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## **Bentonite-Bonded Rammed Olivine and Zircon Molds for Titanium Casting**

**By R. K. Koch and J. M. Burrus**



**UNITED STATES DEPARTMENT OF THE INTERIOR**



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# BENTONITE-BONDED RAMMED OLIVINE AND ZIRCON MOLDS FOR TITANIUM CASTING

by

R. K. Koch<sup>1</sup> and J. M. Burrus<sup>2</sup>

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## ABSTRACT

The Bureau of Mines produced several series of titanium castings in order to investigate the feasibility of producing commercial-grade titanium castings in bentonite-bonded olivine or zircon sand molds. The use of these molds for titanium casting was investigated as a possible alternative to the industrially used rammed graphite process. Parameters investigated were mold mixtures, mulling, gating, venting, drying, and mold washing.

The investigators found that castings with superior ductility and fatigue life, compared with rammed graphite castings, could be made by fume-free processes in molds bonded by western bentonite, using either olivine or zircon sand. Zircon molds were satisfactory for both light- and heavy-sectioned castings. However, olivine molds were suitable only for light-sectioned castings because the mold-metal reaction became excessive during the pouring of heavy-sectioned castings.

## INTRODUCTION

The long-range goals of the Bureau include the minimization of requirements for mineral commodities through conservation and substitution; the minimization of environmental conflicts such as air pollution; and the maximization of productivity and the reduction of capital, labor, and energy requirements of the mining and mineral processing industries. This investigation was carried out at the Bureau's Albany (Oreg.) Research Center in pursuit of these goals.

Titanium, a domestically abundant element, is a viable corrosion-resistant substitute for stainless steel alloys which contain domestically scarce cobalt, chromium, and nickel and are used in marine and chemical processing environments. Because of the phenomenally high strength-to-weight ratio of titanium, its substitution for ferroalloy castings in the transportation industries could result in theoretical energy savings of 43 pct.

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However, wide-scale use of titanium has been inhibited by the cost of titanium castings, which is largely due to the relatively high cost of the current industrial molding procedure.

Most commercial-grade titanium castings are made using the rammed graphite process, a process that was largely established by the Bureau (3-4, 6).<sup>3</sup> In this process, molding mix is used that consists of electric-furnace (artificial) graphite mulled with water and organic binders such as dextrin, cornstarch, and resins. The mix is rammed around a reusable wood or metal pattern in a slip flask to make a mold half. The slip flask is removed and the process is repeated to make the other half. (The top half is called a cope, and the bottom half is called a drag.) The green copes and drags are air-cured at ambient temperature for 24 to 72 hours, depending upon size, then stage-heated in an oven at 140° to 400° F over a 5-hour period. Next the molds are fired at 1,650° F in a reducing atmosphere for 6 to 12 hours. Cores are processed similarly.

About 25 pct of the expended molds is discarded after each pour so that new graphite and binders can be brought into the molding cycle.<sup>4</sup> This represents a large energy loss because 2.2 kwhr of energy is required to make 1 pound of artificial graphite. In addition to the solid graphite loss, the rammed graphite process converts approximately 12 pct of the mold weight to atmospheric pollutants during the firing cycle by partly oxidizing and vaporizing the organic binders.

The rammed graphite process has other inherent defects. Some of the more important are that:

1. Molds and cores frequently warp, crack, or lose dimensions because of shrinkage during the firing cycle.
2. Castings, particularly near the surfaces, are carbon-contaminated, which reduces ductility and fatigue life.
3. Under certain conditions, large titanium carbide scabs are formed and the castings must be scrapped.
4. Mold gases which have a deleterious effect on the castings are generated by the reaction of titanium with residual binders. To offset the effect of these gases, nearly all castings are poured centrifugally.

In this investigation, titanium castings were produced in rammed olivine [(Mg, Fe)<sub>2</sub>SiO<sub>4</sub>] and zircon (ZrSiO<sub>4</sub>) molds that were washed with zirconia and bonded by western bentonite. The molds were cured at a maximum temperature of 980° F and poured statically. Unlike the rammed graphite process, no fumes other than water vapor were evolved. In addition, the molding mixes had enough green strength and flowability for use in match-plate molding or with automatic molding machines.

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<sup>3</sup>Underlined numbers in parentheses refer to items in the list of references preceding the appendixes.

<sup>4</sup>One foundry, however, recycles 98 pct of the expended molding mix, with a 12-pct total addition of new binders.

## MATERIALS

Olivine was chosen for investigation as a molding sand because it reportedly does not cause silicosis in foundry workers (1). Other attributes are low cost, low specific gravity (3.2), low thermal expansion, and relative resistance to attack by molten titanium.

Chemically, olivine is described as magnesium and iron orthosilicate ( $\text{Fe}_2\text{SiO}_4$ ), with ferrous oxide ranging from 5.0 to 30.0 pct.

All of the olivine used in this study was from a deposit in Mount Vernon, Wash., and was classified as foundry-grade olivine. This deposit has been estimated to contain 180 billion tons of olivine under less than 3 feet of overburden. Three crushed and sized sands were employed: No. 70, No. 90, and No. 180 olivine. The chemical analyses of the as-received olivine sands are given in table 1, and the size distribution are listed in table 2.

TABLE 1. - Chemical analyses of as-received olivine sands, pct

Sand (producers' designation)	MgO	FeO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	LOI <sup>1</sup>
No. 70.....	46.1	8.30	42.5	0.45	0.41	0.31
No. 90.....	42.0	8.48	43.7	.65	.54	.30
No. 180.....	45.0	8.65	41.4	.60	.49	.11

<sup>1</sup>Weight loss after 1/2 hour at 1,650° F.

TABLE 2. - Size distribution of as-received olivine sands by U.S. standard sieve size, pct

Sand <sup>1</sup>	Amount retained							
	No. 40	No. 50	No. 70	No. 100	No. 140	No. 200	No. 270	Pan
No. 70.....	0.5	27.2	39.4	22.5	5.3	3.2	1.0	0.9
No. 90.....	0	.1	17.3	43.8	28.3	8.2	1.3	1.0
No. 180.....	0	0	.1	.5	5.4	49.3	27.4	17.3
								100.0

<sup>1</sup>Sizes listed for the as-received sands correspond to grain fineness numbers (as established by the American Foundrymen's Society) of 61 (No. 70), 85 (No. 90), and 182 (No. 180).

Previous Bureau research demonstrated that waterglass-bonded zircon molds produced commercially acceptable titanium castings (13-14). Therefore, bentonite-bonded zircon molds were considered worthy of study, although it is a relatively high-priced foundry sand.

Although zircon is commercially produced in Florida and Georgia, all of the foundry-grade zircon used for this investigation was from Australia because this was the only zircon available at local foundry supply houses at the time of the investigation. The sand had an American Foundrymen's Society grain fineness number (AFSgfn) of 94 and the following composition, in percent: 64.9 ZrO<sub>2</sub>, 34.6 SiO<sub>2</sub>, 0.1 Al<sub>2</sub>O<sub>3</sub>, 0.1 Fe<sub>2</sub>O<sub>3</sub>, 0.2 TiO<sub>2</sub>, 0.1 CaO, and trace quantities of Mg and Mn.

Bentonite was chosen as the binder for the molding mixes because it is an established, readily available, domestically abundant, low-cost binder that produces excellent green strength and good dry strength in rammed sand molds. It is composed of minerals of the montmorillonite family. Montmorillonite ( $\text{MgAl}_2\text{Si}_5\text{O}_{14} \cdot n\text{H}_2\text{O}$  or  $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot n\text{H}_2\text{O}$ , with  $n$  varying from 5 to 8 at 65° F and from 3 to 4 at 212° F) is a hydrous magnesium aluminum silicate.

Foundry-grade bentonite is divided into two general types: western bentonite and southern bentonite. Both types were initially used in the olivine and zircon molding mixes, but it was soon apparent that the molds bonded by western bentonite produced superior castings.

The principal difference between the two clays is that in western bentonite, sodium oxide has substituted for some of the magnesia, whereas calcia has substituted for some of the magnesia in southern bentonite. Chemical analyses of the bentonites used in this study are given in table 3. A water slurry of western bentonite had a pH of 9.5, and a water slurry of southern bentonite had a pH of 8.1. This was normal, since western bentonite tends to be more alkaline than southern bentonite.

TABLE 3. - Chemical analyses of bentonite clays, pct

Bentonite	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	Na <sub>2</sub> O	FeO	CO <sub>2</sub>	LOI <sup>1</sup>
Western.....	1.50	14.3	60.9	1.23	2.26	3.82	0.20	10.3
Southern.....	2.50	13.5	49.8	3.06	.29	4.50	.10	17.8

<sup>1</sup>Weight loss after 1/2 hour at 1,650° F.

## EXPERIMENTAL PROCEDURES AND RESULTS

### Melting and Pouring

Most of the castings described in this report were poured from commercially pure (CP) titanium in a consumable-electrode vacuum-arc skull-casting furnace. A number of castings were poured from Ti-6Al-4V and Ti-6Al-4Zr-2Mo-2Sn alloys, but unless otherwise stated, castings shown or described were poured from CP titanium in the skull-casting furnace at a chamber pressure of 50 to 150μ.

A few titanium castings were poured in an inductoslag furnace at 3.75 psia of helium pressure. Castings so poured are designated as "inductoslag-cast."

The techniques of inductoslag melting (8-10) and skull casting (5) have been thoroughly described by others and so they are not detailed here. Both methods deliver metal to the mold that is equal to or slightly better than the melt stock.

The skull-casting crucible used for most of the castings poured during this study was capable of delivering 16 pounds of titanium to the mold. Small molds were poured in clusters of two to four, and the larger molds were poured singly. The largest molds poured, 6-inch cubes and a 14-inch-diameter

propeller, were cast from a crucible capable of delivering 34 pounds of titanium to the mold.

Molten titanium was tilt-poured from the crucible into a reusable graphite funnel which discharged into a reusable graphite pouring basin. Expendable graphite sprues connected the pouring basin to runners in the sand molds. In the case of the 6-inch cubes and the propeller, the graphite pouring basin was omitted and metal was discharged directly from the funnel into the sand mold because the mold had sufficient volume to take all of the crucible contents.

The furnace chamber pressure at the beginning of the pour was generally between 0.05 and 0.15 torr. Immediately after the pour, the pressure surged to various values depending on the mold under study; in extreme cases, the chamber pressure exceeded the limit of the thermocouple gage (760 torr). Pressure increases from molds prepared from sands mixed in an industrial miller and dried at 975° F generally did not exceed 0.15 torr, except for increases from olivine molds used to produce castings with cross sections greater than 1-3/4 by 1-3/4 inch. In the latter cases, apparent pressures sometimes exceeded the upper limit of the thermocouple gage. The furnace chamber was backfilled with helium within two min after the pour to near atmospheric pressure.

The inductoslag crucible used in this study was capable of delivering about 8.0 pounds of molten titanium directly into the sand mold without the use of graphite pouring basins and sprues.

#### First Casting Series

A 12-inch-long wedge that was 1-3/4 by 1-3/4 inches on the heavy end and tapered to one-eighth inch thick by 1-3/4 inches wide on the light end was chosen as the first shape to be cast in bentonite-bonded olivine and zircon molds. The molding mixes were 65 pct No. 90 olivine, 32 pct No. 180 olivine, with 3 pct western or southern bentonite, or zircon sand with 2.5 pct western or southern bentonite. The sands and bentonite were dry mixed for 2 min in a laboratory 22-pound-batch wheel muller before temper water (4 pct for olivine and 3 pct for zircon) was added. The mulling was then continued for 15 min after the water addition.

#### Mold Drying

The effect of the mold drying temperature on the castings produced was studied by making 12 pours in the skull-casting furnace. Each pour had one mold bonded by western bentonite and one mold bonded by southern bentonite. Twelve molds were made of olivine sand and 12 were made of zircon sand.

Replicate tests were made in molds dried at 260°, 480°, and 1,600° F. None of the castings produced were sound, but the four castings from the olivine molds dried at 480° F had the least gas porosity. The olivine molds bonded by western bentonite produced better castings at every temperature than the olivine molds bonded by southern bentonite. All castings from the zircon molds had washboard surfaces and extensive gas porosity regardless of which binder was used.

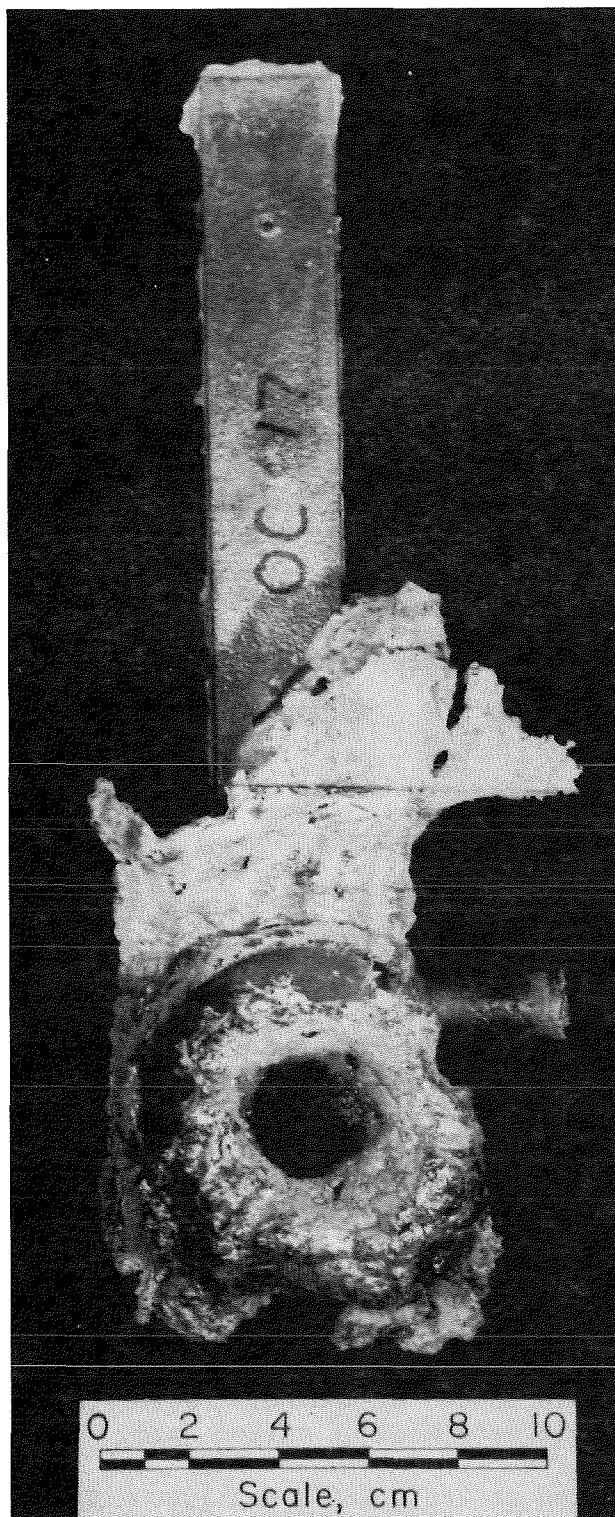


FIGURE 1. - Cope view of 12-inch wedge cast in magnesia-washed olivine mold dried at 480° F (250° C).

Because at this point castings from zircon molds were inferior to those from olivine molds, the study of zircon molds was recessed, and efforts were concentrated on improving the quality of castings made in bentonite-bonded olivine molds.

#### Mold Washes

In an effort to reduce the gas porosity of the wedge castings, various mold washes were tried on olivine molding sands blended in the 22-pound-laboratory muller.

Graphite, magnesia, alumina, and zirconia washes in water or 95-pct industrial-grade ethanol ( $C_2H_5OH$ ) were tried on molds made of No. 90 olivine and 3 pct western bentonite and dried at 480° F.

It was soon found that graphite- and magnesia-washed molds generated more gas than unwashed molds. A casting from a magnesia-washed mold is shown in figure 1. (Note hollow sprue and flash from gas boil.) Alumina-washed molds were somewhat better than unwashed molds but still had too much gas porosity. Zirconia-washed molds, on the other hand, generated less gas during the pour and produced castings with sound surfaces and good detail, as shown in figure 2.

Since the zirconia mold wash had proven effective, it was used in a final attempt to use southern bentonite as a binder for olivine. Two castings were poured in molds of the same composition and history except that one contained 3 pct southern bentonite and the other contained 3 pct western bentonite (fig. 3). The western bentonite casting (bottom of figure 3) was definitely the better casting; the southern bentonite casting (top) had a large gas defect in the cope and a washboard surface in the drag. Consequently, southern bentonite was not investigated further.

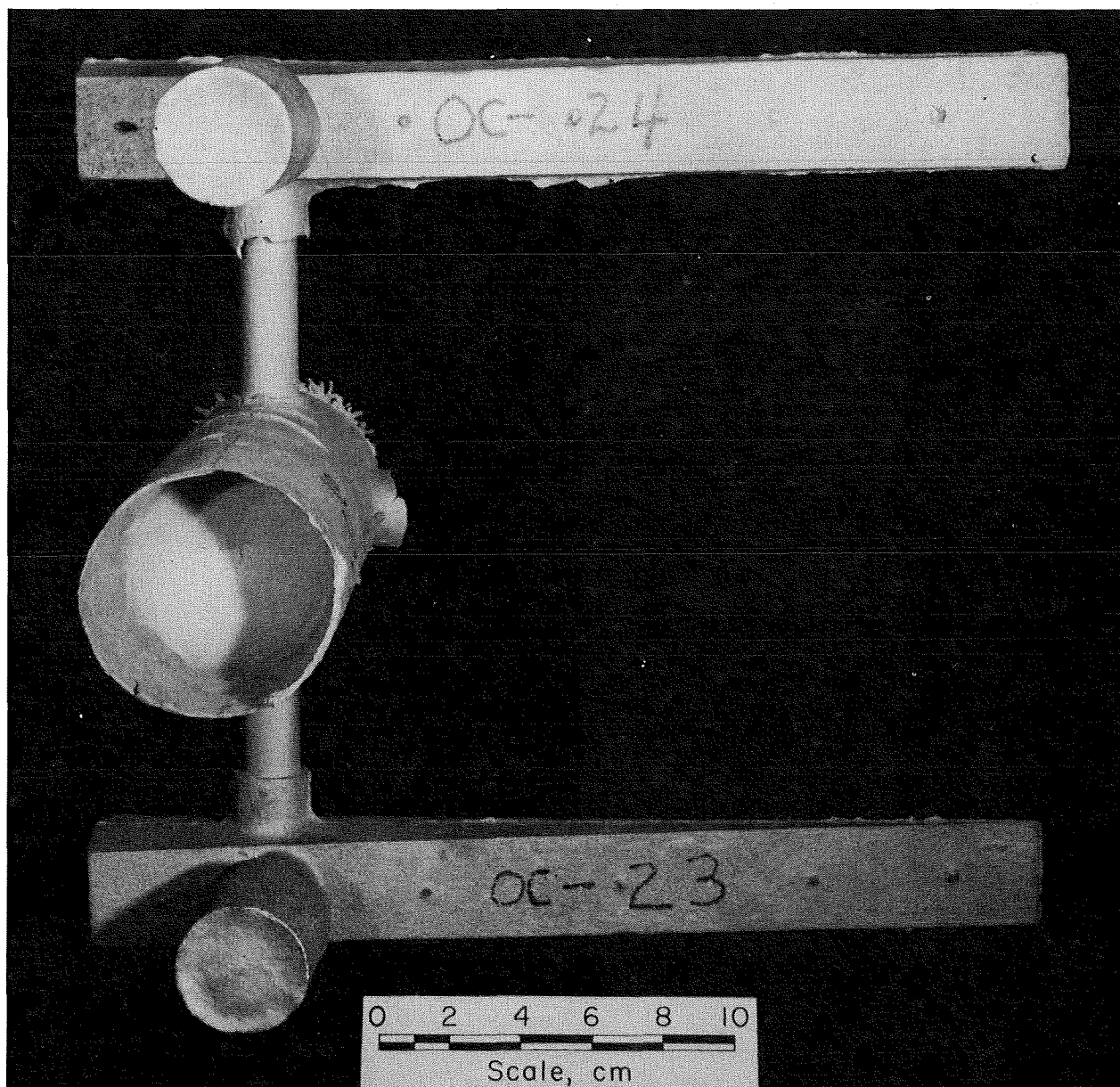


FIGURE 2. - Cope view of wedges cast in zirconia-washed olivine molds dried at 480° F (250° C).



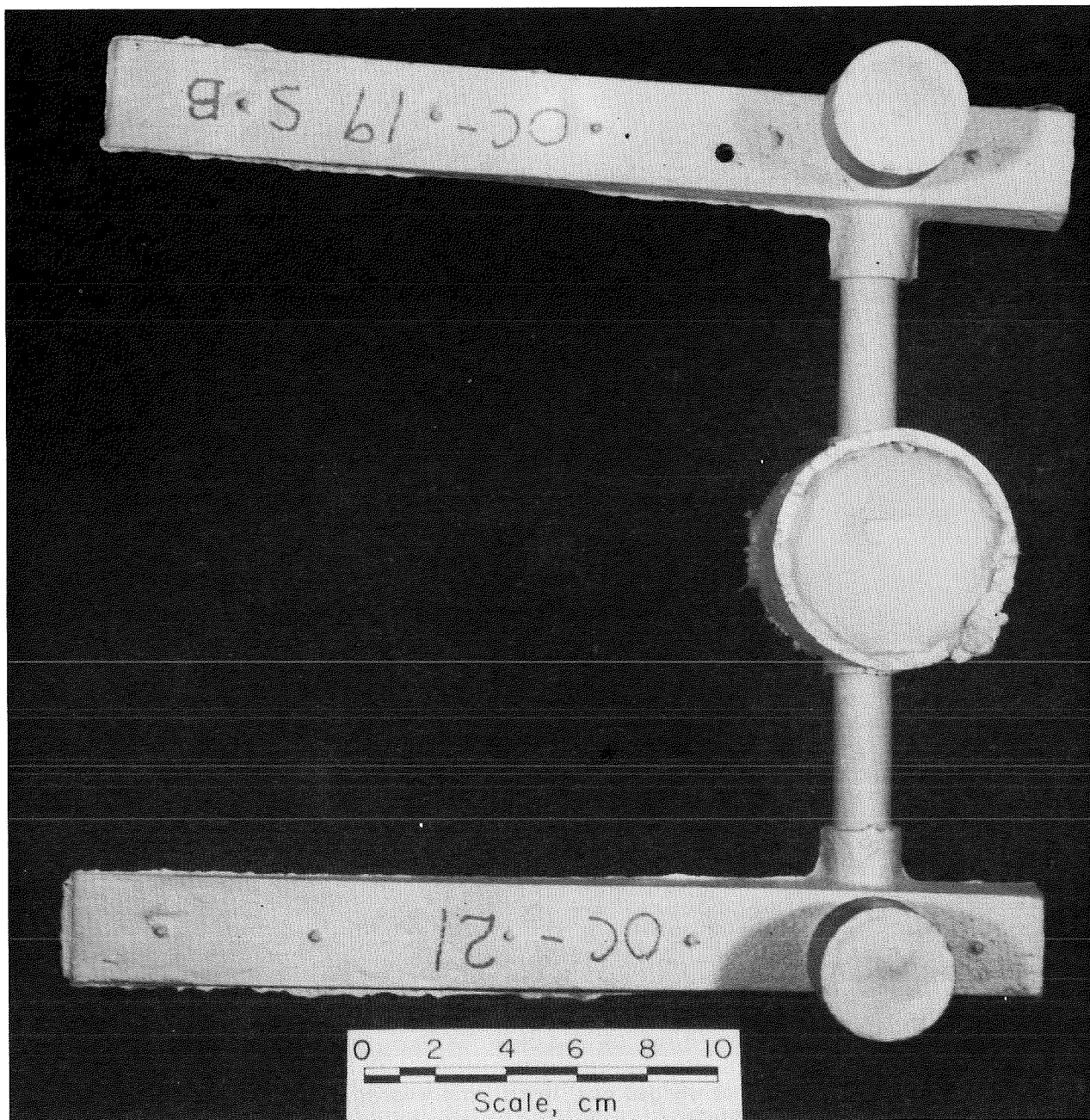


FIGURE 3. - Cope view of wedges cast in zirconia-washed olivine molds bonded by southern bentonite (top) and by western bentonite (bottom).



### Wedge Casting Evaluation

In order to evaluate the composition of the wedge castings, 10 castings (5 heats) were poured in the skull-casting furnace in zirconia-washed molds prepared from recycled (twice-used) 65 pct No. 90 and 32 pct No. 180 olivine sand with 3 pct western bentonite. Used sand was prepared for recycling by crushing in the laboratory wheel muller and screening through a 14- by 16-mesh sieve to remove metallic beads. No makeup bentonite was added, even though the sand was recycled a total of seven times. However, temper water additions were increased to 6 pct for the recycled sand (compared with 4 pct for the virgin sands). The additional temper water was needed to obtain green strength comparable to the strength of virgin sand.

All 10 castings had sound surfaces and good detail. In table 4, the analyses of these castings are compared with the chemical composition requirements for unalloyed titanium as given in specification B367-69 (reapproved 1974) of the American Society for Testing and Materials (ASTM). This comparison showed that all 10 of the castings met the composition requirements for unalloyed titanium for the ASTM's cast grades C-3 and C-4, except for hydrogen content. The ASTM specification requires that hydrogen concentration be 100 ppm or less, and five of the castings did not meet this requirement.

TABLE 4. - Chemical analyses of commercially pure titanium wedges cast in olivine molds dried at 480° F (250° C) compared with ASTM requirements for unalloyed titanium,<sup>1</sup> ppm

	Oxygen	Hydrogen	Nitrogen	Carbon	Copper	Silicon
TITANIUM TEST WEDGES						
Casting:						
1.....	3,290	146	42	113	300	100
2.....	2,200	100	31	160	2,400	<100
3.....	2,380	94	77	63	400	300
4.....	3,145	76	62	66	400	100
5.....	1,360	68	101	84	200	200
6.....	2,275	179	98	95	200	<100
7.....	1,825	188	59	83	100	100
8.....	1,715	100	42	73	100	900
9.....	2,835	221	50	90	400	100
10.....	2,760	174	51	77	400	300
ASTM REQUIREMENTS <sup>1</sup>						
Grade:						
C-1.....	<1,800	<100	<300	<1,000	<1,000	<1,000
C-2.....	<2,500	<100	<300	<1,000	<1,000	<1,000
C-3.....	<3,500	<100	<500	<1,000	<1,000	<1,000
C-4.....	<4,000	<100	<500	<1,000	<1,000	<1,000

<sup>1</sup>Chemical requirements for the four grades of unalloyed titanium listed in ASTM specification B367-69.

### Second Casting Series

A three-specimen 1/4-inch test bar pattern was used for the second series of castings. The main purpose of this series was to obtain test bar blanks

(three-eighths inch in diameter, as cast) that could be machined to either fatigue or tensile specimens (one-fourth inch in diameter) so that the effect of high hydrogen content on the mechanical properties of the castings could be determined. It has been previously reported that high hydrogen contents markedly reduce the fatigue strength of titanium but have little effect on tensile strength or elongation (7, 12). Two castings (six test bars) were poured in each heat in the skull-casting furnace. A typical casting off this pattern is shown in figure 4.

A secondary purpose of this series was to study the effects of various olivine sand sizes and mixes on the quality of castings produced.

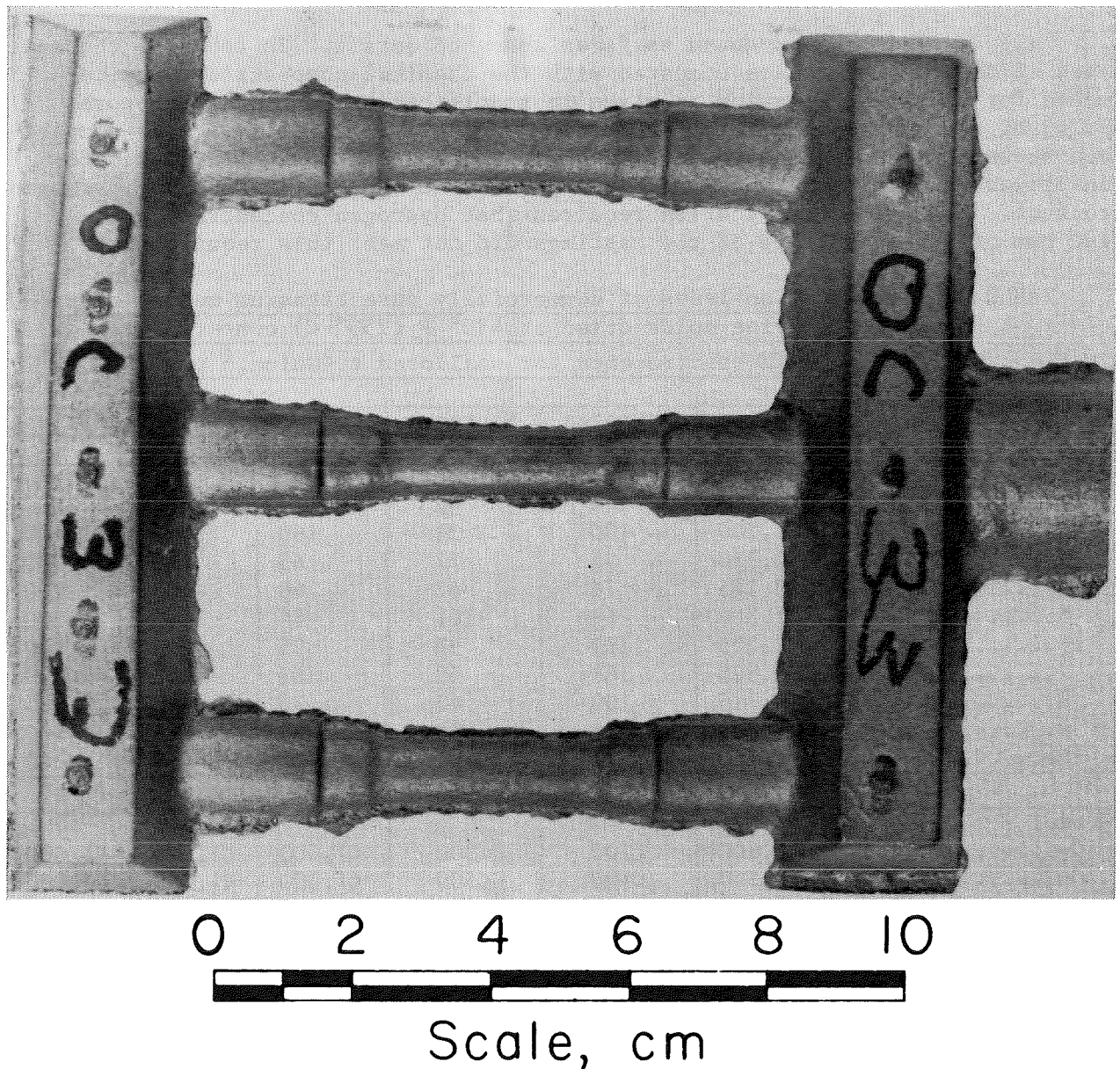


FIGURE 4. - Cope view of test bar casting from zirconia-washed olivine mold bonded by western bentonite and dried at 480° F (250° C).

## Molding Mixes

The compositions of the five mixes studied are shown in table 5. All of the mixes were blended in the 22-pound-batch laboratory muller. Four of the mixes contained 3-pct additions of western bentonite which gave adequate green strength for molding. However, mix 5 (see table 5) needed a 4-pct addition of western bentonite to develop green strength comparable to the other mixes because the potassium fluoborate ( $\text{KBF}_4$ ) exerted a weakening effect. The potassium fluoborate was added in an attempt to reduce hydrogen pickup in the castings. All of the molds were washed with zirconia and dried at  $480^\circ\text{F}$ . The results for each mix are summarized below and in tables 6 and 7.

TABLE 5. - Laboratory-mulled sand mixes for test bar castings, pct

Ingredient	Mix				
	1	2	3	4 <sup>1</sup>	5
Olivine:					
No. 70.....	97	0	0	0	0
No. 90.....	0	97	0	65	0
No. 180.....	0	0	97	32	93
Western bentonite.....	3	3	3	3	4
$\text{KBF}_4$ .....	0	0	0	0	3
Total.....	100	100	100	100	100
Temper water <sup>2</sup> .....	3	6	5	6	5

<sup>1</sup>Sixth recycle of this sand; original composition is listed.

<sup>2</sup>Percent of dry mix weight.

TABLE 6. - Radiographic results for test bars cast in laboratory-mulled olivine molds

Casting	Test bars, number of		Gate riser <sup>1</sup>		Flow-through riser <sup>2</sup>	
	Sound	With voids	Soundness	Voids	Soundness	Voids
1.....	<sup>3</sup> 1	2	S	NV	N	V
1-A.....	3	0	S	NV	S	NV
2.....	1	2	N	V	N	V
2-A.....	3	0	S	NV	S	NV
3.....	<sup>3</sup> 1	2	S	NV	S	NV
3-A.....	2	1	S	NV	S	NV
4.....	3	0	S	NV	S	NV
4-A.....	3	0	S	NV	S	NV
5.....	0	3	N	V	N	V
5-A.....	3	0	S	NV	S	NV

S Sound. N Not sound. NV No voids detected. V Voids were detected.

<sup>1</sup>Riser closest to ingate; inspected by sectioning.

<sup>2</sup>Riser farthest from ingate; inspected by sectioning.

<sup>3</sup>Internal porosity revealed during machining of test bar to final dimensions.

TABLE 7. - Chemical analyses of test bars from laboratory-mulled olivine molds and from a rammed-graphite mold, ppm

Casting	Hydrogen	Nitrogen	Oxygen	Carbon
1.....	205	44	2,515	510
1-A.....	132	49	3,235	300
2.....	37	40	780	135
2-A.....	84	40	680	200
3.....	27	95	1,145	245
3-A.....	30	74	1,085	290
4.....	40	40	770	130
4-A.....	215	41	1,670	235
5.....	24	42	720	410
5-A.....	18	62	810	170
Rammed graphite <sup>1</sup> .....	35	50	1,500	400

<sup>1</sup>Test bar provided by a local titanium founder.

#### Casting Integrity and Composition

The two molds prepared from mix 1 (table 5) produced only four radiographically sound test bars (castings 1 and 1-A in table 6). Casting 1 had gas voids in two test bars and in the flow-through risers. Casting 1-A, on the other hand, appeared to be free of gas defects.

Mix 2 (table 5) produced castings 2 and 2-A as listed in tables 6 and 7. The two castings were produced in duplicate molds in the same heat, but again there was considerable disparity between them. Casting 2 had one radiographically sound test bar and gas voids in the gate riser and flow-through riser, whereas casting 2-A was sound in all respects. The sound casting has the higher hydrogen content, as shown in table 7.

Mix 3 (table 5) produced castings 3 and 3-A (tables 6 and 7), which were more similar to one another than were the castings from mixes 1 and 2. Neither casting had three sound test bars, although both were free of gas voids in the risers.

Castings 4 and 4-A (tables 6 and 7) were prepared from mix 4 (table 5). These two castings appeared to be duplicates from a visual and radiographic viewpoint, but there were considerable differences in their hydrogen and oxygen contents. However, both molds produced sound castings. These were the only castings in this series that were made in recycled sand.

Mix 5 (table 5) failed to yield consistent results, as shown by the data for castings 5 and 5-A (table 6). Casting 5 had gas defects in all bars and both risers, while casting 5-A was sound in all respects. Mix 5 produced the two castings with the lowest hydrogen content. This may have been due to the potassium fluoborate inhibitor in the molding mix; however, casting 5 and 5-A were not significantly lower in hydrogen content than castings 3 and 3-A, which did not contain potassium fluoborate in the molds.

The widely varying gas porosities and chemical compositions of castings from replicate molds, as shown in tables 6 and 7, indicate that at least one major variable was not adequately controlled during mold preparation. However, the data do not give enough information to determine which variable (or variables) needs better control.

#### Mechanical Evaluation

Table 8 lists the results of mechanical testing for the five molding mixes evaluated in the second casting series. Also listed in table 8 are the mechanical testing results for three test bars cast in rammed graphite molds and the minimum mechanical requirements for unalloyed titanium grades C-1 through C-4 per ASTM specification B367-69. Since specification B367-69 lists no minimum fatigue life requirements, comparison of the fatigue lives that resulted when the five mixes were used was restricted to comparison with the results for the rammed graphite castings. Details of the fatigue testing program used in this evaluation may be found in appendix B.

All test bars evaluated in the second casting series had tensile elongation properties that exceeded the ASTM's requirements for grade C-1 and also exceeded the tensile elongation result obtained for the test bar cast in rammed graphite. Those specimens chemically classifiable as grade C-1, per specification B367-69, produced tensile and yield strengths exceeding the minimum requirements for grade C-1, as did the other test bars. The fatigue lives of the sand-cast test bars compared favorably with the fatigue lives of the test bars cast in rammed graphite.

TABLE 8. - Mechanical properties of test bars cast in laboratory-mulled olivine molds with comparative data

	Average strength, ksi <sup>1</sup>		Elongation in 1 inch, pct	Tensile specimens tested	Average fatigue life, <sup>2</sup> ×10 <sup>6</sup> cycles	Fatigue specimens tested	Applicable ASTM grade, <sup>3</sup> per speci- fication B367-69
	Tensile	Yield (0.2 pct offset)					
TEST BARS CAST FROM LABORATORY-MULLED OLIVINE							
Mold mix:							
1.....	49.7	36.8	47	2	1.46	1	None
2.....	49.9	34.1	49	2	2.14	2	C-1
3.....	64.1	50.9	30	2	NAp	0	C-1
4.....	52.6	40.0	45	2	6.50	4	None
5.....	50.6	37.3	47	2	7.01	1	C-1
FOUNDRY-CAST TEST BARS <sup>4</sup>							
Rammed- graphite cast	67.0	54.0	25	1	0.60	2	C-1
ASTM REQUIREMENTS <sup>5</sup>							
Grade:							
C-1.....	35.0	25.0	24	NAp	NAp	NAp	C-1
C-2.....	50.0	40.0	20	NAp	NAp	NAp	C-2
C-3.....	65.0	55.0	15	NAp	NAp	NAp	C-3
C-4.....	80.0	70.0	12	NAp	NAp	NAp	C-4

NAp Not applicable.

<sup>1</sup>Ksi=1,000 lb/in<sup>2</sup>.

<sup>2</sup>See appendix B for testing procedure and details.

<sup>3</sup>Classified by chemical composition. (Requirements for grade C-1 are, in pct: N<0.03; C<0.1; H<0.01; Fe<0.20; O<0.18; and other <0.10 each and <0.40 total.)

<sup>4</sup>Rammed graphite provided by a local titanium founder.

<sup>5</sup>Minimum requirements for unalloyed titanium, per ASTM specification B367-69.

### Third Casting Series

This series of molds and castings was made to determine why replicate molds generally failed to produce castings with similar degrees of gas porosity.

A cored 1-inch pipe tee with a nominal 1/8-inch wall was chosen as the test pattern because cored castings are more sensitive to gas-related defects than are solid castings. Two to four castings were poured per heat in the skull-casting furnace. A single casting and mold are shown in figure 5.

Sand was mixed in the 22-pound-batch laboratory wheel muller. Molds for the first four heats were made from 65 pct No. 90 and 32 pct No. 180 olivine with 3 pct western bentonite. Temper water varied from 4 to 6 pct, depending on whether new or recycled sand was employed. Cores were made from the same mix. Both molds and cores were dried at 480° F for a minimum of one hour per inch of thickness, then sprayed with an 80-pct minus-325 mesh suspension of



FIGURE 5. - One-inch titanium pipe tee and zirconia-washed olivine mold with core in place.

monoclinic zirconia in 190-proof ethyl alcohol. After spraying, the molds and cores were redried at 480° F before the cores were set and the molds were closed.

Of the 16 castings made in these molds, none were radiographically sound in the cope metal. In general, the castings from recycled sand had fewer and smaller gas voids in the cope metal than did castings from new sand. About half the castings from both the new and recycled molds showed signs of sand wash.

In order to make a stronger mold, the mix composition was increased to 4 pct western bentonite and the mulling cycle was increased from 15 min to 30 min. This effectively stopped the sand wash, but it did not reduce gas porosity in the cope metal.

#### Molding Process Variables

It was apparent from the foregoing tests that the basic mold preparation steps had to be studied in order to make sound cored titanium castings in bentonite-bonded olivine molds.

The fundamental variables of any dry sand molding process are sand mixing, gating, venting, mold washing, and drying. These steps were studied in the order that was most compatible with the available equipment.

#### Venting

The ability of molds to expel gas can be increased by three techniques: (1) By increasing the diameter and/or number of vents, (2) by using coarser grained sand, or (3) by using a lighter ram during mold compaction.

All three methods were tried with no apparent success. The sand size was increased to all No. 70 olivine. The size and number of the vents in each cope were increased from four 1/8-inch-diameter vents to three 1/4-inch-diameter vents plus one 1/2-inch-diameter vent in the center of the cope. Ramming pressure was decreased to the minimum amount of compaction that would keep the molds together. These changes, however, did not noticeably decrease the degree of gas porosity in the cope metal of cored tees.

#### Mold and Cores Washes

The effect of thicker zirconia mold washes was studied by building deeper coats through successive spraying of molds until a zirconia layer approximately one-sixteenth inch thick covered the mold and cores. It was found that coats thicker than one-sixty-fourth of an inch produced slightly adverse effects. That is, castings from molds with the heavy coats had a somewhat higher degree of gas porosity. Presumably, this was due to decreased mold and core permeability.



### Gating

In all of the cored castings produced up to this point, the area of the gate cross section in the sand mold was approximately the same as the cross-sectional area of the graphite sprue. Because it was theorized that this 1:1 gate-to-gate sprue ratio might be causing turbulent flow in the molds (and thus trapping gas in the casting), the gate-to-sprue ratio was increased to 4:1. The effects of this change were immediately apparent and beneficial. About one out of every four castings was sound, and gas porosity in the remaining castings was significantly reduced. However, increasing the gate-to-sprue area ratio above 4:1 did not result in a further increase in the percentage of porosity-free castings.

### Mulling and Drying

Proper mixing of sand, binder, and water is an important operation in sand molding regardless of the metal to be cast. This is because the sand grains should be as evenly coated as possible with clay (bentonite) in order to develop maximum strength for a given addition of clay. Uneven dispersion of bentonite in olivine molding sands results in the formation of clay aggregates. These aggregates grow when the molds are dried. For a given mix, the extent of aggregate growth during drying is dependent on the quantity of temper water used and the drying temperature. The greater the quantity of free water and the higher the drying temperature, the larger the clay particles will grow in the mold surface.

The effects of water concentration and drying temperature on the segregation of western bentonite are shown in figures 6 through 9. The mold halves depicted in these illustrations were prepared by dry mixing No. 70 olivine with 5 pct western bentonite for 2 min in the 22-pound-batch laboratory muller; then, 8 pct temper water was added, and the mix was mulled for 30 min. The same process was repeated with a second batch of sand, except that only 4 pct temper water was added. Four half molds were hand-rammed from each batch in a 6-by-6-by-1-3/4-inch slip flask; and the mold halves were dried on metal plates at 65°, 175°, 480°, and 975° F for periods of 120, 24, 4, and 4 hours, respectively. Top and bottom views of these mold halves are shown in figure 6 through 9.

The dried molds were examined visually, and samples for clay analyses were scraped from the top and bottom surfaces of each mold. The visual inspection revealed that all of the dried molds had macrosegregation of clay and sand. Moreover, the individual zones of high clay concentration in size as drying temperature increased, although the number of these clay-rich zones decreased. This is illustrated in figures 6 through 9, where the clay-rich zones are visible as the lighter colored areas. It was also found that the average of the clay-rich zones area was larger at each drying temperature in the molds containing 8 pct temper water than it was in the molds containing 4 pct temper water. However, the differences in the areal extent of the clay zones due to initial water content were not nearly as great as the differences produced by the various drying temperatures.

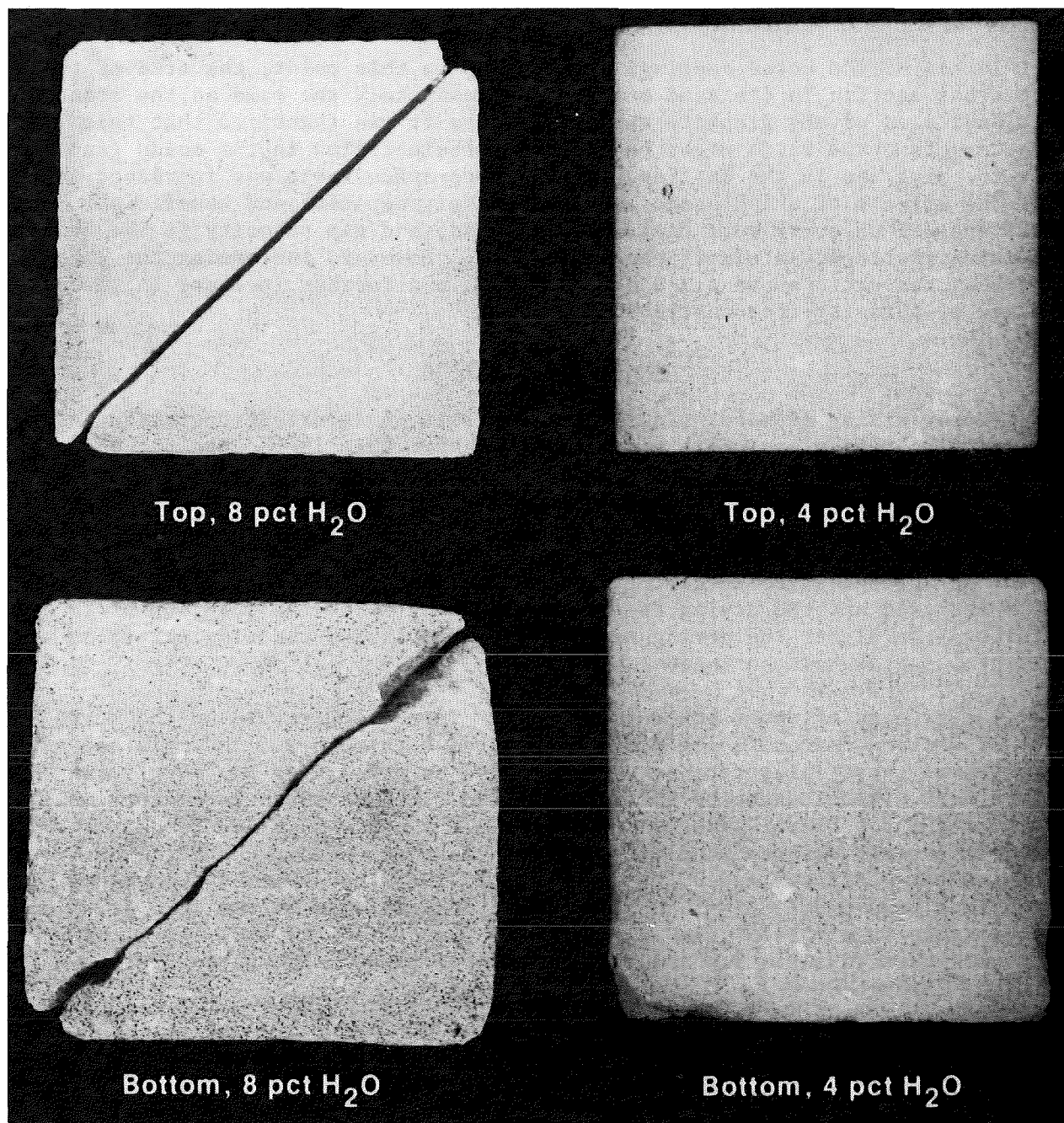


FIGURE 6. - Initial water concentration effect on segregation of western bentonite in laboratory-mulled olivine molds dried at 65° F (18° C).

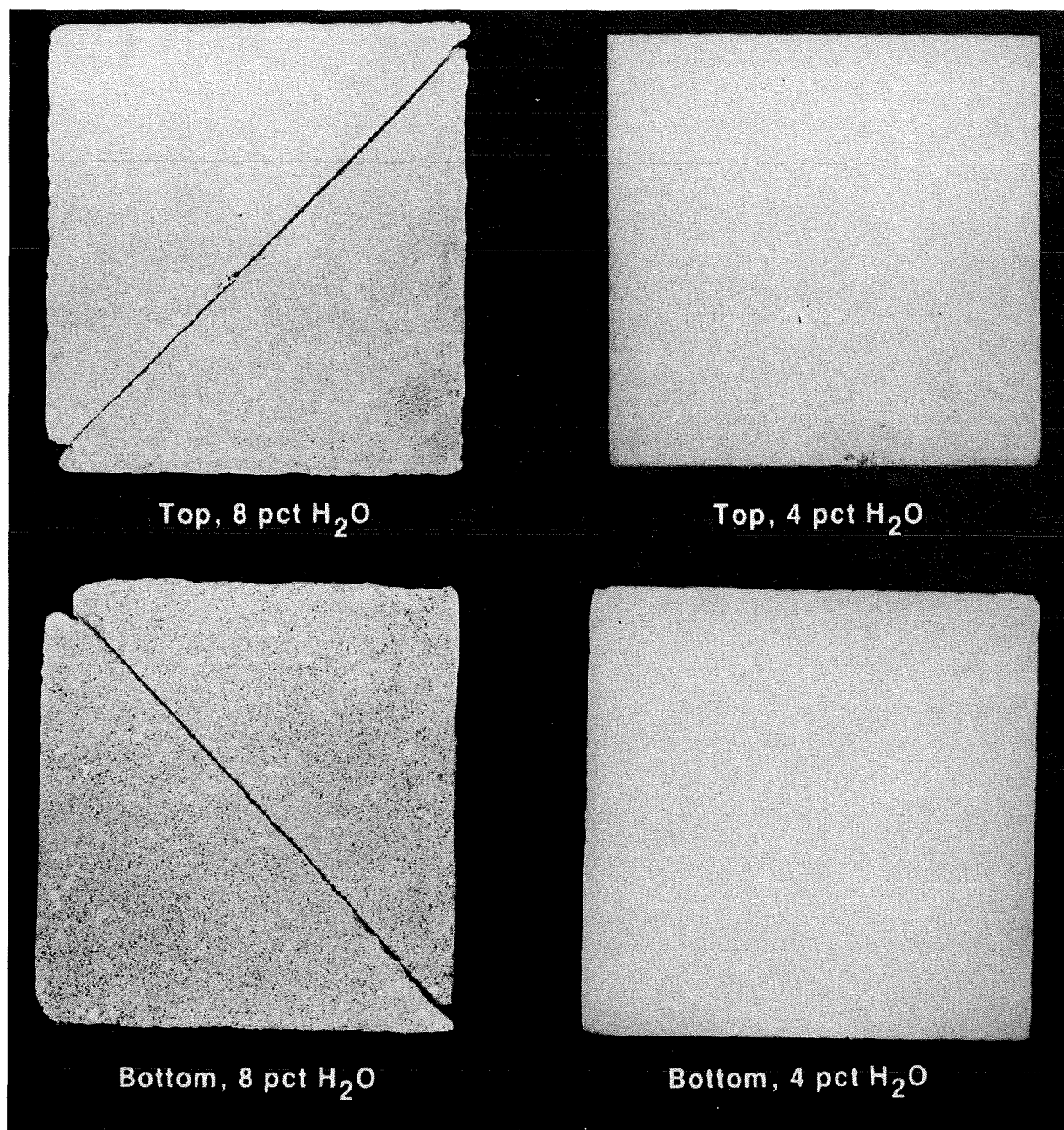


FIGURE 7. - Initial water concentration effect on segregation of western bentonite in laboratory-mulled olivine molds dried at 175° F (80° C).

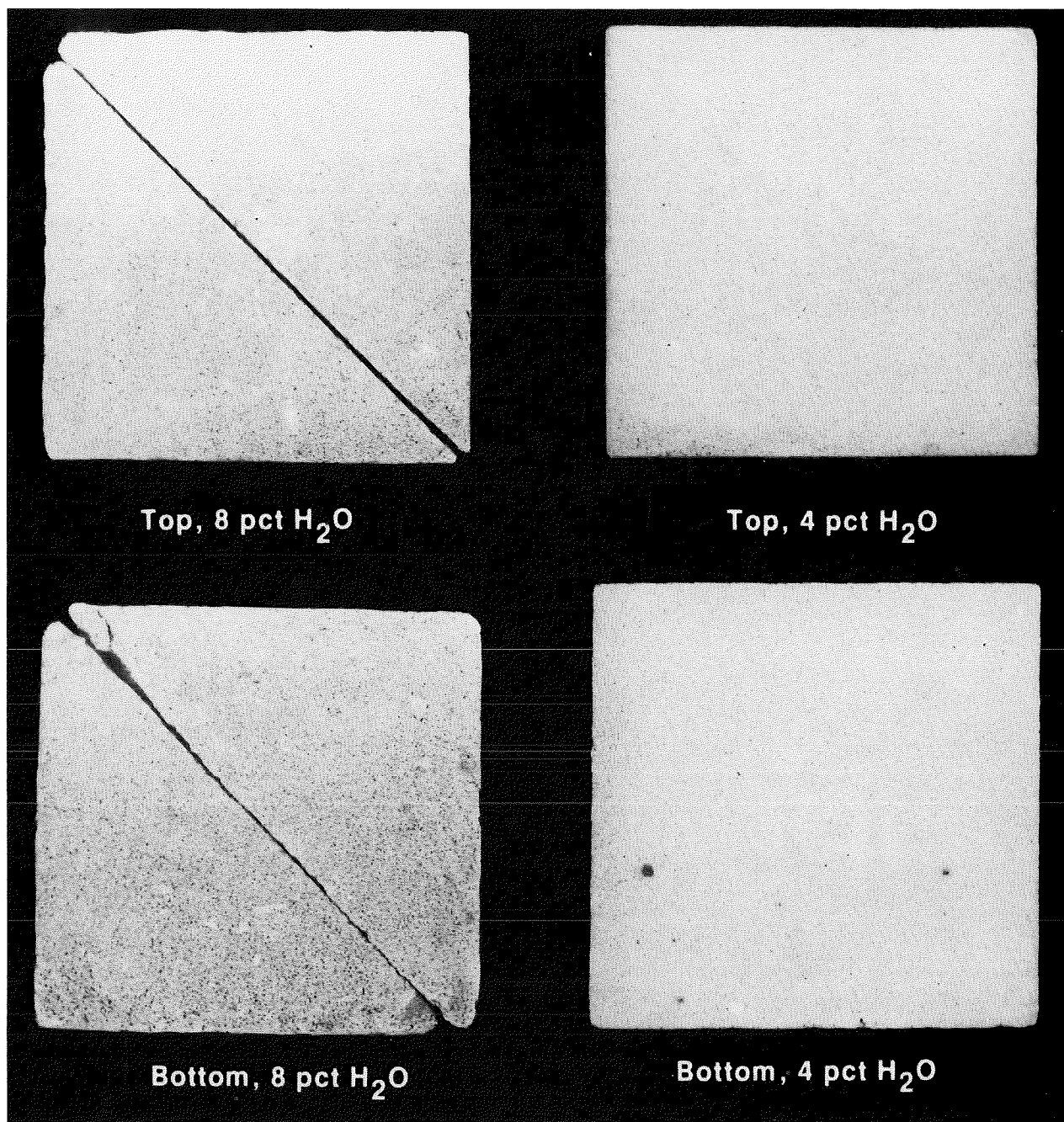


FIGURE 8. - Initial water concentration effect on segregation of western bentonite in laboratory-mulled olivine molds dried at 480° F (250° C).



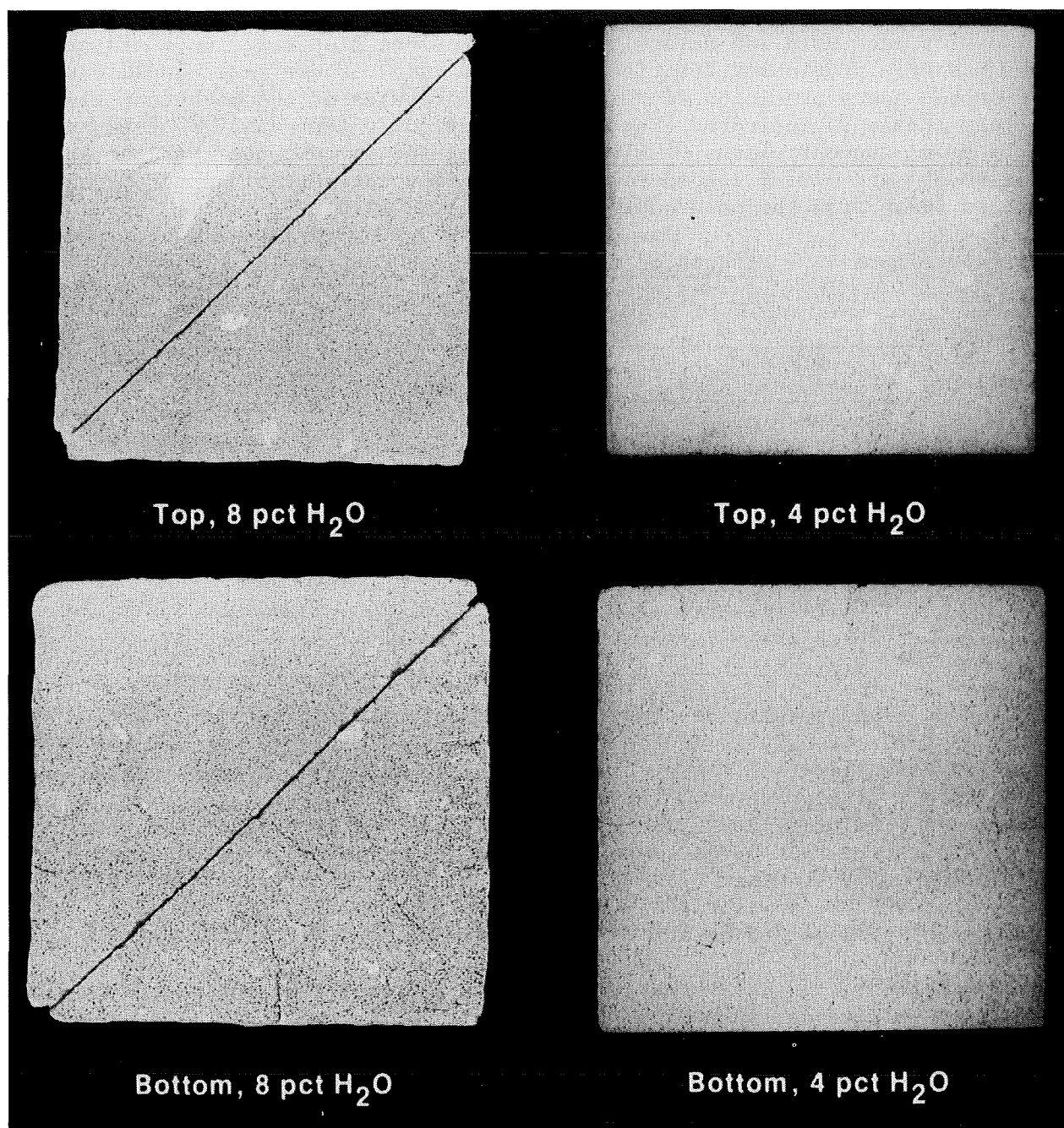


FIGURE 9. - Initial water concentration effect on segregation of western bentonite in laboratory-mulled olivine molds dried at 980° F (525° C).

The percent of active clay in the samples taken from the top and bottom surfaces of each mold was determined by a methylene blue test, in a manner which has been previously described by others (11). Under test conditions, this method had a precision of  $\pm 0.2$  pct. The results of the methylene blue analyses (table 9) indicated that the molds dried at 480° and 975° F had nearly equal concentrations of clay at the top and bottom, but that the molds dried at 65° and 175° F tended toward higher clay concentrations at the bottom surfaces (away from the mold cavity in a complete mold).

TABLE 9. - Effects of temper water and drying temperature on western bentonite segregation in olivine containing 8 and 4 pct H<sub>2</sub>O

Drying temperature, ° F	Western bentonite, pct	
	At top surface	At bottom surface
8 pct H <sub>2</sub> O:		
65.....	5.6	6.6
175.....	5.4	5.8
480.....	5.6	5.2
975.....	4.6	4.6
4 pct H <sub>2</sub> O:		
65.....	6.0	5.8
175.....	5.8	6.4
480.....	5.2	4.8
975.....	4.4	4.6

The combined results of the visual examinations and the clay analyses indicated that slow drying at low temperatures (below 212° F) causes the formation of many clay-rich zones of small (individual) area, whereas high-temperature drying produces a far smaller number of clay-rich zones but of much larger (individual) area. The clay analyses indicated that the total mass of bentonite that migrates to the surface is greater in molds dried below the boiling point of water (212° F) than it is in molds dried above 212° F. However, at 975° F, some of the clay may have been calcined to the point where it could not be detected by active clay analysis.

In an effort to achieve better homogeneity, the wet mixing period in the laboratory muller was extended to 90 min. However, visual examinations and clay analyses did not disclose any improvement in the dried molds produced.

#### Reaction of Titanium With Mold Materials

Three tests were made to obtain data on the severity of reaction between molten titanium with olivine and with western bentonite. These tests were conducted in the inductoslag furnace under a helium pressure of 3.2 psia.

The material to be tested was rammed in the bottom of a waterglass-bonded zircon pouring cup that had been fired at 1,600° F. Previous research had proven that waterglass-bonded zircon is a relatively inert mold material for titanium (13). Therefore, if extensive reaction took place, it would be ascribed to the material rammed in the bottom of the zircon cup.

In the first test, moistened western bentonite was rammed in the bottom of a zircon cup and oven-dried for 2-1/2 hours at 975° F. The composite mold was loaded hot into the inductoslag furnace and the mold cooled to an estimated 200° F during furnace pumpdown, backfill, and melting.

When molten titanium was poured into the composite mold, the furnace chamber pressure surged to 7.3 psia (compared with 3.2 psia initial pressure), and metal drops (splatter) and smoky fumes erupted from the mold.

After the mold was removed from the furnace, it was found that 3.1 pounds of metal stayed in the pouring cup and 0.7 pound had been expelled as splatter. The metal remaining in the pouring cup had a sponge-like texture and was so brittle that it was easily crushed in a titanium mortar and pestle for analytical samples.

The second test was conducted in the same way as the first test, except that No. 70 olivine was tamped in the zircon cup. When the molten titanium contacted the olivine, the furnace chamber pressure jumped from 3.2 psia to 4.5 psia, and considerable smoke plus a small amount of splatter was evolved from the mold.

The casting weighed 2.7 pounds, and the splatter weighed less than 0.1 pound. The casting was sectioned by sawing, and it was found that it contained many large gas voids separated by solid, seemingly ductile titanium. Samples for chemical analysis were obtained by drilling.

The third test differed from the second only in the calcining temperature used. In this test, No. 70 olivine in a zircon pouring cup was calcined at 2,190° F for 2-1/2 hours and then furnace-cooled to 975° F before loading into the inductoslag furnace.

When the composite mold was poured with titanium, the furnace chamber pressure surged from 3.2 psia to 6.2 psia, and large volumes of dark smoke and splatter were generated. The resultant casting weighed 3.5 pounds, and the splatter weighed 0.6 pound. The sectioned casting looked very similar to the casting from the test just described, but there appeared to be a greater number of gas voids, and the solid metal seemed to be harder. Samples for analyses were obtained by drilling.

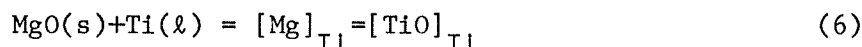
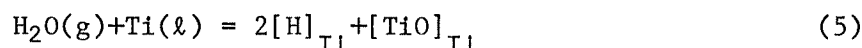
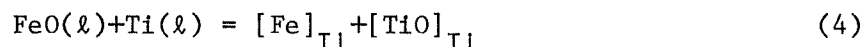
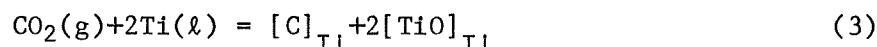
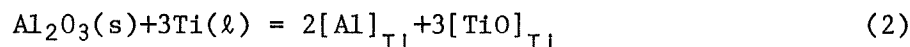
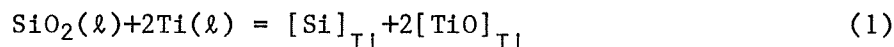
The results of the chemical analyses for all three of the reaction tests are compared in table 10, which includes a typical analysis of a piece of melt stock for comparative purposes. The large increase in oxygen content of the metal in contact with bentonite mirrored the visual observations of the pours. The large increases in the silicon and aluminum contents indicated that most of the oxygen buildup in the casting was the result of titanium reduction of silica and alumina. Table 10 also indicates that ferrous oxide, water, and carbon dioxide contributed minor amounts of oxygen.

TABLE 10. - Impurity content of titanium after reaction with western bentonite and olivine, pct

Mold material	O	N	H	Si	Fe	Mg	Al	C
Western bentonite calcined at 975° F.....	2.59	0.009	0.011	0.63	0.30	0.035	0.76	0.050
No. 70 olivine calcined at: 975° F.....	.28	.009	.004	.11	.10	.016	.09	.053
2,190° F.....	.46	.013	.013	.15	.31	.035	.10	.022
Melt stock, approximate composition <sup>1</sup> .....	.11	.006	.002	.01	.05	.001	.01	.016

<sup>1</sup>Typical analysis of miscellaneous pieces of CP titanium that comprised the melt stock for all three heats.

Until the exact mechanisms are known, the reactions of titanium with western bentonite can be represented, in order of apparent oxygen contribution, by the following simplified reactions:



where  $\ell$  represents liquid, s represents solid, g represents gas, and  $[\ ]_{\text{Ti}}$  represents an element or compound dissolved in titanium. These reactions, which assume complete solubility of all reaction products and ignore known lower oxides of Si, C, and Al, can be used as approximate mechanisms for the reaction of molten titanium and olivine, although the order of oxygen contribution changes somewhat, as shown in table 11.



TABLE 11. - Calculated and analyzed oxygen gains of titanium cast in western bentonite and olivine, pct

	Western bentonite calcined at 975° F	No. 70 olivine	
		Calcined at 975° F	Calcined at 2,190° F
Calculated oxygen gain: <sup>1</sup>			
Silicon.....	0.71	0.114	0.160
Aluminum.....	.67	.071	.080
Carbon.....	.091	.099	.016
Iron.....	.072	.014	.074
Hydrogen.....	.072	.016	.088
Magnesium.....	.022	.010	.022
Total calculated oxygen gain	1.637	.324	.440
Analyzed oxygen content.....	2.59	.28	.46
Less oxygen in melt stock.....	-.11	-.11	-.11
Analyzed oxygen gain.....	2.48	.17	.35

<sup>1</sup>Based on element changes.

Using these reactions, the oxygen gain for the three materials listed in table 10 was calculated from the increases in the Si, Al, C, Fe, H, and Mg contents of the cast products. The calculated total oxygen gains are compared with the analyzed oxygen gains in table 11. The fact that the calculated oxygen increase exceeded the analyzed oxygen increase in two cases and was less than the analyzed increase in one case indicates that the differences may have been caused by the cumulative analytical error for the individual elements. Therefore, the simplified equations might closely approximate the reactions taking place.

#### Industrial Muller

From the foregoing studies on the inhomogeneity of clay distribution in the dried molds and on the severity of the reaction between western bentonite and molten titanium, it was clear that better mulling of the sand and clay was needed.

An industrial vertical-wheel muller of the type used in many sand-molding foundries was obtained to determine if it would provide more uniform distribution of the clay content of the molding mix. Preliminary tests revealed that the blending action of the 250-pound-batch industrial muller was much better than could be obtained with the laboratory muller. Clay particles in the dried molds were too small to be detected by the naked eye.

A typical mulling procedure was to dry-mix 100 pounds of No. 180 olivine with 100 pounds of No. 90 olivine for 1 min, then add 4 pct temper water, mix for 2 min, add 3 pct western bentonite, and then mull the batch for 10 min before discharging it.

Twelve molds of the cored tee were rammed from the foregoing mix, washed with zirconia, dried at 975° F, and poured in the skull-casting furnace in three heats (four castings per heat). The first two heats produced eight sound castings. The third heat produced two sound castings and two castings with small but weldable gas holes in the cope metal.

#### Mulled Sand Storage

The third heat in the skull-casting furnace, the heat produced two inferior castings, was composed of molds made from industrially mulled sand that had been stored for 40 days in a closed container. Further investigation of this stored green sand (sand containing free water) revealed a visible growth of clay particles on the top surface of the sand heap. The investigators believe this growth was the result of a refluxing action within the container; that is, fluctuations in ambient temperature caused water to evaporate and condense on the cover, the condensate dripped down on the mix, and the cycle was repeated. Bentonite tends to migrate toward the region of greatest water concentration, which in this case was the top surface of the stored mix. To compensate for this in subsequent heats, sand that was stored for over 14 days after the first mulling was recharged to the muller and mixed for 10 min to redistribute the bentonite before any molds were made.

#### STANDARD PROCEDURE

Because of the encouraging results obtained with the industrial muller using olivine molding mixes, the investigators decided to resume studies on zircon molding mixes. Preliminary tests led to adoption of the standard practices described below for sand mulling and mold ramming, gating, venting, washing, and drying. These practices were employed in subsequent molding systems that used olivine or zircon bonded by western bentonite.

#### Mulling

The procedure used to process sands in the industrial muller was basically the same for both olivine and zircon sands. Each sand was mulled for 2 min with the required quantity of temper water (4 pct for virgin olivine and 2.5 pct for virgin zircon). Next, western bentonite was added (3 pct for olivine and 2.5 pct for zircon), and mulling was continued for 10 min before the mix was discharged. The batch weights were between 100 and 250 pounds each. The green sand was stored in closed containers, and any sand not used within 14 days was remulled as previously described.

#### Ramming, Gating, and Venting

Regardless of the sand used, the molds and cores were rammed to a B-scale green hardness of 70 to 90 using a 7.0-mm-radius ball impressor (a 980-gram load results in a reading of 100), which produced green compressive strengths of 6 to 15 psi. The cross-sectional gate-to-sprue area ratio was maintained at 4:1. The high points in the cope mold cavities were vented with 0.190 to 0.250-inch-diameter vents.

### Washing and Drying

Green molds were sprayed with slurries containing 0.87 ounce of 80-pct minus-325 mesh zirconia per fluid ounce of 95-pct ethanol (industrial grade). Cores were dried at  $190^{\circ}\pm 10^{\circ}$  F for a minimum of 2 hours per inch of thickness and then sprayed with the same zirconia-ethanol slurry that was used on the molds. The washed molds and cores were either air-dried at  $65^{\circ}$  F for a minimum of 2 hours or oven-dried at  $190^{\circ}$  F for a minimum of 30 min. The cores were then set and the molds closed, and the assembly was dried at  $980^{\circ}\pm 10^{\circ}$  F for a minimum of 1 hour per inch of mold thickness. The dried mold assemblies were stored at  $250^{\circ}\pm 10^{\circ}$  F (for not more than 3 weeks) until they could be poured.

### EVALUATION OF STANDARD PROCEDURE

The standard procedure was used to make olivine and zircon molds which were poured statically in the skull-casting furnace and the results are described below.

#### Olivine Molds and Castings

##### Tees

The 12 1-inch olivine pipe tees mentioned previously were radiographed after the 2 tees that had gas defects had been welded. All of the tees were found to be sound except for minor centerline shrink in the bosses. The tees were threaded and hydraulically tested to 40,000 psi. One tee failed at 39,000 psi, but the others were leaktight. The tee that failed had a sand pit on the surface (with no weld repair) which reduced the nominal 1/8-inch thickness, and the failure was ductile fracture at the same pit site.

For comparison, five commercial steel tees of the same design were tested, and all of them failed at less than 7,500 psi. Therefore, even the titanium tee that failed at 39,000 psi should be considered as a commercially acceptable casting.

##### Cubes

A 6-inch solid cube mold was prepared from olivine, and a casting was poured from Ti-6Al-4Zr-2Mo-2Sn alloy. About 5 sec after the pour, most of the mold contents erupted from the mold, leaving only a shell approximately one-half inch thick which lined the mold cavity. Samples of the shell at the mold-metal interface were taken for microprobe analysis.

The results of the microprobe analysis indicated that the principal reactions occurring at the mold-metal interface involved Fe, Si, and Al compounds. A loose scale approximately 0.015 inch thick on the casting surface contained (in percent) 6.2 Fe, 5.5 Si, 6.1 Al (the matrix contained 5.1 Al), and 73.6 Ti. Unlike the aluminum concentration in the scale, the aluminum concentration detected in the casting did not exceed that of the matrix. To a depth of 0.035 inch, the casting contained iron (0.2 pct) and silicon (0.4 pct) in

greater concentrations than were found in the matrix (less than 0.1 pct for both elements), but beyond depths of 0.037 inch, the concentrations of these elements also did not exceed those of the matrix. The microprobe results appeared to confirm the data listed in table 10, which indicate that Si, Fe, and Al compounds in bentonite and olivine are the principal sources of titanium casting contamination.

A 4-inch cube mold was also prepared, in an effort to determine whether a 16-square-inch cross-sectioned casting could be successfully poured in olivine bonded by western bentonite. Again, the mold contents erupted, leaving only a thin layer of frozen metal in the mold cavity.

The results of this test, together with the results previously obtained using wedge castings, indicate that between a casting cross-sectional area of 3.1 square inches and a cross-sectional area of 16 square inches, the thermal stress in bentonite-bonded olivine molds exceeds a critical limit. When the limit is exceeded, reaction between titanium and the molding mix proceeds at a rapid rate. It appears that bentonite must enter into this reaction, since titanium castings with 36-square-inch cross sections have been successfully cast in waterglass-bonded olivine molds (1). Unless a suitable inhibitor is found to repress this reaction, bentonite-bonded olivine cannot be considered suitable as a mold material for producing heavy-walled titanium castings.

#### Test Bars

The initial test bar pattern shown in figure 4 was modified so that five 1/4-inch test bar specimens could be cast in each mold. This was accomplished by placing a 1-inch half-round runner on each side of the pattern drag between the feed and flow-through risers. The runners were used for the two extra test bars in each mold.

Two olivine molds were made off the revised test bar pattern. One mold was dried at the standard 980° F and the second was dried at 480° F. When the mold dried at 980° F was statically poured with CP titanium, the furnace chamber pressure increased by only 25  $\mu$ ; but when the mold dried at 480° F was cast, the pressure surged to 1,000  $\mu$ . A zircon test bar mold with the same drying history was included in each heat. All of the test bars were radiographically sound, including the runners. However, the risers of the casting from the olivine mold dried at 480° F contained larger gas-shrink voids than were found in the risers of the casting from the olivine mold dried at 980° F. There was also a noticeable difference in the surface smoothness of the test bars; the specimens from molds dried at higher temperatures were superior in this respect. The castings from these heats are shown in figures 10 and 11.

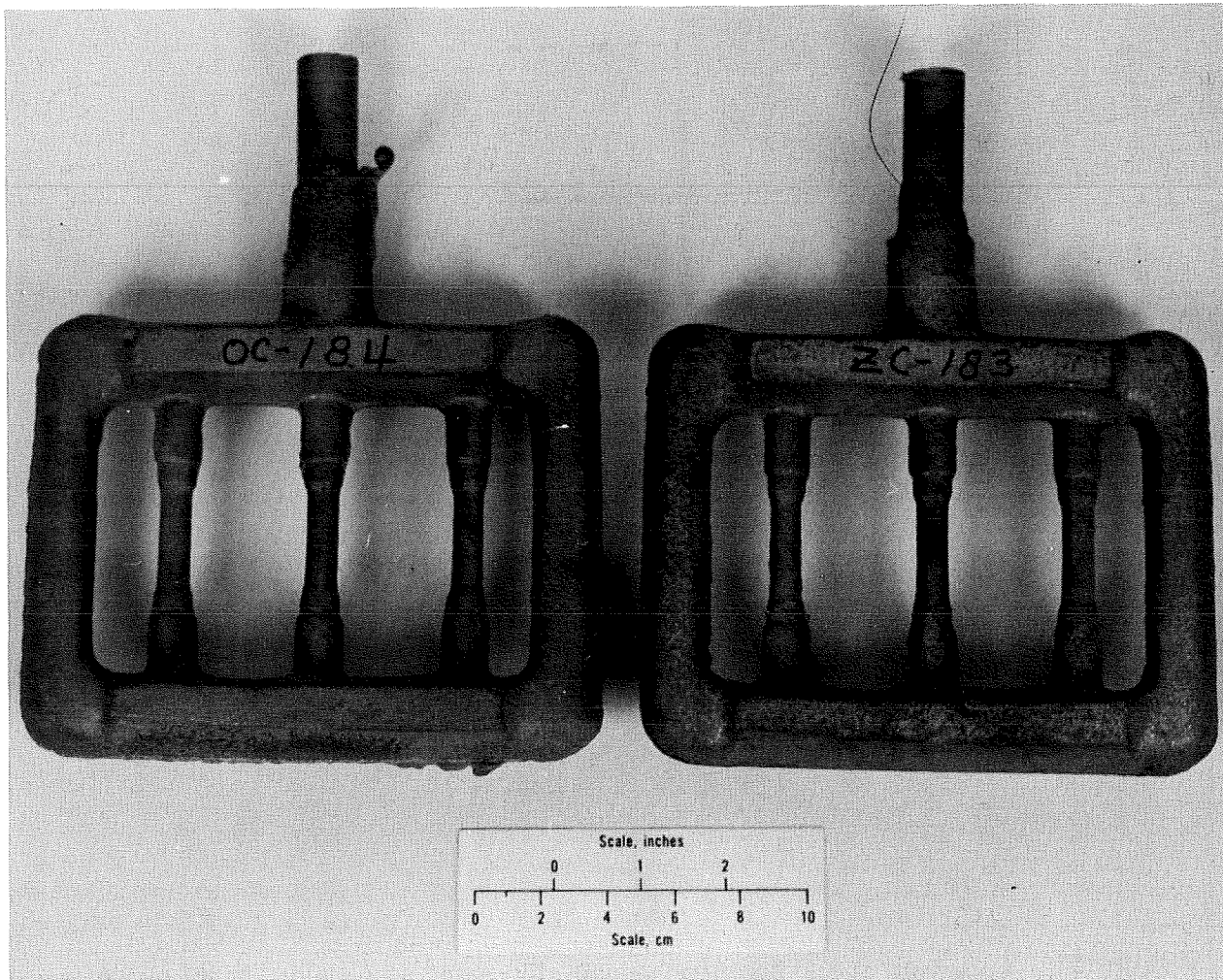


FIGURE 10. - Drag view of test bars from industrially mulled sand molds bonded by western bentonite and dried at 480° F (250° C). Olivine mold was used for casting at left; zircon mold was used for casting at right.

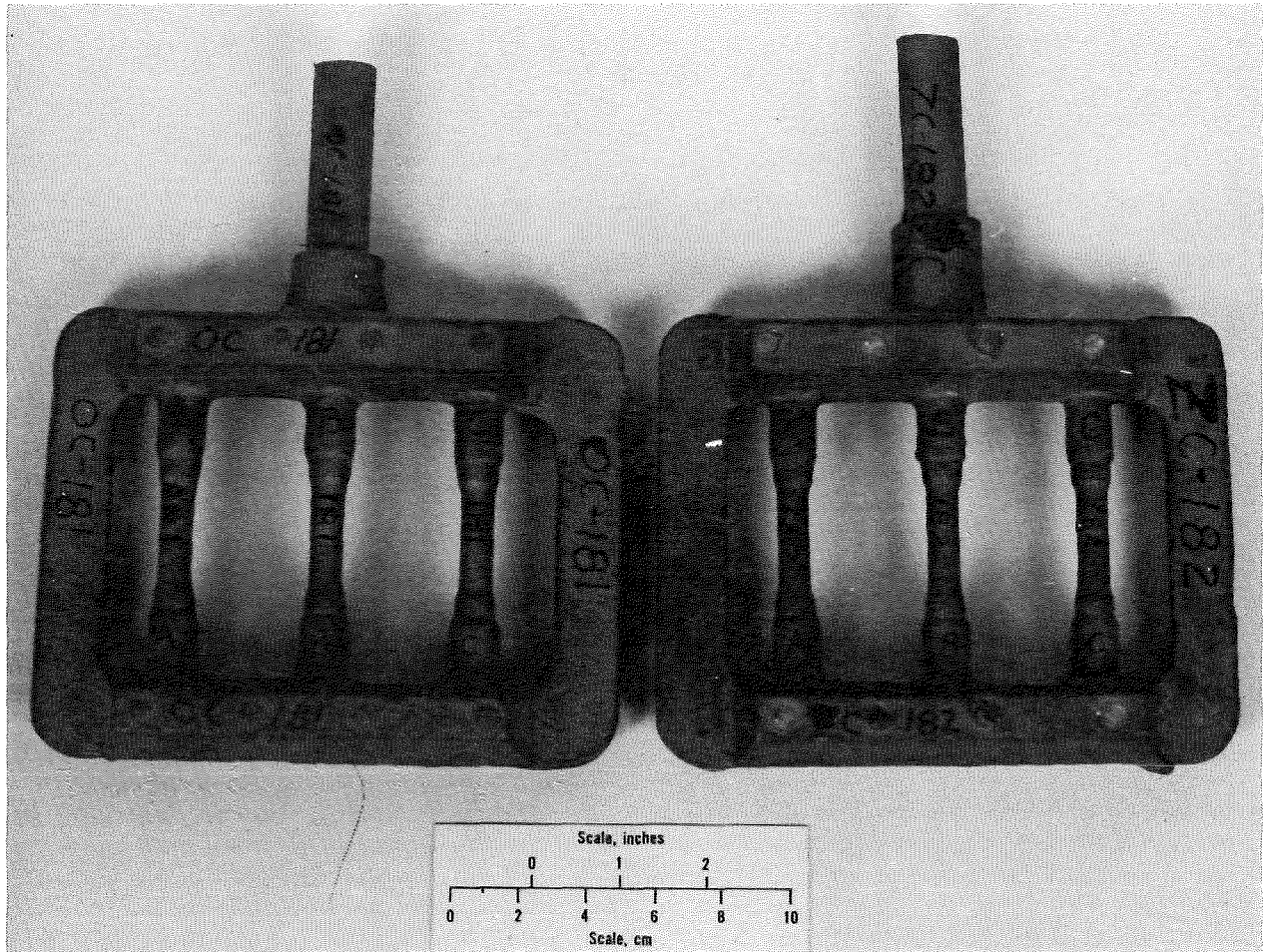


FIGURE 11. - Cope view of test bars from industrially mulled sand molds bonded by western bentonite and dried at 980° F (525° C). Olivine mold was used for casting at left; zircon mold was used for casting at right.

#### Mechanical Evaluation of Olivine Castings

Table 12 lists the mechanical properties of the test bars cast in olivine-bentonite molds prepared from industrially mulled molding mixes. The tensile properties of these castings were essentially identical whether the molds were dried at 480° F or whether they were dried at 980° F. In both cases, the tensile properties exceeded the minimum requirements for grade C-1 unalloyed titanium, as set forth by ASTM specification B367-69. The fatigue lives of these castings, which again were determined as described in appendix B, compared quite favorably with the results obtained for the test bars cast in rammed graphite (table 8). Also listed in table 12 are the mechanical test results for test bars that were poured in zircon-bentonite molds in conjunction with these olivine-bentonite test bar castings. There was no significant difference between the test bars cast in either sand. Chemical analyses of castings from both sands are given in table 13.

TABLE 12. - Mechanical evaluation of test bars cast in olivine and zircon molds bonded by western bentonite and prepared from industrially mulled molding mixes

Sand drying temperature, ° F	Average strength, ksi		Elongation in 1 inch, pct	Tensile specimens tested	Average fatigue life, <sup>1</sup> ×10 <sup>6</sup> cycles	Fatigue specimens tested	Applicable ASTM grade, <sup>2</sup> per specification B-367-69
	Tensile	Yield (0.2 pct offset)					
Olivine:							
480.....	50.5	34.5	44	2	<sup>3</sup> >5.64	3	( <sup>4</sup> )
980.....	50.4	33.6	44	2	<sup>5</sup> >8.16	3	C-1
Zircon:							
480.....	50.2	34.5	46	2	<sup>6</sup> >2.05	3	C-1
980.....	50.0	33.8	47	2	<sup>7</sup> >7.94	3	C-1

<sup>1</sup>See appendix B for testing procedure and details.

<sup>2</sup>Classified by chemical composition.

<sup>3</sup>One specimen failed at a gas void; one failed at a thread root; and one exceeded 10<sup>7</sup> cycles without failure.

<sup>4</sup>Hydrogen content exceeded classification limits.

<sup>5</sup>One specimen failed at a thread root; the other two each exceeded 10<sup>7</sup> cycles without failure.

<sup>6</sup>One specimen exceeded 10<sup>7</sup> cycles without failure.

<sup>7</sup>Two specimens exceeded 10<sup>7</sup> cycles without failure.

TABLE 13. - Chemical analyses of test bars cast in olivine and zircon molds bonded by western bentonite and prepared from industrially mulled molding mixes, ppm

Sand drying temperature, ° F	O	H	N	C	Cu	Si	Fe	Mg	Al
Olivine:									
480.....	725	113	49	110	<10	<50	40	<10	<10
980.....	895	31	53	110	<10	<50	60	<10	10
Zircon:									
480.....	785	42	50	100	20	<50	300	<10	10
980.....	740	33	57	160	20	<50	300	<10	50

#### Zircon Molds and Castings

##### Cube

A 6-inch zircon cube mold was prepared by the standard process and poured in the skull-casting furnace from Ti-6Al-4Zr-2Mo-2Sn. The furnace pressure increased by only 50  $\mu$  after the pour. The casting exhibited no visible signs of mold-metal reaction other than a barely detectable reaction at the sharp edges of the cube. Only a very thin layer of sintered sand adhered to the casting surface.

##### Propeller

A loose pattern and core box for a 14-inch-diameter four-bladed propeller was borrowed from a commercial rammed graphite founder. The propeller had proven difficult to cast with titanium in rammed graphite because high thermal stresses caused the formation of titanium carbide at the interface of the hub core and the titanium. Thus, the propeller presented a unique opportunity to qualitatively compare the heat resistance of zircon bonded by western bentonite with that of rammed graphite cores without exceeding the weight capability of the furnace used in this investigation.

A mold and a core were made using the standard procedure. Because of space limitations in the furnace, it was necessary to gate the 1-inch-diameter sprue directly into one of the blades. The other three blades had 1/4-inch-diameter vents at the high point of the cope. The hub core was dried separately at 480° F and pasted in the green cope with a waterglass-zircon cement. The green cope and drag were then spray-coated with a total quantity of slurry composed of 8.7 ounces of 80-pct minus 325-mesh monoclinic zirconia in 10 fluid ounces of 95-pct ethanol. The cope and drag were then dried (open) for 5 hours at 980° F and furnace-cooled to 250° F. When the dried mold sections were closed, it could be seen that cracks originating at the 1/4-inch vents had propagated across the cope. However, the cracks did not hinder closing the mold and resulted in only one small vein on the casting, which is shown in figure 12.

The mold was statically poured with CP titanium in the skull-casting furnace using the large crucible. The crucible contents were discharged into a 12-inch-diameter pouring basin which was made from the standard zircon molding mix and fed directly into the mold sprue. The pouring basin had been previously sprayed with a zirconia-ethanol slurry and dried at 980° F.





FIGURE 12. - Cope view of titanium propeller cast in zircon mold bonded by western bentonite and dried at 980° F (525° C).

The casting produced did not show signs of extensive reaction at the interface of the hub core and titanium, and the core separated cleanly from the casting cavity. However, near the bottom of the cored cavity there was a noticeable depression of the titanium hub surface. This depression had the appearance of a shrink-induced surface defect; defects of this kind are frequently associated with fairly large subsurface shrink voids, but radiographic examination indicated that there was no subsurface void in the area of the surface defect. The radiographic examination also indicated that the only internal voids were in the upper central area of the hub (which was the last part of the casting to freeze). The results of this test confirmed that the standard zircon molding procedure can be used to produce molds and

cores that are more resistant to molten titanium than are commercial rammed graphite molds and cores.

#### Wedges

Two 12-inch-long tapered wedges were cast from Ti6Al-4V alloy in molds made by the standard zircon-bentonite process. The castings were indistinguishable from the Ti-6Al-4V wedges made in olivine molds bonded by western bentonite and were commercially acceptable with regard to soundness and detail.

#### Test Bars

Two test bar molds were made by the standard process for zircon bonded by western bentonite. One was dried at 980° F, and the other was dried at 480° F. Both were cast from CP titanium but were poured in separate heats. Each heat contained an olivine test bar mold with the same drying history as the zircon mold. The results for the zircon castings were the same as those for the olivine castings. That is, the test bar castings from the molds dried at 980° F had superior surface detail and smaller gas-shrink voids in the risers than the castings from the molds dried at 480° F. These results proved that 980° F is a better drying temperature than 480° F for both zircon and olivine molds when western bentonite is used as the binder. The castings are shown in figures 10 and 11.

#### Mechanical Evaluation of Zircon Castings

It is apparent from table 12 that the tensile properties of the test bars cast in zircon molds bonded by western bentonite were essentially identical whether the molds were dried at 480° F or at 980° F. In both cases, the tensile properties exceeded the minimum requirements set forth for grade C-1 unalloyed titanium in ASTM specification B-367-69. The fatigue life values listed in table 12 were determined as described in appendix B and compare favorably with the results for commercial rammed graphite cast test bars (table 8).

#### Case Effect in Olivine and Zircon Castings

Metallography specimens were obtained from a riser of each of the test bar castings for observation and microhardness testing. The case of hardness of the olivine castings was approximately 700 KHN (Knoop hardness number) at a point of 0.008 inch from the cast surface. The casting from the olivine mold dried at 480° F had a case with an apparent depth of 0.036 inch, compared with a case depth of 0.032 inch for the casting from the olivine mold dried at 980° F. The zircon castings had a lower case hardness, with a maximum case hardness of 479 KHN at a point 0.008 inch from the cast surface. The castings produced from zircon molds dried at 480° F and at 980° F both had shallower case depths than the castings produced from olivine molds. The case depth of the casting produced in the zircon mold dried at 480° F was 0.028 inch, and the case depth of the casting from zircon mold dried at 980° F was 0.020 inch.

In each casting, a softer zone occurred at the surface, and the maximum case hardness was found approximately 0.008 inch from the cast surface. The average hardness of the core area was 144 KHN. A composite of the photomicrographs from the test bar castings produced using both sands, and at both mold drying temperatures, is shown in figure 13. Both microhardness data and the

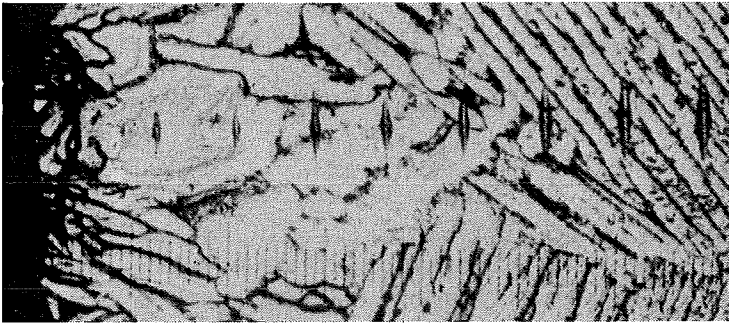
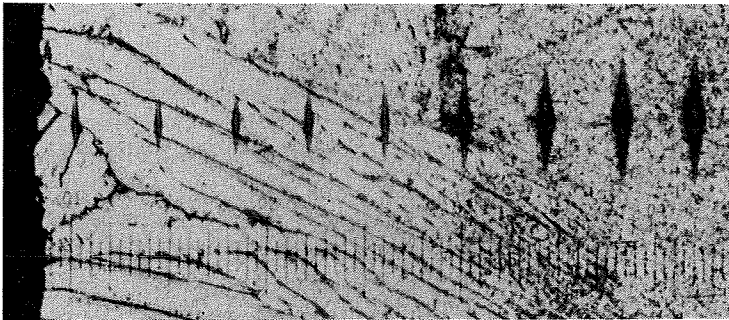
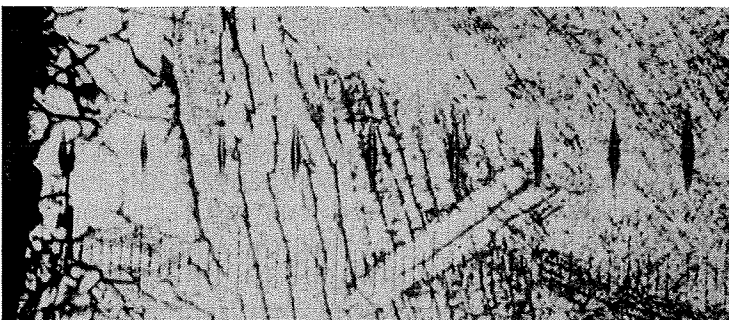
**A****B****C****D**

FIGURE 13. - Partial microhardness traverses of titanium cast in olivine and zircon sand molds dried at 480° F (250° C) and 980° F (525° C). Sections shown were taken from the risers of the test bar castings produced from: A, olivine mold and B, zircon mold, both dried at 480° F; and C, olivine mold and D, zircon mold, both dried at 980° F. Sections were taken from the corresponding test bar castings shown in figures 10 and 11, and indentations were produced using a Knoop indenter with a 200-gram load.

**100X**

photomicrographs indicate that the case depth was shallower in molds dried at 980° F than it was in molds dried at 480° F, for both the olivine and zircon molds. In all cases, the zircon molds appeared to produce castings with less intense and shallower contamination than did the olivine molds.

#### CONCLUSIONS AND DISCUSSION

Commercial-grade titanium castings can be statically poured in olivine and zircon sand molds bonded by western bentonite. Olivine sand molds are satisfactory for castings with cross sections of 3 square inches but are unsatisfactory for casting cross sections of 16 square inches because of mold-metal reaction. Zircon sand is satisfactory for casting a 6-inch cube (the largest volume castable in Bureau furnaces).

The ductility and fatigue life of titanium cast in either olivine or zircon sand molds bonded by western bentonite markedly exceeds the ductility and fatigue life of titanium cast in organically bonded rammed graphite molds.

Bentonite-bonded olivine and zircon sand molds do not generate noxious fumes during curing at 980° F, or at any other process step. In contrast, organically bonded graphite molds generate large volumes of noxious fumes during curing at 1,650° F.

Olivine and zircon sand molds are dimensionally stable during curing (that is, there is no measureable shrink or warp). Rammed graphite molds, however, are subject to about 5-pct shrink and warpage during 1,650° F curing.

Olivine and zircon sand molding mixes possess greater green strength and flowability than the rammed graphite mixes do and can be used industrially with automatic molding machines. Historically, rammed graphite mixes have not been amenable to machine molding because the graphite flakes (which are shaped like sharp-edged shingles) lock under pressure and create a high resistance to flow.

To make porosity-free titanium castings by static pours in either olivine or zircon sand molds, it is imperative that the western bentonite be thoroughly dispersed during the mulling operation in order to avoid clay segregation when the molds are rammed and dried. A zirconia-based mold wash is needed to reduce mold-metal reaction, and the minimum diameter of the cope vents should be 0.190 inch to reduce gas entrapment by the molten titanium while the mold is filled. It is also essential when the mold is poured statically, to maintain a 4:1 gate-to-sprue cross-sectional ratio to avoid turbulent filling of the mold cavity and consequent gas entrapment. When these precautions are taken, commercial-grade titanium castings can be statically poured in olivine or zircon sand molds bonded by western bentonite. Olivine molds are suitable only for light-walled castings, but zircon molds can be used for either light- or heavy-walled castings.

## REFERENCES

1. American Metal Market/Metalworking News. Researchers Say Olivine Eliminates Silicosis Risk. July 25, 1977, p. 11.
2. American Society for Testing and Materials. Constant Amplitude Axial Fatigue Tests of Metallic Materials. E466-76 in 1978 Annual Book of ASTM Standards: Part 10, Metals--Mechanical, Fracture, and Corrosion Testing; Fatigue; Erosion; Effect of Temperature. Philadelphia, Pa., 1978, pp. 546-551.
3. Ausmus, S. L., and R. A. Beall. Expendable Casting Molds for Reactive Metals. BuMines RI 6509, 1964, 44 pp.
4. Ausmus, S. L., F. W. Wood, and R. A. Beall. Casting Technology for Titanium, Zirconium, and Hafnium. BuMines RI 5686, 1960, 31 pp.
5. Beall, R. A., and others. Cold-Mold Arc Melting and Casting. BuMines Bull. 646, 1968, 151 pp.
6. Beall, R. A., F. W. Wood, J. O. Borg, and H. L. Gilbert. Production of Titanium Castings. BuMines RI 5265, 1956, 42 pp.
7. Boyer, R. R., and W. F. Spurr. Characteristics of Sustained-Load Cracking and Hydrogen Effects in Ti-6Al-4V. Met. Trans., v. 9A, January 1978, pp. 23-29.
8. Clites, P. G. (assigned to U.S. Department of the Interior). Cold Crucible, U.S. Pat. 4,058,668, Nov. 15, 1977.
9. Clites, P. G., and R. A. Beall. Inductoslag Melting of Titanium. BuMines RI 7268, 1969, 20 pp.
10. \_\_\_\_\_. Preparation of Ingots and Shaped Castings by Inductoslag Melting. 5th Internat. Symp. on Electroslag and Other Special Melting Technologies, Oct 16-18, 1974, Pittsburgh, Pa., Part 11, ed. by G. K. Bhat and A. Simkovich. Carnegie-Mellon Inst. of Research, Pittsburgh, Pa., 1975, pp. 477-496.
11. Farquinio, F., and D. Bolding. Sand Control With the Methylene Blue Test. Foundry, v. 97, No. 2., February 1969, pp. 119-124.
12. Jaffee, R. I. Memorandum on Hydrogen in Titanium and Its Alloys. Titanium Metallurgical Laboratory, Battelle Memorial Inst., Columbus, Ohio, Sept. 30, 1957, 23 pp.
13. Koch, R. K., and J. M. Burrus. Shape-Casting Titanium in Olivine, Garnet, Chromite, and Zircon Rammed and Shell Molds. BuMines RI 8443, 1980, 33 pp.
14. Koch, R. K., J. L. Hoffman, M. L. Transue, and R. A. Beall. Casting Titanium and Zirconium in Zircon Sand Molds. BuMines RI 8208, 1977, 44 pp.

## APPENDIX A.--MECHANICAL TEST PROCEDURE

To demonstrate that the molding and casting processes examined in this study did not adversely affect the mechanical properties of cast titanium, the specimens were prepared and tested as nearly as possible in accordance with ASTM specification B367-69. This specification sets certain standards for the testing of the specified cast materials (including titanium). According to the specification, the following must be adhered to:

"8.2 tension test specimens shall be machined and tested in accordance with ASTM Method E8, Tension Testing of Metallic Materials. Tensile properties shall be determined using a strain rate of 0.003 to 0.007 in/in/min through the specified yield."

ASTM method E8 states that after the material under test passes through yield, the strain rate may be increased to a rate of up to 0.05 in/in/min, but this is not required by the specification.

Because of equipment limitations, the authors were not able to reach the 0.003 to 0.007 in/in/min strain rate requirement set forth in ASTM specification B367-69; a strain rate of 0.01 in/in/min was the closest that could be achieved. Since it would have been necessary to interrupt tests in order to change the strain rate indicators on the test machine used, and since the ASTM specification only suggests (but does not require) a change in strain rate, the single strain rate of 0.01 in/in/min was used throughout each test.

The specimen configuration chosen for this study was a standard 0.250-inch-diameter threaded tensile specimen (fig. A-1) which conformed to the applicable ASTM recommendation. Testing was carried out on a 60,000-pound-force universal testing machine equipped with a stress-strain recorder.

Each set of specimen blanks (blanks to be used for either room-temperature tensile or fatigue specimens) was cast to shape using the indicated casting method and mold. After casting, the specimen blank and runners were radiographed to check their internal integrity. Specimens with significant discontinuities were discarded. Following radiographic inspection and sorting, specimens were arbitrarily selected for either tensile testing or fatigue testing. Those specimens chosen for tensile testing were finish-

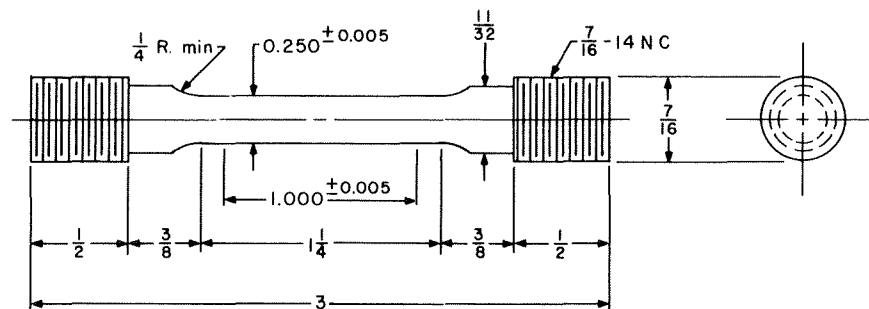


FIGURE A-1. - Standard configuration of cast titanium tensile specimens. (Measurements in inches.)

the specimens were marked with individual test numbers and inspected using dye-penetrant. The inspection results were noted and used to qualify the tensile test results.

After inspection, the specimens were gage-marked and prepared for

tensile testing. The gage-marked tensile specimens were then placed in the grips of the testing machine and the extensometer was attached to the specimen and the stress-strain recorder. The tensile test was then performed as previously described, and a post-test examination of the specimen was made. Any results from specimens that failed either the pre-test dye-penetrant examination or the post-test examination were qualified by notation.

# APPENDIX B.--FATIGUE TEST PROCEDURE

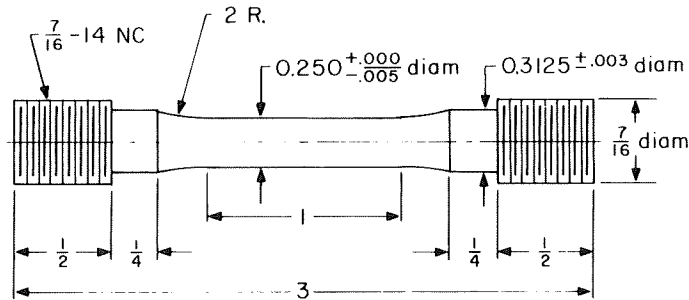


FIGURE B-1. - Standard configuration of cast titanium fatigue specimens. (Measurements in inches.)

Fatigue testing was carried out to determine if the molding techniques under investigation had a detrimental effect on the cast metal. For this phase of the research program, round axial fatigue specimens which conformed to the recommendations of ASTM E466-76, section 5.2.1 (2) were used (fig. B-1).

The fatigue tests were performed on an electrohydraulic closed-loop test machine. A sinusoidal tension-tension load program was used in which the maximum tensile stress ( $S_{max}$ ) was equal to 95 pct of the room-temperature yield strength. The minimum tensile stress ( $S_{min}$ ) applied to the specimen was determined by the formula  $S_{min} = S_{max} (R)$ , in which  $R$ , the ratio of  $S_{min}$  to  $S_{max}$ , was arbitrarily chosen to equal 0.25. The frequency of the sinusoidal load program used was 10 hertz.

Each set of specimen blanks (blanks to be used for either room-temperature tensile or fatigue specimens) was cast to shape using the indicated casting method and mold. After casting, the specimen blanks and runners were radiographed to determine their internal integrity. Specimens with significant discontinuities were discarded. Following radiographic inspection and sorting, specimens were arbitrarily selected for either tensile testing or fatigue testing. Specimens chosen for fatigue testing were finish-machined to conform with the configuration shown in figure B-1. Subsequently, the specimens were marked with individual test numbers and inspected using dye-penetrant. The inspection results were noted and used to qualify the fatigue test results.

After the dye-penetrant inspection, the specimens were measured to determine the minimum cross-sectional area of each specimen. This measurement was used in calculating the loads required to achieve the maximum and minimum stresses. After the maximum and minimum loads required for the fatigue program were determined, the test machine controls and monitors were adjusted to achieve these requirements. The specimen to be tested was then loaded into the test machine and the program was initiated. The test was periodically monitored until specimen failure occurred.









