaluated. These are:

	Lampblack	Flux	Alcohol
A	10 parts	15 parts	100 parts
B	5 parts	15 parts	50 parts

The mold washes were brushed onto flux-rammed graphite mold surfaces, though spray coating or dip coating is certainly feasible, and, in fact, is common foundry practice especially for cores. The alcohol was then ignited and allowed to burn to completion.

Both coatings were very smooth, filling in all voids after alcohol ignition. The mold having coating A was then fired at 1400° F for 15 minutes in order to glaze the coating. Cracking or spalling on the coating was observed after glazing. The mold employing coating B was fired at 1400° F for 10 minutes. The resulting glazed coating did not spall, but impregnated the mold resulting in a smoother mold wall surface. However, it was rougher than an unglazed, but washed rammed graphite mold surface. Employing this technique and wash composition would require several coating and glazing operations in order to obtain a uniformly smooth mold surface. The coatings after alcohol ignition abrade somewhat, whereas coatings after glazing are hard, adherent, exhibit increased scratch resistance and do not abrade. This is important because it may minimize carbide formation between the titanium and the graphite mold during solidification of the casting.

Mold washes were employed on zircon and shell molds. Three test castings were evaluated. Mold 22A was spray coated with only a light coating of flux. Mold 22B was lightly coated with mold wash composition B, the alcohol was ignited and allowed to burn to completion. Mold 22C was lightly coated with mold wash composition B, ignited and allowed to burn to completion, then lightly spray coated with flux. Casting 22B exhibited considerable surface porosity, but had excellent dimensional retention and no apparent cold shuts. Casting 22C exhibited some porosity, though less than 22B, but it did not retain its dimensions. Casting 22A exhibited very little surface porosity, but exhibited somewhat inferior detail.

Mold washes were also applied to flux-rammed graphite molds. Castings 23A and 23B were made in molds of composition 51 coated with mold wash B which was applied by brush. Both molds were baked 16 hours at 300° F prior to casting. The mold wash on mold 23B was glazed. The unglazed wash did not adhere as adequately as desired and appeared to erode during casting. The glazed coating did not erode during castings. Castings 23B showed no physical or chemical reaction with the mold while the surface of casting 23A exhibited a marked reaction. These results appear promising and indicate that mold coatings incorporating the MITRON flux are practical for improving the surface quality of titanium castings. It should be pointed out that castings with excellent surface quality have been produced using the developed rammed graphite mold composition.

IV CONCLUSIONS

A chemically inert binder for producing water soluble rammed graphite molds and cores for titanium castings has been developed. The optimum compositions determined are:

	79	80
graphite	100	100 pbw
flux	20	20
starch	2	
sodium silicate		5
water	10	10

Molds and cores of these compositions have been made by employing standard commercial practices and have been evaluated under standard foundry conditions. Castings have been obtained which are of acceptable commercial quality. The analyses of test castings weighing from 2 to 45 pounds have indicated that the mechanical properties of castings from flux-rammed graphite molds of the above composition are equivalent to castings from identical commercial rammed graphite molds. In addition, chemical analyses indicate that the presence of flux in rammed graphite molds appears to slightly reduce the carbon pickup in thin sections by the metal during solidification and cooling in the mold.

A processing technique, which produces molds with excellent scratch hardness and strength has been developed. This technique consists of baking at 250° F for 8 hours followed by heating the surfaces of the mold cavities with a torch so as to burn out the combustible materials remaining in the mold to a depth of about 0.250 inches. Actual time required varies as a function of mold design. For example, three minutes of torch heating is recommended for each half of the gate valve mold exhibited in Figure 33. The applicability of this process for producing premium quality titanium castings using the graphite-flux-starch-water system is demonstrated by the excellent castings obtained under actual foundry conditions.

The low degree of reactivity of flux incorporated zircon and graphite shell molds has been demonstrated during this program. With further development, flux incorporation is expected to make standard shell molding techniques feasible when applied to small titanium castings. In addition, it is felt that the feasibility of rammed flux-sand molds has been demonstrated by the work with the zircon-sand for at least small titanium castings.

The application of the MITRON flux to rammed graphite molds for producing titanium castings has resulted in several improvements. Mold processing has been simplified and the time required for processing significantly reduced. Core removal has been simplified as a result of the water solubility of the developed system. This water solubility also permits the casting of intricately cored shapes not currently attempted. Mold/metal reactions have been somewhat reduced because the flux, used as a binder or mold coating, is nonreactive with titanium. Surface laps and other surface defects caused by the high heat extraction of the graphite have also been reduced by the flux.

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