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An Investment Mold for Titanium Casting

By E. D. Calvert

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The Bureau of Mines, in its effort to promote greater utilization of domestically abundant materials, conducted research on an alternate mold material that has commercial potential for titanium investment casting. Using variations of the conventional lost wax molding process, investment shell molds were formed entirely of fused, calcia-stabilized ZrO_2 and a ZrO_2-forming binder. Optimization of binder/slurry properties, stucco grain size and distribution, and curing practices resulted in a structurally sound investment shell that was distortion free and thermally stable. Small titanium castings, weighing up to 10 pounds, were prepared in unheated molds by both static and centrifugal casting techniques. Microstructural examination of the castings revealed that mold fill and surface quality were enhanced by centrifugal casting, although good results also were obtained from the statically poured molds. Microstructural and electron microprobe examinations showed that excessive, brittle case formation could be avoided by curing the dried shell molds in air for at least 2 hours at 1,400° C. Increasing curing temperature and time above these levels yielded added benefits. Molds fired in vacuum at 1,500° C for 4 hours yielded castings essentially free of case formation. The tensile properties of as-cast test specimens (no surface conditioning performed) and the chemical composition of representative metal samples showed that castings produced were comparable to Grades C-1 and C-2 unalloyed titanium. This indicated that no significant degradation of metal properties resulted from mold/metal interaction.

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AN INVESTMENT MOLD FOR TITANIUM CASTING

by

E. D. Calvert[1]

ABSTRACT

The Bureau of Mines, in its effort to promote greater utilization of domestically abundant materials, conducted reasearch on an alternate mold material that has commercial potential for titanium investment casting. Using variations of the conventional lost wax molding process, investment shell molds were formed entirely of fused, calcia-stabilized ZrO_2 and a ZrO_2-forming binder. Optimization of binder/slurry properties, stucco grain size and distribution, and curing practices resulted in a structurally sound investment shell that was distortion free and thermally stable.

Small titanium castings, weighing up to 10 pounds, were prepared in unheated molds by both static and centrifugal casting techniques. Microstructural examination of the castings revealed that mold fill and surface quality were enhanced by centrifugal casting, although good results also were obtained from the statically poured molds. Microstructural and electron microprobe examinations showed that excessive, brittle case formation could be avoided by curing the dried shell molds in air for at least 2 hours at 1,400° C. Increasing curing temperature and time above these levels yielded added benefits. Molds fired in vacuum at 1,500° C for 4 hours yielded castings essentially free of case formation.

The tensile properties of as-cast test specimens (no surface conditioning performed) and the chemical composition of representative metal samples showed that castings produced were comparable to Grades C-1 and C-2 unalloyed titanium. This indicated that no sifnificant degradation of metal properties resulted from mold/metal interaction.

INTRODUCTION

One of the goals of Bureau of Mines research is to promote greater utilization of domestically abundant materials, particularly those that resist deterioration and are suitable for use at high temperature or under other adverse conditions encountered in chemical and metallurgical operations. Titanium is one of these materials, and it has many desirable properties, such

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as a high-strength-to-weight ratio and good corrosion resistance. However, special foundry techniques are required because liquid titanium reacts readily with most solid, liquid, and gaseous materials. Brittle compounds that result from these reactions render titanium unfit for almost all engineering applications.

For several years, the Bureau of Mines has been intermittently engaged in research to determine foundry practices required to prepare engineering-quality titanium castings. The first industrially accepted molds for titanium casting were machined from high-density graphite and were semipermanent in nature. These molds were expensive to make in terms of labor and material costs and, in addition, had undesirable thermal properties. Later, by adaptations of conventional sand foundry techniques (3),[2] the Bureau of Mines produced molds made by ramming mixtures of graphite powders and organic binders onto suitable patterns. This is the primary technique used today in the titanium casting industry; castings of fairly complex shapes weighing up to several hundred pounds are routinely made for the chemical and marine industries.

Even though both large and small castings of acceptable quality for most applications can be made in rammed graphite molds, investment castings are the more practical choice if maximum surface smoothness, close dimensional tolerances, or very complex shapes are required, as for example in aircraft engine and airframe applications.

The lost-wax process for making investment shell molds is an established foundry technique. However, the author of this report is aware of only three systems of investment molds in use today for titanium casting: (1) ceramic oxide molds faced with thoria (hazardous radioactivity); (2) graphite molds formed with carbon binders (undesirable thermal properties); and (3) ceramic oxide molds faced with refractory metals (undesirable thermal properties, expensive, and/or imported materials). The disadvantages presented by each of these mold systems tend to restrict full utilization of titanium, even though the inherent properties of this metal present many advantages over those materials conventionally used. The use of titanium will grow when improved methods and materials are found that will lower manufacturing costs and maintain product quality. The specific objective of this research, therefore, was to devise an investment mold for titanium casting that would minimize the disadvantages of the presently used commercial mold systems.

BACKGROUND

The general process for making investment molds is well known throughout the precision casting industry. It involves forming a disposable pattern from waxes, plastics, or wax-plastic mixtures. These materials are injected, while in the molten or semiplastic state, into a metal die that contains a cavity (or cavities) formed to the configuration of the desired casting. The patterns thus formed have the exact geometry of the finished casting, but the patterns are made slightly larger to compensate for volumetric shrinkage of

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[2] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

the mold during curing and of contraction of the cast metal during solidification.

After the patterns have solidified, they are removed from the dies and attached to a suitable gating and risering system also made of the disposable pattern material. They are then dipped into a slurry made up of a finely ground refractory material in a fluid binder and are subsequently sprinkled, while still wet, with a ceramic or refractory grain. (This is called stuccoing, the powder or grain being the stucco.) This procedure is repeated several times using progressively coarser grades of stucco until a self-supporting shell is formed around the pattern. The shell thickness may vary from 3/16 to 5/8 inch, depending upon the strength requirements and mold properties being sought.

After air drying, the patterns are removed from the shell by heating or by chemical dissolution. The resultant monolithic shell molds thus formed are then fired in air at medium temperatures (200° to 400° C) to remove the last traces of pattern material and slurry vehicle volatiles. This heating cycle is followed by firing at high temperatures to attain a high-temperature bond and a certain degree of permeability before the molds can be filled with metal.

The Rem Metals Corp. has revealed its technique for making investment molds in a patent issued to R. A. Brown and C. A. Brown (4). The essence of this technique is the facing coat (interior) of finely divided metals, such as columbium, molybdenum, tantalum, or tungsten. This refractory metal lining gives the potential for zero interface reaction when casting titanium in a heated mold. The higher melting point metals, columbium and molybdenum, have been cast into molds of this type with encouraging results.

The chief advantages of the investment molding technique lie in the complexity, smooth finish, and dimensional accuracy of the shapes cast. Disadvantages, of course, include the relatively high cost of materials (which are normally not recyclable), the complex process, and the highly undesirable possibility of mold reaction with molten titanium.

In reviewing the properties of a suitable investment mold for titanium, first consideration is given to reactivity. The reacted materials dissociate and decompose to form mold gases. Some of these gases may be dissolved into the liquid titanium and may cause deleterious embrittlement and degradation of properties. Even trace amounts of the interstitial elements oxygen, hydrogen, nitrogen, and carbon produce this result. Therefore, if the mold (including residual binder) reacts with titanium, the casting may be loaded, in severe cases, with defects such as reaction zones, blow holes, and porosity; in a minimal situation, the casting may have a brittle case comprising a compound of titanium and the reacted mold material. In this latter instance, the case may be partially or completely removed by chemical milling.

Beyond the ever-present hazard of reaction, a mold must produce castings that are competitive with existing commercial products in the cost of materials and process. Finally, the mold must have dimensional stability and handling strength.

ACKNOWLEDGMENTS

The author gratefully acknowledges the counsel of Robert A. Brown of Rem Metals Corp. who initially provided guidance in the art of the lost-wax process and who made his facilities available for one-time tests that otherwise could not have been made.

PROCEDURES FOR MOLD PRODUCTION

In order to make titanium investment castings cost and quality competitive with superalloy investment castings, the disadvantages found in currently used mold systems and the casting defects commonly encountered must be minimized. A combination of procedures and materials was determined that appears to meet these demands.

Selection of Mold Materials

In this investigation, over 100 castings were poured into a variety of molds representing numerous refractory materials, binders, face coat and backup coat slurries and stuccos, and curing-firing schedules. Some of the more promising materials that were evaluated and their influence on the characteristics of unalloyed titanium castings are summarized in table 1. The data presented in this table consider only the composition of the face coat slurry and the temperature at which the mold was cured. These are the most important considerations from the viewpoint of mold-metal reaction, face coat integrity, and casting surface conditions. The backup coats of all the molds evaluated were essentially identical, being formed from size-graded layers of stabilized ZrO_2 and/or of Al_2O_3 refractory grains. They, therefore, were not considered as a variable for this evaluation.

TABLE 1. - Influence of mold face-coat composition and firing conditions on characteristics of titanium investment castings

Mold inner-face composition		Firing conditions		Casting defects[1]	
Refractory grain	Binder	Temp., ° C	Atmosphere	Internal soundness	Surface conditions
Stabilized ZrO_2[2]	Syton F.M.[3]	1,200	Air	Blow holes, porosity	Pin holes, no other defects.
Do.	do	1,400	Air	Porosity	Do.
Do.	do	1,500	Vacuum	No defects	Scattered pin holes, no other defects.
Do.	Ludox A.S.[4]	1,500	do	do	Minor pin holes, no other defects.
Do.	Zirconium acetate[5]	1,200	Air	Porosity	Pin holes, reaction zones, scab.
Do.	do	1,200	Vacuum	No defects	Pin holes.
Do.	do	1,400	Air	do	No defects.
Do.	do	1,400	Vacuum	do	Do.
Do.	do	1,500	do	do	Do.
Do.	Zirbind[6]	1,400	Air	do	Do.
Monoclinic zirconia (ZrO_2)	do	1,400	Air	do	Alligator skin surface,[7] fins.
Do.	Zirconium acetate.	1,400	Air	do	Alligator skin surface,[7] fins, scales.
Zircon ($ZrSiO_4$)	Syton F.M.	1,400	Air	Blow holes, porosity	Reaction zones, fusion.
Do.	do	1,500	Vacuum	Porosity	Do.
Do.	Ethyl silicate[8]	1,400	Air	Blow holes, porosity	Do.
Do.	do	1,500	Vacuum	Porosity	Do.
Do.	Zirconium acetate.	1,500	do	No defects	Pin holes, fusion.
Alumina (Al_2O_3)	do	1,400	Air	do	Fusion.
Do.	Zirbind	1,400	Air	Minor porosity	Do.
Do.	Colal P[9]	1,500	Vacuum	Porosity	Fusion, pin holes.
Do.	Ludox A.S.	1,500	do	do	Do.
Cerium zirconate ($CeZrO_4$).	Zirconium acetate.	1,400	Air	No defects	Fusion.
Do.	do	1,500	Vacuum	do	Do.
Yttria (Y_2O_3)	Syton F.M.	1,500	do	Porosity	Rough surface.[10]
Do.	Zirconium acetate.	1,500	do	No defects	Do.[10,11]
Yttria (Y_2O_3)[12]	do	1,500	do	Porosity[12]	No defects.

[1] Description of casting defects listed is in reference 2.

[2] Fused ZrO_2 stabilized to the cubic structure with 3.5 to 4.0 pct CaO.

[3] Aqueous, colloidal silica.

[4] Ammonia-stabilized, aqueous, colloidal silica.

[5] 22 pct ZrO_2 in H_2O solution, converts to colloidal ZrO_2 after dehydration at room temperature.

[6] Hydroxy nitrate of zirconic acid, converts to colloidal ZrO_2 after dehydration at room temperature and to crystalline form at elevated temperatures; evolves nitric acid.

[7] These defects are due to shrinkage of monoclinic ZrO_2 during firing.

[8] Alcohol dispersion of colloidal silica.

[9] Aqueous dispersion of colloidal silica + colloidal alumina.

[10] Mold surface cracked and spalled owing to high alkalinity of the Y_2O_3 flour.

[11] Casting surface rough and uneven owing to rapid gellation of face coat slurry caused by acid (binder) base (Y_2O_3) reaction, which also evolved considerable heat and rapid drying.

[12] H_2SO_4 added to slurry in an attempt to retard gellation. Porosity probably caused by residual sulfur from the H_2SO_4.

Dip coat slurries for pattern investment were made by mixing fused, calcia-stabilized ZrO_2 with a ZrO_2-forming binder. The binder selected for use in this research was zirconium acetate. It is a mild acid with a pH of 3.2 comprising 22 pct ZrO_2 in water solution. A typical analysis of this binder is shown in table 2. Slurries formulated from these materials are stable over a long period and display no tendency to gel prematurely. Either refractory oxide or binder can be added to change the viscosity of the slurry without seriously affecting slurry life or quality.

TABLE 2. - Typical analysis of zirconium acetate binder[1]

Analytical technique	Elements detected, pct					
	B	Mg	Na	Si	Ti	Zr
Qualitative spectrographic..........	0.001 0.01	0.0003 0.003	0.03 0.3	0.003 0.03	0.003 0.03	10.0 100.0
Wet chemical........................	ND	ND	0.16	ND	ND	38.0

ND Not detected.

[1] Typical ZrO_2 contents = 22.0 pct (vendor).

Zirbind[3] (hydoxy nitrate of zirconic acid), also a ZrO_2-forming binder, was examined as an alternate binder. It is a strong acid with a pH of 0.7. Molds made with ZrO_2 and this material were strong and had good properties after being properly cured and fired. However, because of the corrosive nature of the binder (HNO_3 evolved) and resultant damage to furnace elements during firing, further use was ruled out.[4]

On the basis of the data shown in table 1, the following general conclusions were made:

1. Monoclinic ZrO_2 is dimensionally less stable than cubic ZrO_2 and is therefore inferior as a mold material. This conclusion is supported by Garvie (8), who reports that a large volume expansion is involved in the transition of monoclinic to tetragonal ZrO_2. This change in volume prevents the refractory properties of pure zirconia from being used in structural ceramics.

2. Stabilized ZrO_2 (cubic ZrO_2) with ZrO_2 forming binders (zirconium acetate and Zirbind) is suitable for the inner-face layer of molds for titanium casting, provided the molds are fired at a high-enough temperature. Vacuum firing appears to offer added benefits.

3. Aluminum oxide seems to be unsuitable for titanium investment shell molds because of mold fusion and surface wetting that occur when contacted by molten titanium. This appears true ragardless of the binder used or the mold firing conditions.

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[3] Reference to specific trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

[4] Only electric furnaces were available for mold firing. If gas-fired furnaces, with adequate ventilation systems were available, which could reach sufficiently high temperature, this binder would likely be very good.

4. Zirconium silicate (zircon sand) also is unsuitable because of mold-metal reaction and fusion.

5. Cerium zirconate (not economically practical) tends to fuse when in contact with molten titanium; however, no reaction was detected.

6. Firing temperatures greater than 1,200° C are required to remove mold gases and promote thermal stability and structural soundness in investment molds intended for titanium casting.

7. Yttria may be an acceptable, nonreactive material for the inner face of molds, provided means can be determined to minimize rapid and premature gellation of slurries and the tendency of the coating to crack and spall during mold firing.

8. Slurries formulated with silica sols are not acceptable as face coats for titanium investment molds because of gases evolved from the dissociation of silica.

Other refractory metal oxides, carbides, nitrides, and silicides were considered as possible candidates for this research, but were rejected because of their incompatibility with suitable binders and refractories, thermodynamic instability at the temperatures and pressures ($\sim 10^3$ torr) encountered when melting and casting titanium, economic considerations, or potential health hazards. Among these materials were TiC, ZrC, TiN, ZrN, BN, BeO, MgO, HfO_2, and ThO_2. Molds were prepared with each of the listed materials (except BeO and ThO_2) at the inner face. However, none was cast because in all instances the material failed during high-temperature firing.

It is well known throughout the industry that a system utilizing ThO_2 is used with excellent results by one of the more prominent industrial titanium investment casters in the United States. This system, however, involves exposure to low-level radioactive material. Two other systems, ceramic oxide faced with refractory metal, and graphite molds, are also used commercially with good results. Both, however, have thermal characteristics that contribute to cold shuts, and castings poured into the metal-faced molds occasionally have hot tears. In addition, as previously stated, the metal-faced molds are particularly expensive to make because of the high costs of materials.

On the basis of these facts and the data presented in table 1, molds made from fused, calcia-stabilized ZrO_2 with a ZrO_2-forming binder were selected for optimization. Typical analyses of the ZrO_2 used for slurry preparation and stucco grain are presented in table 3.

TABLE 3. - Typical analysis of ZrO_2 used in shell mold preparation[1]

Particle size range, mesh	Primary structure	Major elements, pct					Total other impurity elements, pct
		Zr[2]	Ca[3]	Si	Fe	Al	
Minus 325...........	Cubic....	69.40	3.66	0.21	0.05	0.05	0.05
Minus 50 plus 100...	...do....	68.70	3.92	.57	.06	.21	.074
Minus 30 plus 50....	...do....	67.10	3.41	.33	.03	.03	.125
Minus 12 plus 30....	...do....	68.50	5.27	1.20	.01	.06	.275

[1] All ZrO_2 was stabilized with CaO, fused and attrition ground to size.
[2] Zr present as ZrO_2.
[3] Ca present as CaO.

Pattern Preparation

A small-scale, commercial, manually operated air pressure wax injector with a capacity of 4 quarts of molten wax was used to prepare disposable patterns. Either molten or semisolid wax was injected into permanent metal dies that were preheated to ~100° F to improve flow characteristics of the pattern material. This operation is illustrated in figure 1 showing closed die and injection equipment.

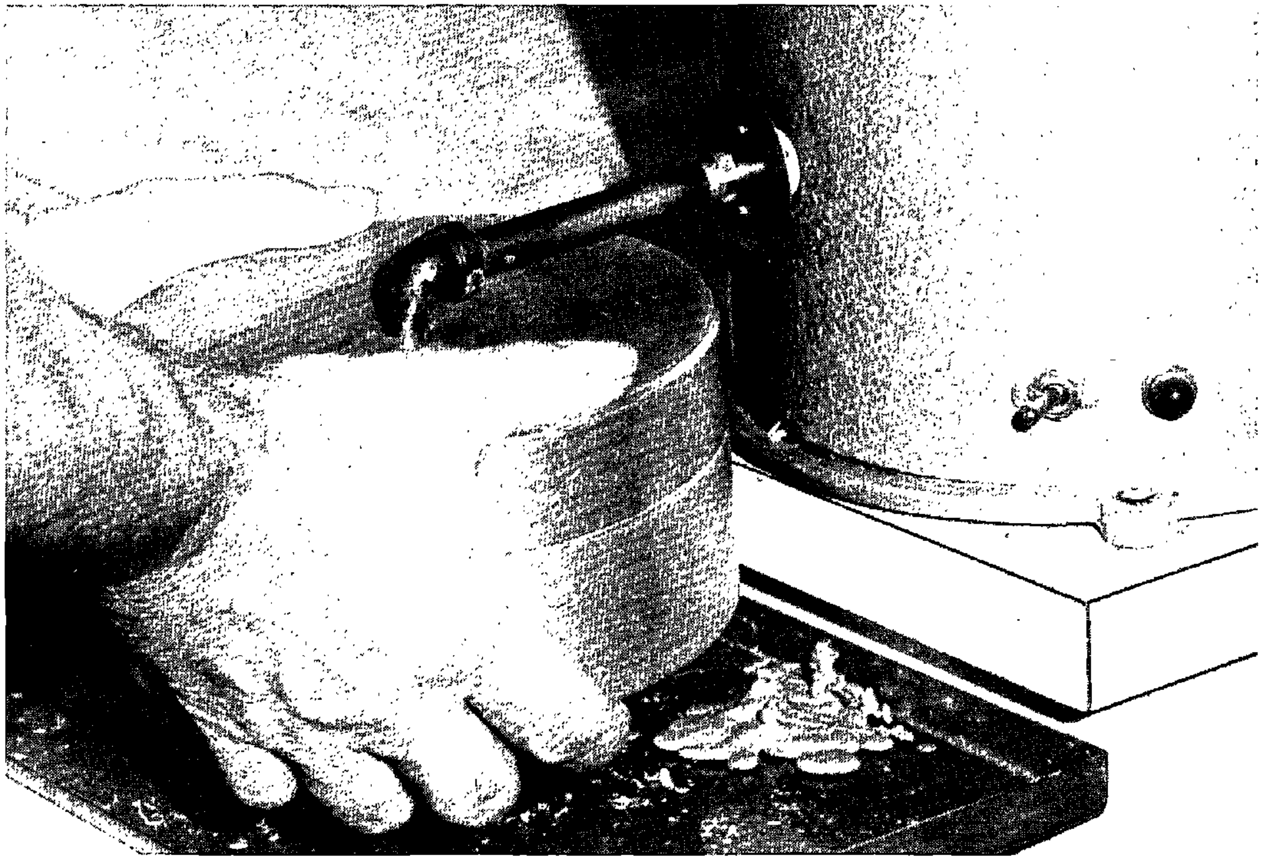

FIGURE 1. - Injection of metal die with wax to prepare a disposable pattern.

An industrial-type pattern wax was used. This wax has an injection temperature range of 132° to 140° F and a melting point range of 158° to 160° F. It was selected because it undergoes a minimum amount of cavitation, has a constant shrink factor, and produces good surfaces. To improve die-fill and minimize flow lines in the finished patterns, the wax was injected at a pressure of ~15 psi and at or slightly above the upper end of the injection temperature range. The temperature was maintained below the lower end of the melting point range of the wax, because injection of the wax as a semisolid decreases the amount of cavitation in the patterns and tends to shorten the injection cycle.

Figure 2 shows a typical wax pattern, in the shape of an integral turbine wheel-blade configuration, being removed from the tooling after solidification of the pattern material.

Other pattern components, such as sprues, gates, and risers, are made in similar fashion in appropriate dies. They are "wax welded" to the pattern body to complete a pattern assembly. In the instance where multiple parts are attached to a single sprue, this assembly is termed a pattern cluster or tree.

Before investing the prime coat onto the pattern assembly, silicone release agents used to prevent patterns from adhering to dies were removed. This was accomplished by washing the pattern in a 50-50 vol-pct mixture of acetone and trichlorotrifluoroethane. Removal of release agents is necessary to prevent nonadherence of the slurry to the pattern assembly. Wax residues and the solvent mixture can be recovered by distillation. However, recovery of these materials was considered to be impractical in this case because of the small quantities used in this research.

Pattern Investment

The prime coat slurry, which forms the mold face coat, was mixed from minus 325-mesh, fused, stabilized-ZrO_2 flour and zirconium acetate. Small amounts of other materials were added to the slurry mix, such as polyvinyl alcohol to improve mold green-strength and inhibit redissolution of partially dried coatings, methyl cellusolve or glycerine to develop plasticity, ethyl hexanol to suppress foam formation, and various nonionic wetting agents.

Slurry viscosities were determined and reproduced by means of a standard #4 Zahn viscosimeter and were recorded as Zahn #4 seconds; that is, the time interval required for 44 cm^3 of a liquid (capacity of Zahn #4 cup) to flow through the 0.168-inch-diameter orifice at the bottom of the cup. The viscometer is accurate to within 2 seconds, so reproducibility poses no problem. There is no general formula for converting Zahn measurements to other terminology, such as centipoise, because all liquids do not have the same flow characteristics with respect to the cup's surface even though they have the same absolute viscosity. It follows, therefore, that Zahn-second values are equal to other unit values only when referred to a specific liquid. The technique used for taking viscosity measurements is illustrated in figure 3.

FIGURE 2. - Removal of disposable pattern from permanent metal dies.

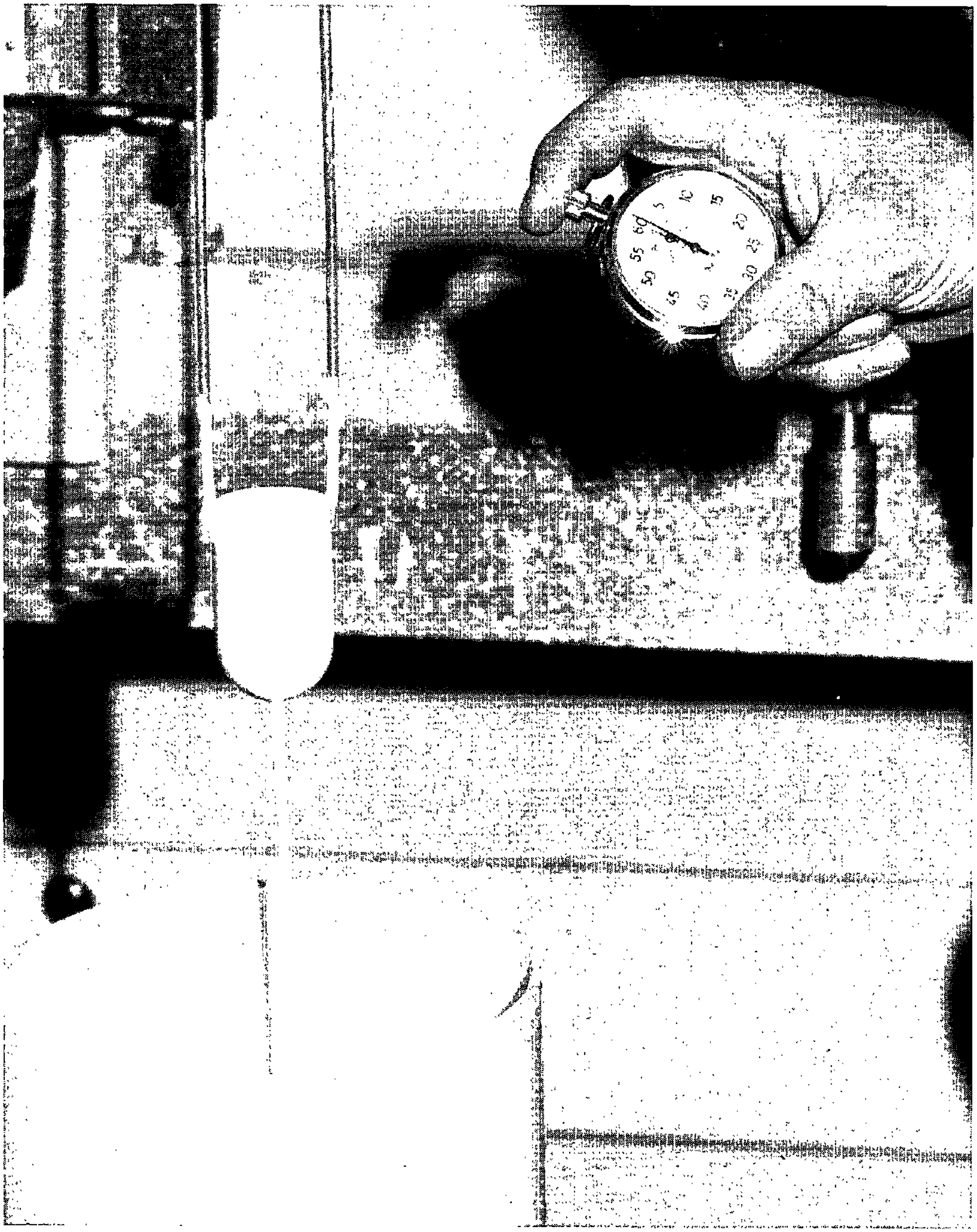

FIGURE 3. - Equipment and technique used for determination of slurry viscosity.

After the pattern assembly is cleaned, it is dipped into the primecoat slurry and rotated to assure complete coverage, after which it is withdrawn and allowed to drain to remove excess slurry. This is illustrated in figure 4.

Care should be exercised to avoid the formation of folds and sags in the prime coat, because areas of excess thickness may result in non-uniform stresses at these points in the mold and may reduce structural soundness. This can show up as buckles and scales in the casting. Sags and folds on the pattern assembly can be minimized by control of slurry viscosity and temperature, as well as by control of the temperature and humidity in the room. In addition, it is very beneficial to rotate the pattern during drainage in order to equalize the slurry distribution and to apply the first stucco as soon as possible to the wet pattern.

The nearly ideal viscosity for the prime-coat slurry was found to be 30 to 35 Zahn #4 seconds. Lower viscosities resulted in poor and inadequate pattern coverage because of excessive drainage. This in turn resulted in poor adherence of the first stucco coat and/or penetration of stucco grains through the coating. This can result in rough and pitted areas on the casting. On the other hand, if the prime coat slurry viscosity is too high, there is a greater tendency for the formation of dip coat folds, sags, and wrinkles. The effects of this have already been mentioned.

Stuccoing the slurry-coated pattern with refractory grain can be done either by immersing the still-wet pattern into a fluidized bed containing the stucco material or by conveyor belt or hand sprinkling. Because of the relatively small number of molds prepared at any given time and the necessity for frequent changes in stucco composition and grain size, the hand-sprinkling method was used in this investigation. A slurry-coated pattern is shown being stuccoed by this method in figure 5. Fused, calcia-stabilized ZrO_2 with a grain size range of minus 50 to plus 100 mesh was generally used on the inner coats. A finer stucco was also used with satisfactory results, although this practice at times resulted in the backup investment separating from the prime coat. This separation also occurred when the stucco was not applied quickly enough, in which case it did not bond to the slurry. Particle size range and distribution of the oxides used in mold preparation are shown in table 4.

Control of room temperature, humidity, and airflow in the mold room was required in order to avoid cracks and checks in the prime and adjacent prime coatings. Cracks can occur by excess expansion or contraction of the pattern assembly. This problem can be prevented by proper temperature control. The preferred drying temperature range was from 70° to 75° F. Cracks also occurred when the humidity was too low or the airflow over the molds was too high. These conditions resulted in rapid drying. The problem was solved by installing air conditioning in the mold room, limiting traffic through this area, and utilizing a specially constructed closed drying chamber. An independent heat source in this chamber allowed the temperature to be controlled to ±2° F.

TABLE 4. - Particle size range and distribution of oxides used in preparation of investment shell molds

Particle size distribution	Screen opening, inch	Distribution, pct
MINUS 12- PLUS 30-MESH[1] ZrO_2		
Plus 12-mesh......................	>0.0555	0.80
Minus 12-mesh......................	.0555	20.35
Minus 14-mesh......................	.0469	15.20
Minus 16-mesh......................	.0394	11.35
Minus 20-mesh......................	.0331	12.90
Minus 24-mesh......................	.0278	12.00
Minus 28-mesh......................	.0234	10.45
Pan.............................	<.0234	16.95
MINUS 30- PLUS 50-MESH[1] ZrO_2		
Plus 28-mesh......................	>0.0234	0.23
Minus 28-mesh......................	.0234	.24
Minus 32-mesh......................	.0197	.38
Minus 35-mesh......................	.0165	>.75
Minus 42-mesh......................	.0139	53.05
Minus 48-mesh......................	.0117	34.55
Pan.............................	<.0117	3.80
MINUS 50- PLUS 100-MESH[1] ZrO_2		
Plus 48-mesh......................	>0.0117	0.62
Minus 48-mesh......................	.0117	6.65
Minus 60-mesh......................	.0098	36.90
Minus 65-mesh......................	.0083	23.85
Minus 80-mesh......................	.0070	17.48
Minus 100-mesh.....................	.0059	11.80
Pan.............................	<.0059	2.70
MINUS 28- PLUS 48-MESH[1] Al_2O_3		
Plus 28-mesh......................	>0.0234	0.05
Minus 28-mesh......................	.0234	.50
Minus 32-mesh......................	.0197	1.40
Minus 35-mesh......................	.0165	10.70
Minus 42-mesh......................	.0139	24.20
Minus 48-mesh......................	.0117	29.55
Pan.............................	<.0117	33.60
MINUS 60-MESH[1] Al_2O_3		
Plus 60-mesh......................	>0.0098	4.45
Minus 60-mesh......................	.0098	1.20
Minus 65-mesh......................	.0083	3.00
Minus 80-mesh......................	.0070	6.55
Minus 100-mesh.....................	.0059	8.10
Minus 115-mesh.....................	.0049	6.25
Pan.............................	<.0049	70.45

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[1] Tyler equivalent mesh.

FIGURE 4. - Draining excess refractory slurry from pattern assembly after dip coating.

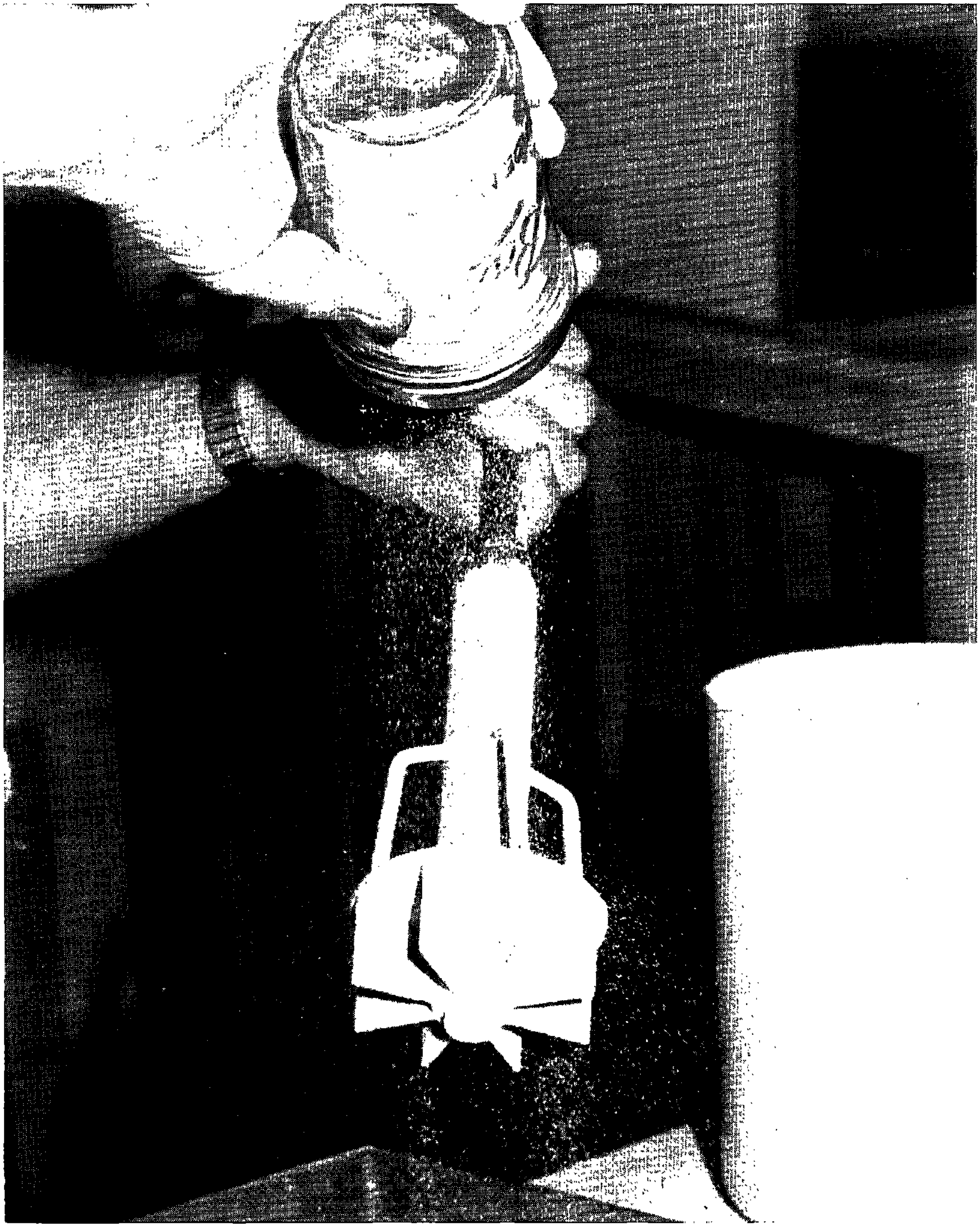

FIGURE 5. - Sprinkling refractory grain (stucco) on wet pattern assembly.

After the first stuccoed coat is allowed to dry to a maximum solvent content of ~20 pct, a second dip coat of the same composition as the first, but of only about half the viscosity, is applied. The coated pattern is then drained and stuccoed as in the preceding operation and allowed to dry before application of a following coat. According to Brown and Brown (4), the solvent content of the coatings should fall in the range of ~20 pct maximum to ~2 pct minimum.

If the solvent content of the previous coat is too high, that coating may be dissolved by the following dip coat. On the other hand, if the solvent content falls below ~2 pct, the coating will lose resiliency and become brittle. It may then crack and spall because it can no longer expand and contract with thermal changes. Thus, the solvent content is especially critical if slurry and room temperatures are not closely controlled. It is highly desirable that this practice be followed for each coating step involved in building up the mold shell.

The reason for significantly lowering the viscosity of the second dip coat is to thoroughly wet the first and thus minimize the formation of unfilled air voids between the two coatings. This procedure gives added strength to the mold and prevents molten metal from penetrating the relatively thin prime coat during the casting operation. In order to form mold shells of desired thickness, and of adequate strength and permeability, a gradual increase was made in the refractory stucco particle size and in the distribution and concentration of coarse and fine grain solids in the dip coat slurry. Work indicated that after progression to the coarsest stucco (minus 12- plus 30-mesh), no benefits were realized by further increasing the stucco grain size, changing slurry characteristics, or continued application of the minus 12- plus 30-mesh backup stucco. Therefore, minus 30- plus 50-mesh grain was used to achieve the desired rapid buildup of shell thickness with good strength and permeability.

Typical formulations for two alternate successful mold systems are presented in tables 5 and 6. Table 5 represents a mold made entirely of fused, stabilized ZrO_2, and table 6 represents a ZrO_2-faced mold backed by Al_2O_3 from the third to the final coat. The use of Al_2O_3 at the inner face of molds for titanium was ruled out because of mold fusion. However, Al_2O_3-backed molds with an inner face of the more refractory ZrO_2 might be a practical way to reduce production cost. We found that mold fusion and mold/metal reaction could be avoided by this means, but that other problems occurred. The Al_2O_3-backed molds often cracked during firing, thus rendering them useless. Whether this was caused by an expansion mismatch between the ZrO_2 and the Al_2O_3 or by a volumetric change during a phase transformation was not determined. Besides this, the frequency of misruns in thin sections of casting was quite high because of the high thermal conductivity of the molds with Al_2O_3 backing.

TABLE 5. - Formulation for 100-pct, fused, stabilized ZrO_2 investment shell mold

Dip coat	Slurry composition[1]	Slurry viscosity[2]	Stucco
Prime.....	Minus 325-mesh ZrO_2[3]........	35	Minus 50- plus 100-mesh ZrO_2.
Adjacent prime.	.....do.....................	15	Do.
1st backup	Minus 325-mesh ZrO_2 (50 pct) + minus 50- plus 100-mesh ZrO_2 (50 pct).	25	Minus 30-plus 50-mesh ZrO_2.
2d backup.	.....do.....................	25	Do.
3d backup.	.....do.....................	25	Minus 12- plus 30-mesh ZrO_2.
4th backup	.....do.....................	25	Minus 30- plus 50-mesh ZrO_2.
5th backup	.....do.....................	25	Do.
6th backup	.....do.....................	25	Do.
Seal coat.	.....do.....................	15	None.

[1] Zirconium acetate used as binder/slurry vehicle for all coats.
[2] Slurry viscosity values in Zahn #4 seconds.
[3] All ZrO_2 used was fused and stabilized with CaO.

TABLE 6. - Formulation for Al_2O_3 investment shell mold faced with fused, stabilized ZrO_2

Dip coat	Slurry composition[1]	Slurry viscosity[2]	Stucco
Prime..........	Minus 325-mesh ZrO_2[3]...........	35	Minus 50- plus 100-mesh ZrO_2.
Adjacent prime.	.....do........................	15	Do.
1st backup.....	Minus 325-mesh ZrO_2 (50 pct) + minus 50- plus 100-mesh ZrO_2 (50 pct).	25	Minus 30- plus 50-mesh ZrO_2.
2d backup......	.....do........................	25	Minus 12- plus 30-mesh ZrO_2.
3d backup......	Minus 325-mesh ZrO_2 (50 pct) + minus 60-mesh Al_2O_3 (50 pct).	25	Minus 28- plus 48-mesh Al_2O_3.
4th backup.....	.....do........................	25	Do.
5th backup.....	.....do........................	25	Do.
6th backup.....	.....do........................	25	Do.
7th backup.....	.....do........................	25	Do.
Seal coat......	.....do........................	15	None.

[1] Zirconium acetate used as binder/slurry vehicle for all coats.
[2] Slurry viscosity values in Zahn #4 seconds.
[3] All ZrO_2 was fused and stabilized with CaO.

Mold strength and permeability are dependent on the particle sizes, concentration, and distribution of the materials composing the stucco, as well as on the concentration of the solids in the binder and water slurry vehicle, and on the number of coatings that form the shell. As shown in tables 5 and 6 the final coat was not stuccoed; a thin dip coat was applied to seal the outer surface, thus preventing poorly bonded stucco from sloughing off.

Pattern Removal

After the final investments are applied to the patterns, they are set aside in the drying chamber and allowed to air dry to a low moisture content (~2 pct) to avoid the possibility that water trapped beneath the face coat might cause spalls and cracks. The disposable patterns are then removed by melting the thermoplastic material and allowing it to run out of the shell. This is the most common practice used in the industry. A risk of cracking the shell is presented by this practice, however, because the patterns expand at a faster rate than does the refractory shell, and they exert strong pressures on the relatively weak shell. The frequency of cracking can be lowered considerably by a flash firing technique, where the mold is heated at a sufficiently high rate to cause the surface of the wax in contact with the mold to fluidize before the bulk of the pattern begins to expand. Because of the high temperature required in flash firing, the pattern material burns or degrades and cannot be recycled.

An industrial method, initially used in the Bureau's research, is solvent dissolution of the pattern. Molds containing disposable patterns are inverted on a suitable rack or basket in a chamber with an organic solvent such as trichlorolethylene or perchlorolethylene. The solvent is heated, and vapors circulating through the closed tank dissolve the wax. This process also results in loss of the wax, although this work shows that it is economical to reclaim the solvent by distillation. Approximately 95 pct of the solvent used was recovered and suitable for reuse. This technique was discontinued because mold shells tended to soften and become saturated with solvent-bearing waxes that had to be burned off by firing in air at 400° C. Large quantities of fumes were evolved, and excessively high ash residue remained on mold surfaces. Roughness and irregularities on casting surfaces often resulted.

Finally, microwave heating was used to remove the patterns. The technique has the advantage of flash firing because heat is generated by the action of microwave energy on water molecules in the mold shell and is then conducted from the mold to the pattern. The pattern surface is melted and freed from the mold. Pattern expansion does not occur, and no stresses are applied to the mold shell. A major portion of the wax is removed as a solid and is readily recovered for use without any further treatment. Pattern removal by this method is cheap, fast, and clean. Only a thin film of wax is left in the mold, and this wax is readily eliminated by firing to 400° C. Because of these advantages, the microwave dewax technique was adopted as a standard operating procedure.

Curing Cycle

The best molds were obtained when the shells were placed in a drying oven at 200° C as soon as possible after pattern removal. This drained the residual wax and prevented moisture pickup. The molds were stored at this temperature until just prior to prefiring (high-temperature air cure). To accomplish the curing operation, the molds were rapidly transferred from the drying oven to the electric (Super Kanthal element) muffle furnace, which had been preheated to 200° C. After the transfer was complete, the furnace temperature was increased slowly to 400° C and held at this temperature in an oxidizing atmosphere for a minimum of 12 hours. The reason for the rapid mold transfer and slow temperature change after the transfer was to minimize the possibility of face coat buckle during this early phase of the heat curing cycle. The reasons for the 400° C curing step are to burn off any remaining pattern residues, to effect the removal of pattern and binder volatiles, and to begin formation of a bond between the colloidal oxide binder and the oxides that comprise the mold shell.

Bonding is accomplished by conversion of colloidal ZrO_2 in the zirconium acetate binder to the crystalline form. The conversion is apparently complete at 400° C. A desiccated sample of the binder heated for 12 hours at this temperature was examined by X-ray diffraction, and cubic ZrO_2 was detected. Monoclinoc ZrO_2 was the crystalline form expected after heat treatment. However, according to Duwez and Odel (7), if the average mean crystallite size of ZrO_2 is very small, X-ray patterns will show cubic ZrO_2 even though no modifiers are present. Further heating of the sample to 1,450° C caused the structure to transform to the monoclinic form. The exact temperature at which this occurred was not determined. However, it is assumed that the transformation resulted from grain growth of the crystallites and undoubtedly occurred at less than 1,000° C.

Following the prefiring operation at 400° C, the molds, which had already developed a fair amount of strength, were fired to temperatures for their final cure. Those molds to be tested after curing at 1,200° C were left in the prefiring furnace in order to avoid unnecessary handling and thermal cycling. Ransom and Randolph (9) listed this condition (too fast or uneven firing cycles) as a possible cause for cracks in the mold face coat and resulting flash lines on castings. Molds cured at 1,400° C were fired in an oxidizing atmosphere in a silicon carbide element furnace, and some also were fired in a tungsten element vacuum furnace at this same temperature. This latter furnace also was used for all firing operations above 1,400° C or requiring a controlled atmosphere.

Firing at these high temperatures, which completed the final phase of the curing cycle, was done to complete the formation of a high-temperature bond between the mold particles and to remove the final vestiges of any volatiles remaining in the mold. This step is extremely important in the formation of sound molds that must have a high resistance to both chemical reaction and erosion when in contact with molten metal.

Mold Structure After Firing

According to information advanced by the Zirconia Products Division of the Corning Glass Works (6), monoclinic ZrO_2 crystals transform to tetragonal shape at about 1,000° C, with a volume shrinkage of ~7 pct. This transformation was confirmed by Garvie (8) and was mentioned previously. The transformation is believed to be martensitic, and this form cannot be retained in bulk material at room temperature and atmospheric pressure regardless of quenching procedures because the products are metastable and the transformation is fast and diffusionless. This is unfortunate because tetragonal ZrO_2 has a lower thermal expansion curve than does cubic ZrO_2 and, if the tetragonal ZrO_2 were to be combined with cubic ZrO_2, the product would be useful in the formation of molds having less tendency toward thermal shock and dimensional changes during thermal cycling.

However, when fully stabilized ZrO_2 is mixed with the monoclinic structure, a partially stabilized material forms that has a lower thermal expansion than the fully stabilized form (the expansion curve is still uniform and nearly linear). This form is more useful for molds than is fully stabilized cubic ZrO_2, which is subject to thermal shock.

ZrO_2 in the zirconium acetate binder was converted from noncrystalline to cubic and, ultimately, to the monoclinic form with increasing temperature; retention of the monoclinic form through firing (at least up to 1,450° C) resulted in a partially stabilized ZrO_2 mold that was quite resistant to thermal shock.

X-ray diffraction pattern data showing these transformations in the binder solids and the prime coat slurry solids are presented in table 7. The prime coat slurry was formulated with zirconium acetate and minus 325-mesh, fused ZrO_2 stabilized with CaO, as mentioned previously.

TABLE 7. - Effects of temperature on the polymorphism of ZrO_2 in binder solids and oxide grains used to prepare investment shell molds

Oxide source	Processing temp., ° C	Structure		
		Amorphous, pct	Monoclinic	Cubic
Binder...........	200	100	None...........	None.
Prime coat slurry[1]	200	0	Trace[2].........	Primary phase.[3]
Binder...........	400	0	None...........	Only[4] cubic ZrO_2.
Prime coat slurry.	400	0	Trace..........	Primary phase.
Binder...........	1,450	0	Only monoclinic ZrO_2.	None.
Prime coat slurry.	1,450	0	Trace..........	Primary phase.

[1] Prime coat slurry formulated with zirconium acetate (ZrO_2 forming binder) and fused, CaO-stabilized ZrO_2.
[2] Trace = 1.0-10.0 pct.
[3] Primary phase = 40.0-100.0 pct.
[4] The oxide examined had a very small mean crystallite size.

Mold curing temperatures of 1,000°, 1,200°, and 1,000° C in air at atmospheric pressure and of 1,400° and 1,500° C under vacuum were investigated to determine the interrelated effects of these parameters on mold and casting characteristics. Care was taken to stay below the temperature at which sintering would occur in order to avoid distortion and maintain the close dimensions of the mold. A rough rule of thumb advanced by Brown and Brown (4) suggests that mold curing temperature should range from 60 to 75 pct of the temperature at which the metal to be cast will melt. Temperatures within and somewhat above this range were evaluated, and the results of tests are presented in table 8. These data show that the strength, reactivity, and volatile gas contents, as well as the quality of castings produced, are related to both temperature and time at temperature. Further improvements result by vacuum firing.

TABLE 8. - Effects of firing parameters on the interrelated properties of stabilized ZrO_2 investment molds and cast titanium shapes

(ASP--alligator skin pattern; B--buckles; BH--blow holes; FC--fine cracks; G--grainy; ND--not detected; PH--pin holes; RZ--reaction zone; S--scab; SFL--small flash lines)

Mold curing conditions			Mold and casting characteristics						
Temp., ° C	Time, hours	Atmosphere	Molds face coat			Molds shell hardness[1]	Internal	Castings surface	Case penetration, inch
			Defects	Color	Hardness[1]				
1,000.....	4	Air...	G	Light cream	5	6	Porosity...	PH, RZ, BH	>0.025
	6	Air...	G	...do......	6	6	...do......	PH, BH, RZ	> .025
	8	Air...	ND	...do......	6	7	...do......	PH, BH....	0.020-0.025
1,200.....	2	Air...	ND	Light tan..	6	7	...do......	PH, RZ....	.015- .020
	4	Air...	B	...do......	7	8	...do......	PH, S, RZ.	.015- .020
1,400.....	4	Vacuum	ND	...do......	7	8	No defects.	PH........	.015- .020
	2	Air...	FC	Light beige	8	9	...do......	SFL, ASP..	.007- .010
	4	Air...	ND	...do......	8	10	...do......	No defects	.003- .007
1,500.....	4	Vacuum	ND	...do......	9	10	...do......	...do.....	.001- .004
	2	..do..	ND	Beige......	9	10	...do......	...do.....	.001- .003
	4	..do..	ND	Light brown	10	10	...do......	...do.....	.000- .001

[1] No quantitative hardness measurements available. Hardness is reported on a relative, arbitrary scale of 1 to 10 with the highest number indicating the hardest surface.

MELTING AND CASTING

The melting and casting procedures have been described elsewhere in detail (3, 5). The skull casting process described was devised by the Bureau of Mines and has been adopted as the standard industrial practice for casting titanium and other reactive and refractory metals. The process involves vacuum melting a consumable electrode (of the material to be cast) into a tiltable, water-cooled copper crucible. A high, direct current electric arc is used as the energy source. After the required amount of metal is melted, the arc power is terminated, the crucible is tilted, and the contents are poured into appropriately located molds in a lower portion of the vacuum chamber. The skull casting technique eliminated any possibility for reaction between metal and crucible because the metal is melted in a shell, or skull of metal, which has solidified on the crucible wall.

Typically, a casting heat was conducted using an electrode fabricated from previously melted, commercially pure, vacuum-distilled titanium sponge. On occasion, however, scrap titanium metal was used for melting stock. This was done for screening purposes only, because the high-level of interstitial impurities in the scrap titanium that was used affected mechanical properties but not castability. An analysis of the titanium sponge used for this study is presented in table 9.

TABLE 9. - Analysis of titanium sponge melt stock

Element[1]	Composition of sponge, pct
Titanium	99.8
Carbon	.01
Oxygen	.04
Hydrogen	.002
Nitrogen	.006
Manganese	.02
Iron	.02
Magnesium	.04
Chlorine	.08
Silicon	.01

[1] Elements not reported were not detected.

All castings for this evaluation were made in molds that had been held in a drying oven at 200° C after high-temperature firing. The purpose was to prevent the molds from taking on water prior to casting; water vapor would contribute to casting defects such as porosity, pinholes, and blowholes. The majority of the shapes were statically cast in order to evaluate mold strength. To enhance filling, some were centrifuged at a speed calculated to impart to the casting a force of ~14 times that of gravity. Figure 6 shows a typical arrangement of mold, mold fixture, gating system, and down sprue mounted for centrifugal casting. All components named, except the mold, were machined

FIGURE 6. - Typical arrangement of mold, mold fixture, and sprue/gate system for vertical axis centrifugal casting.

from high-density industrial graphite. Before being closed, the mold fixture was filled with coarse ZrO_2 (grog) to support the mold. A graphite plate was secured to the top of the box to prevent the grog from being thrown from the box during centrifuging.

Molds for static casting were located in the same chamber as the centrifuged molds and were supported vertically in a fixture that also was filled with zirconia grog. The grog was used as an expedient means to support the odd-shaped molds. In addition, it served to isolate the molds from the cold furnace parts and thus prevent unduly rapid chilling of cast metal. No efforts were made to heat the molds beyond the temperature retained from the drying oven because, as can be readily understood, the incidence and severity of mold-metal reaction increases with temperature.

The static molds were filled through a machined-graphite funnel arrangement. Metal entered downward into a ceramic sprue that was an integral part of the mold. A typical, statically cast titanium, integral turbine wheel-blade configuration is shown in figure 7. The imperfections and flow lines seen are reproductions of the wax pattern; they are not casting flaws and defects. The cross section of the blades, or vanes, taper from 0.060 inch at the bottom to 0.150 inch at the location where they join the bottom of the disk. Figures 8A and 8B show side and bottom views of a similar turbine wheel-blade prepared by centrifugal casting.

The dark, mottled pattern shown on the wheel bottom in figure 8B results from uneven grit blasting used to remove mold materials adhering to the casting after knockout or to partially remove the brittle case formation. Figures 9A and 9B show a profile and a bottom view of an alternate centrifugal-casting gating system. This casting was bottom fed with the vanes upright through the "L" shaped gate. Metal flow is less turbulent in this arrangement, and fewer casting defects result. As should be expected, centrifugal casting, regardless of the gating arrangement employed, enhances mold filling. This method is strongly recommended in order to minimize the frequency of misruns in thin sections of unheated molds.

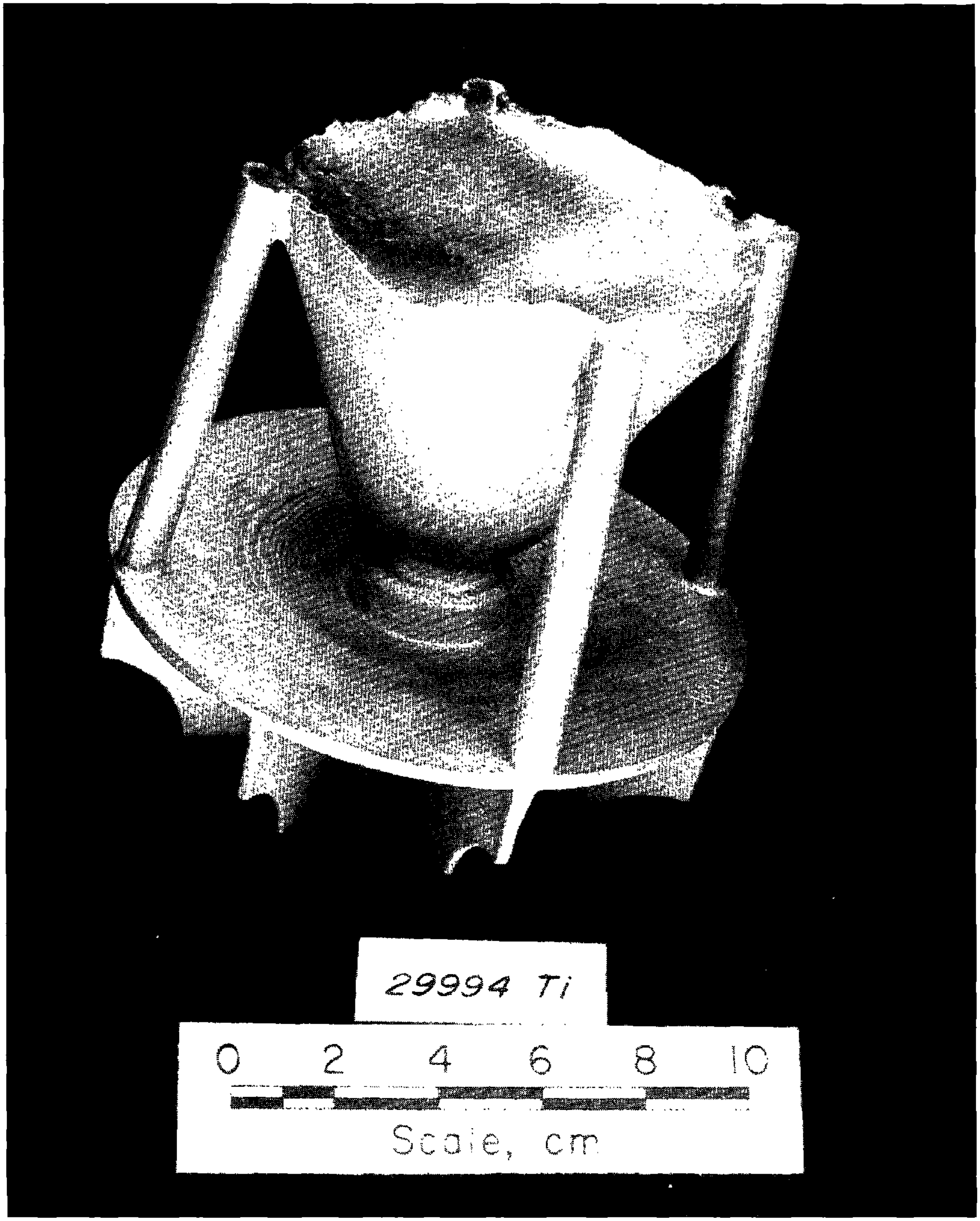

FIGURE 7. - Typical static-cast integral turbine wheel-blade assembly.

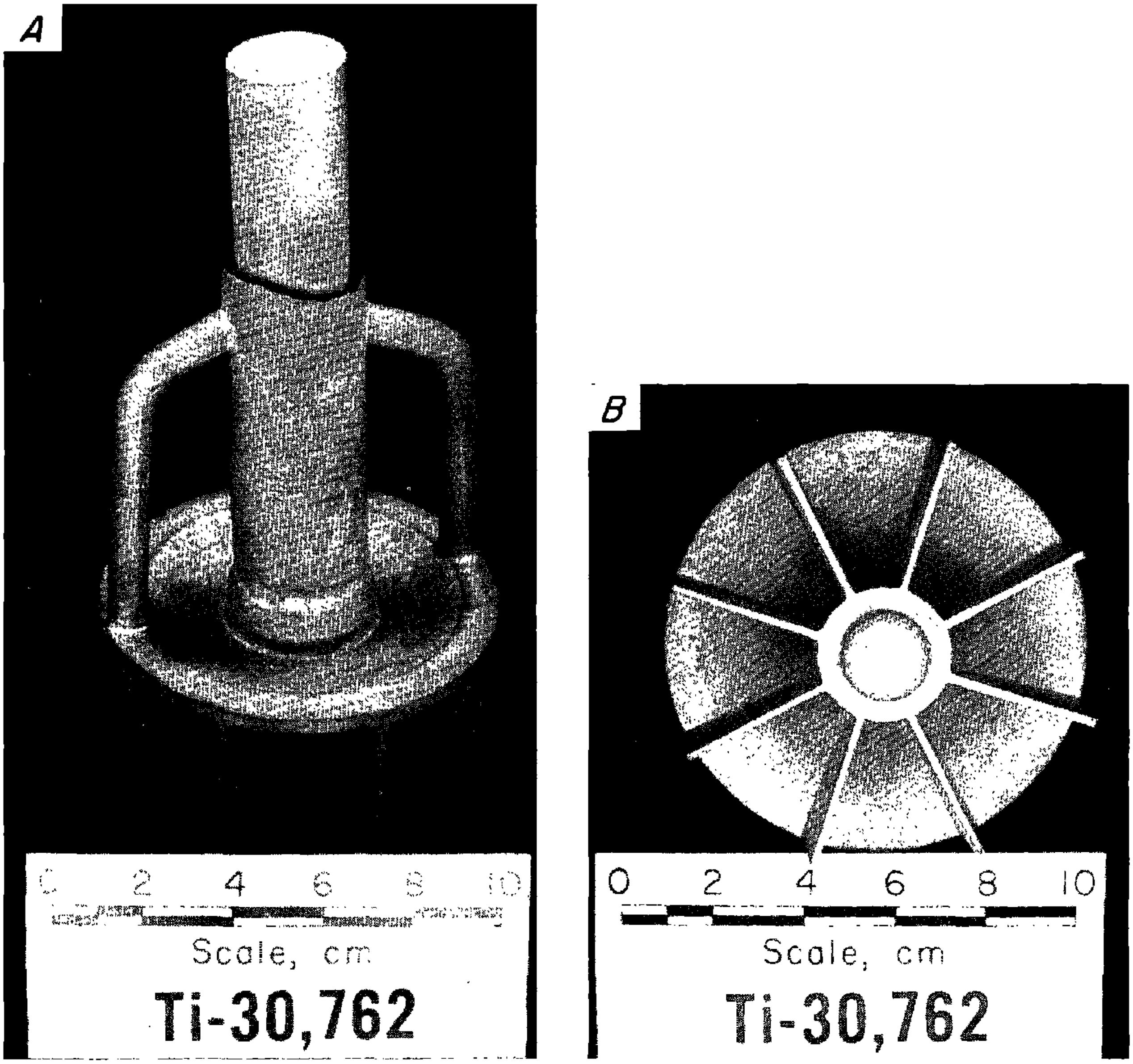

FIGURE 8. - Side (A) and bottom (B) views of a turbine wheel-blade centrifugally cast using a direct straight runner-gate system.

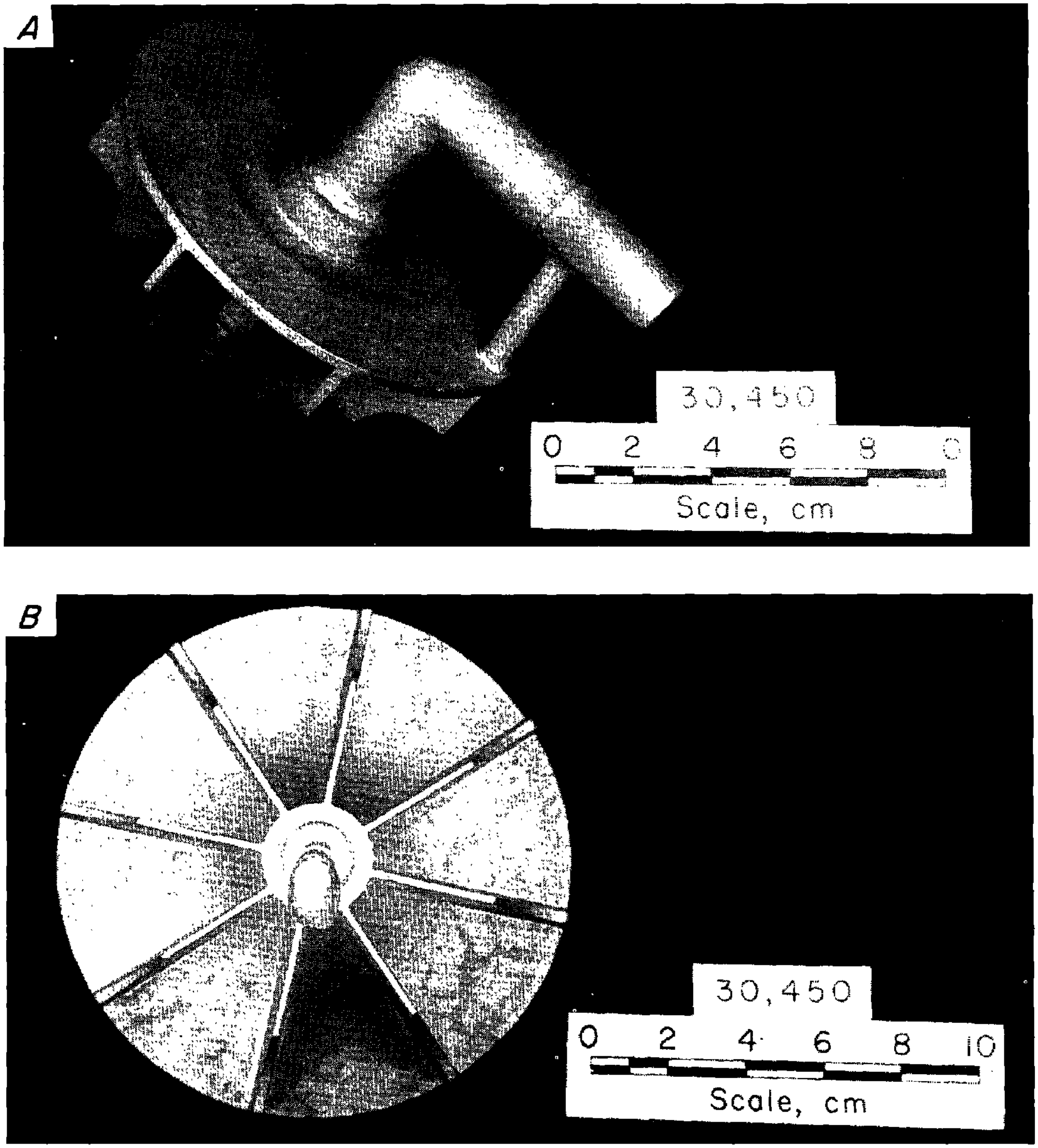

FIGURE 9. - Profile (A) and bottom (B) views of turbine wheel-blade centrifugally cast using a bottom-fed horn gate system.

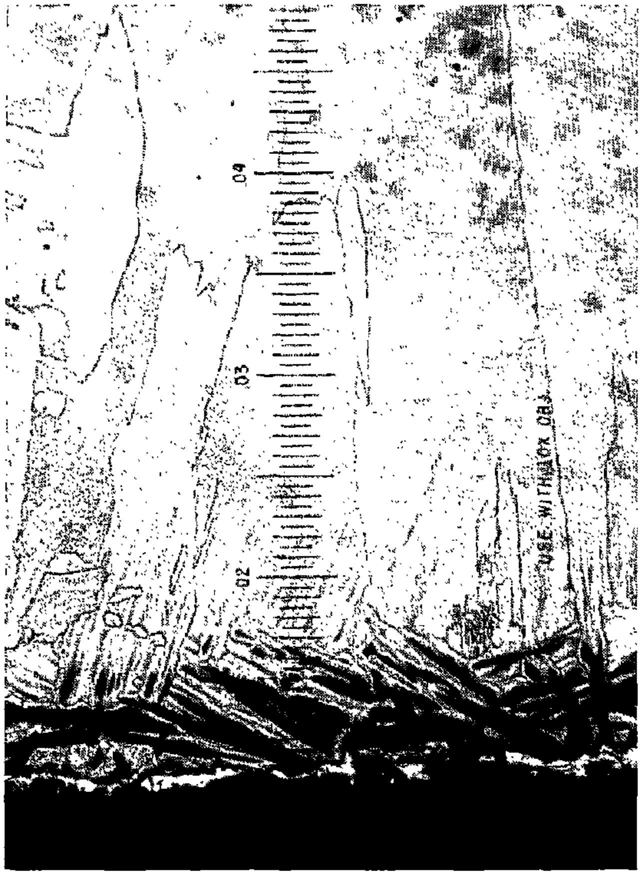

FIGURE 10. - Optical micrograph showing the structure of C. P. titanium poured in a ZrO_2 mold fired for 2 hours at 1,400° C showing case formation (X 100).

EVALUATION

Molds made under conditions judged to be optimum or near optimum were cast with titanium and examined by optical microscopy, electron microprobe, and mechanical testing. Results of these evaluations are discussed below.

Optical Microscopy and Electron Microprobe

A microscopic study was made of specimens taken from several castings to determine the extent of case formation as a function of mold firing temperature. All specimens were taken from areas of nearly equal cross section to minimize the effects of chill time on case penetration. Figure 10 shows an optical micrograph of titanium poured into a mold that had been fired in air for 2 hours at 1,400° C. A brittle, alpha-titanium enriched metal case ~0.0075 inch thick is shown to exist. A thin, nearly continuous phase surrounds the alpha-titanium band. This band, which appears lighter both optically (fig. 10) and in an electron micrograph (fig. 11), contains more oxygen than the darker material. The darker material evidently consists of two fine-grained phases.

It is speculated that the light grains contained enough oxygen to have solidified as the alpha phase, whereas the dark material probably solidified as beta and then transformed to alpha plus beta during the cooling process.

FIGURE 11. - Electron micrograph showing continuous alpha band (X 300).

A few isolated grains containing zirconium were observed at the edge, but not consistently enough to account for changes in microstructure. Figure 12 is a zirconium X-ray micrograph that shows an area where the largest concentration of zirconium can be observed at a distance of roughly 100 micrometers from the surface. Figure 13 is an oxygen X-ray micrograph of the same area, and figure 14 is an optical micrograph at X 300, which clearly delineates the area of the concentration. These areas show a titanium grain rich in oxygen, a void, and a zirconium-rich zone.

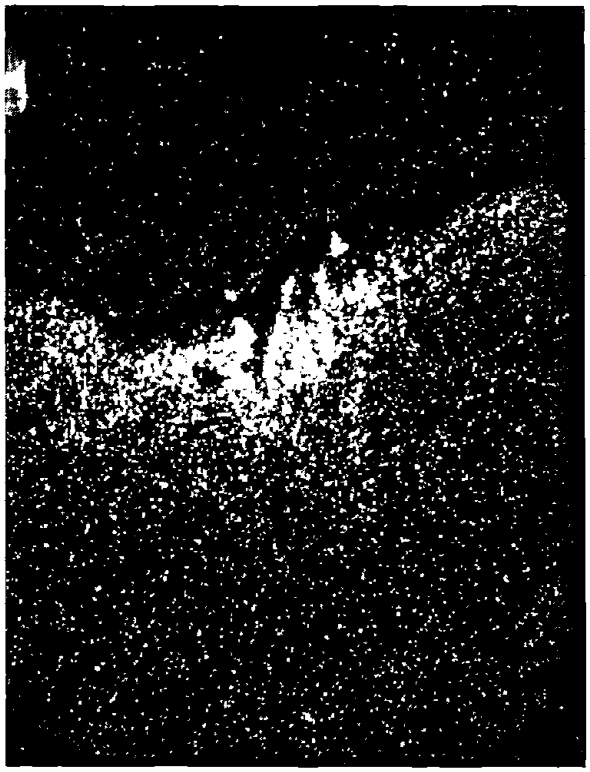

FIGURE 12. - Zirconium X-ray micrograph showing area on casting surface containing zirconium (X 300).

FIGURE 13. - Oxygen X-ray micrograph of the same area (X 300).

FIGURE 14. - Optical micrograph showing area of zirconium-oxygen concentration (X 300).

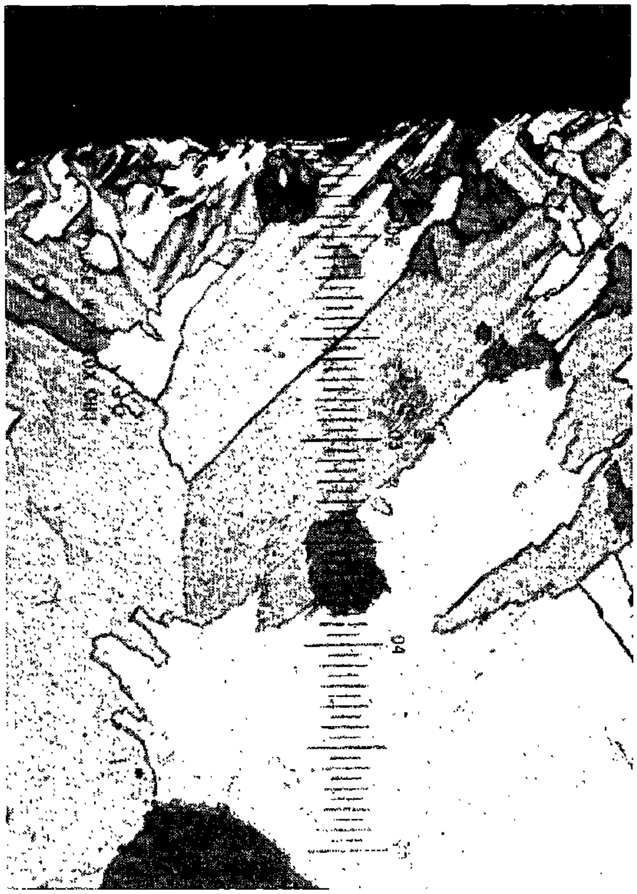

FIGURE 15. - Optical micrograph showing the structure of C. P. titanium cast into a ZrO_2 mold fired to 1,400°C for 6 hours (X 100).

FIGURE 16. - Optical micrograph showing the structure of C. P. titanium cast in a ZrO_2 mold vacuum fired at 1,500° C for 4 hours (X 100).

The extent of case formation on titanium castings poured into molds that were fired to 1,400° C in air for 6 hours is shown in figure 15. This photomicrograph shows that the case depth is considerably less than on the casting from the previous mold. Apparently, the increased time at temperature rendered the mold more resistant to attack by the molten titanium; hence, less oxygen was available for alpha case formation. Penetration of the reacted layer as shown in this figure was approximately 0.003 inch.

Of all the conditions examined, curing in vacuum at 1,500° C for at least 4 hours was the most conducive to preparation of castings having no apparent reacted surface layer. Figure 16 shows the as-cast structure of commercially pure (C.P.) titanium cast into a zirconium oxide mold thus fired. No alpha case is apparent; only an extremely narrow band of very fine grained titanium can be seen at the mold/metal interface. For the first time, no effects of mold reaction can be observed. Only the effects of rapid quenching on the cast structure can be seen. There was no zirconium found by microprobe examination in the area shown in the photomicrograph.

A Knoop microhardness traverse was made of the specimens in an attempt to relate the depth of observed case penetration with the hardening depth. These data are shown in table 10 and are discussed later.

TABLE 10. - Hardening depth of C.P. titanium cast in ZrO_2 molds as a function of reaction case penetration

Observed case depth, inch	Depth of metal hardness, inch
0.0075	0.019
.003	.012
<.001[1]	.002

[1] No alpha case observed; hardening due to quench effect of rapid chilling.

Mechanical Testing

Room-temperature tensile properties of C.P. titanium were determined on standard 1/4-inch-diameter, round, threaded-end, tension test specimens shown in the ASM Metals Handbook (1). Tests were conducted on as-cast specimens. No attempt was made to remove case formation, other than that the case inadvertently thinned during grit blasting to eliminate residual mold materials from the metal surfaces. The strength and ductility, therefore, are representative of unconditioned castings and are not properties of conventionally processed titanium metal. The only machine conditioning performed on the specimens was the reshaping of some of the threaded ends that had not filled completely. The other threaded ends were cleared with a die nut to assure a proper fit with the grips of the test machine.

Test data were obtained on a 60,000-lb capacity hydraulic universal test machine. This machine has a lower limit of 0.01 in/in/min, which is above the ASTM recommendation of 0.003 to 0.007 in/in/min for titanium. This higher rate affects the yield strength and ductility measurements, but does not affect the tensile strength. Thus, the strength data can be used for comparison but not for classification. Elongation and reduction in area were determined in the normal manner after the test. Data from tests performed are presented in table 11.

TABLE 11. - Tensile properties of C.P. titanium cast in ZrO_2 investment shell molds

Test group number[1]	Tensile strength, psi	Yield strength, 2-pct offset, psi	Elongation, pct	Reduction in area, pct
1	60,410	49,900	15.00	19.00
2	54,526	36,483	37.00	60.00
3	53,027	35,299	38.75	58.25
4	52,392	34,767	45.50	50.60
5	52,391	33,696	42.00	69.00

[1] Each test group represents an individual casting. The values presented for each group are an average of 4 determinations.

Each of the castings tested was subjected to a complete chemical and spectrographic analysis. Data are listed in table 12.

TABLE 12. - Chemical composition of titanium castings represented in tension tests[1]

Test group number	Concentration of interstitial and metallic impurity elements, ppm				
	O	H	N	C	Total other elements
1	1,178	38	85	447	1,225
2	847	42	42	414	1,325
3	819	37	43	439	1,410
4	816	26	42	439	1,018
5	784	24	43	400	1,440

[1] Samples for analyses were obtained from tensile specimens after testing.

According to data presented in tables 11 and 12, all the castings, except those represented by test group 1, are comparable to Grade C-1, cast unalloyed titanium (2). Test group 1 castings could also be compared to Grade C-1 on the basis of composition. However, while its greater strength characterizes it in the Grade C-2, unalloyed titanium classification, Grade C-2 requires 20-pct elongation, and the group 1 castings had only 15-pct elongation. This group therefore cannot be directly compared to any grade.

The higher tensile and yield strengths and lower ductility of specimens from test group 1 undoubtedly result from the somewhat higher concentrations of oxygen and carbon. It is possible that the increases noted could have resulted from mold/metal interaction, but it seems more likely that the increase was due to melting practices.

Both analytical and mechanical test data indicate that the titanium castings prepared in ZrO_2 shell molds are comparable to commercial investment castings.

CONCLUSIONS

Bureau of Mines research on investment shell molds for reactive and refractory metal casting yielded positive results. This research demonstrated that molds prepared from calcia-stabilized zirconia with zirconia-forming binders can be used to prepare precision investment castings of titanium with minimal brittle case formation and cast metal contamination. The significance of this is that ZrO_2, which is readily available, nontoxic in character, and relatively inexpensive, can be successfully substituted for molds that are presently used in the developing titanium-casting industry, but that are produced from materials not meeting all these criteria.

The research demonstrated that distortion and dimensional accuracy, as well as mold integrity, can be controlled by molding and firing practices. In addition, relatively thin (~3/8-inch-thick) zirconia shells can be rendered sufficiently strong to withstand stresses of at least 14 times the force of gravity that occur during centrifugal casting of titanium.

Examinations of C.P. titanium specimens cast into the ZrO_2 molds indicate that the occurrence and depth of brittle case penetration into casting surfaces are controllable to acceptable levels by firing practices. This case penetration is strongly dependent upon the interrelated effects of temperature, time at temperature, and curing-furnace atmosphere. (Only air and vacuum conditions were evaluated.) The minimum conditions for acceptable results were found to be 1,400° C for 2 hours in air. These conditions resulted in a case formation of ~0.008 inch on the casting surface. Continued firing at this temperature in air for 6 hours or at 1,500° C in vacuum for only 2 hours was found to yield nearly identical results. The case formation on castings in these instances ranged from 0.001 to 0.004 inch and from 0.001 to 0.003 inch, respectively. This amount of case can be readily eliminated by grit blasting or chemical milling without affecting dimensional tolerances required for most applications. Continued mold firing under these conditions was found to further benefit the castings. Surface hardening follows the same trends. However, the depth of hardening under a given set of conditions exceeds that of the case.

Both chemical and mechanical properties of the castings prepared were found to be roughly comparable to Grades C-1 or C-2 unalloyed cast titanium, although the strain rate used for evaluation was greater than specified by ASTM designation B-367-69. This indicates that no serious degradation of metal properties results from making titanium castings in this type of mold material. Whether the quality of titanium investment castings made with ZrO_2 molds prepared under the conditions discussed will meet the acceptance standards applied for aircraft usage has not been determined. Nevertheless, an alternate technology for preparing investment molds for titanium investment casting has emerged. Manufacturing materials are cheaper, and some of the problems associated with titamium investment mold materials are avoided. The castings produced are of good quality and should find application in the minerals and metals sector of the economy.

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