AN INVESTIGATION OF YTTRIUM OXIDE AS A CRUCIBLE MATERIAL FOR MELTING TITANIUM

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Naval Ship Research and Development Center

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R. L. Helfrich and C. A. Zanis

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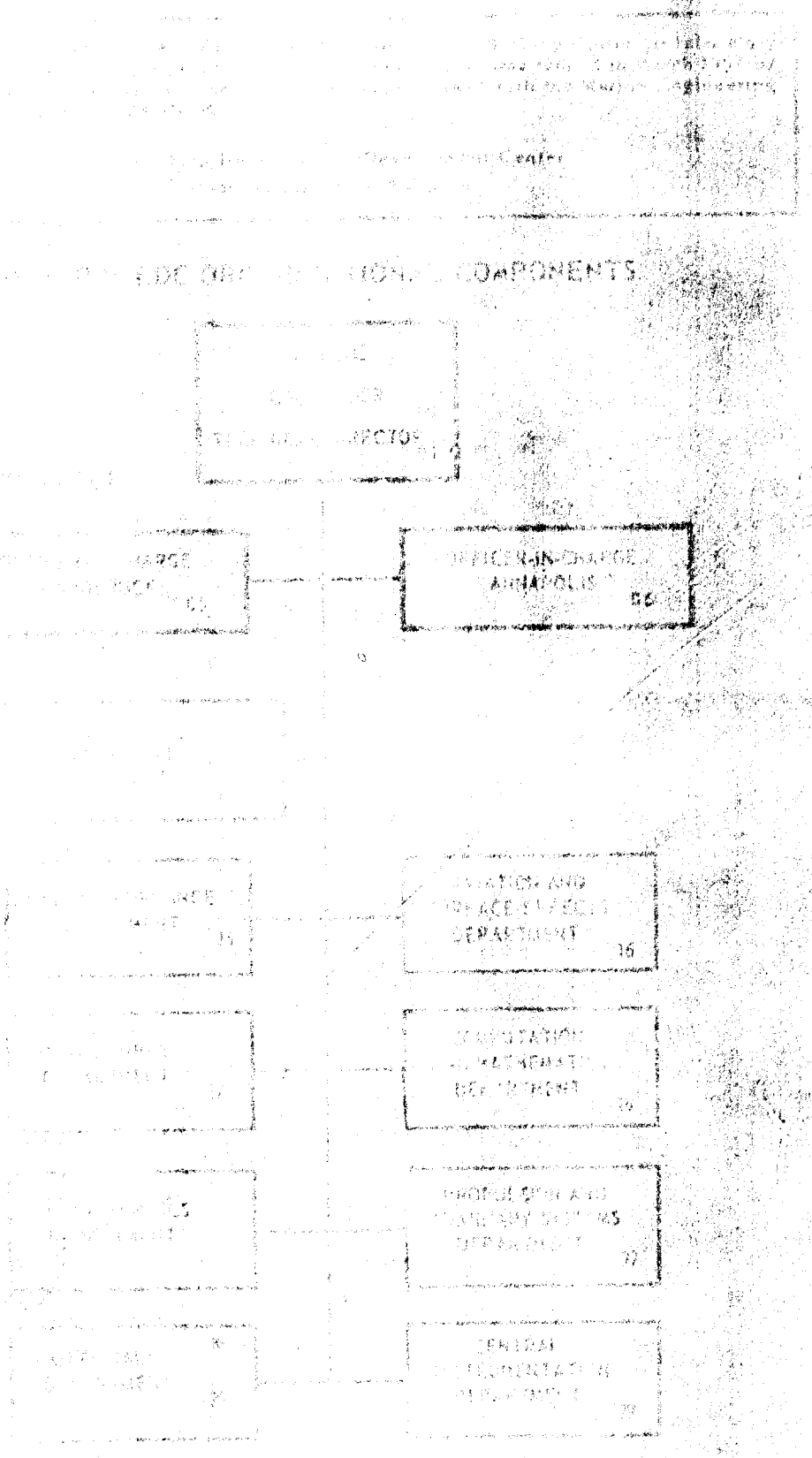

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13 ABSTRACT

The feasibility of using yttrium oxide as a crucible material for induction melting of titanium was investigated. Melting experiments using 10- and 30-gram capacity yttrium oxide crucibles led to the conclusion that molten titanium partially dissociates the yttrium oxide resulting in limited interstitial oxygen contamination of the titanium and in the formation of a titanium-yttrium-oxygen eutectic phase in the cast microstructure. Variation in the crucible density over the range of 70% to 97% of theoretical had no measurable effect on the extent of melt contamination. However, it was noted that melts prepared in oxygen deficient crucibles generally had the highest levels of contamination. Although up to 1.93% yttrium and 0.56% oxygen were picked up from the crucibles, comparison of the results reported in this investigation to those of previous studies on refractory oxides, indicates that yttrium oxide appears to be the best candidate crucible material for melting titanium. Areas requiring additional investigation as well as possible immediate applications for yttrium oxide are suggested.

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INTRODUCTION

The high strength-to-weight ratio and outstanding sea-water corrosion resistance of titanium alloys have long been recognized and have marked titanium as an important structural material in future critical Navy systems. Prior to realizing the full potential of titanium, however, definite advances must be made in processing technology to provide more reliable and economical titanium components. Melting and casting is a specific area in which additional technology will be required for a more effective utilization of titanium alloys in naval service.

The major problem encountered during the melting and casting of titanium is containing the molten metal without detrimental dissolution of the crucible. To circumvent this problem, several melting processes have been developed which utilize a solid titanium film or skull on the inside of a liquid-cooled, copper crucible. Actual melting is accomplished either by striking an arc between a consumable titanium electrode and a titanium skull in the liquid-cooled crucible, or by using an energy source such as an electron or plasma beam to melt a titanium charge in a liquid-cooled crucible. Skull melting is the primary method currently being used by industry to produce cast titanium components.

Consumable electrode skull melting has several disadvantages which may affect the soundness and homogeneity of the resultant castings. The primary disadvantage is that the degree of melt superheat is limited by the presence of a steep thermal gradient adjacent to the liquid-cooled crucible. Other disadvantages of this process include melt splattering, difficulties in controlling total power input, and potential crucible perforation due to arc-wandering. Electron beam skull melting, which allows greater superheat control than the consumable electrode process, is limited by the requirement for larger crucibles, more expensive equipment, and lower power efficiency.[1]

Induction melting is one alternative to skull melting which would eliminate many of the problems cited above, and potentially increase the number of producers of cast titanium. The major obstacle limiting the induction melting of titanium has been the lack of a suitable crucible material capable of withstanding attack by the molten titanium. Numerous investigations[2-11] have been conducted in the past to develop such a material. Oxides, nitrides, carbides, sulfides, refractory metals, and combinations of these materials have been studied. A review of these efforts indicates several areas which require further investigation. For example, many of the materials evaluated and eliminated as possible containers for molten titanium were of relatively

[1] Superscripts refer to similarly numbered entries in the Technical References at the end of the text.

low purity, based upon present standards. Impurities may act as sites for rapid attack by molten titanium. Further, many of the previous investigators utilized low density (approximately 75% to 80%) and commercially available crucibles. Crucible density and the presence of minor defects and binder materials in commercially available crucibles may affect the rate of crucible dissolution and lead to failure. Finally, and perhaps most significantly, many investigators emphasized screening a large number of materials and devoted only limited effort to determine the mode of material or crucible failure.

Finding a suitable crucible for melting titanium requires both a thermodynamic screening of pure refractory materials and development of crucible fabrication techniques which provide an optimum interface with the molten titanium. In addition, a candidate crucible material for titanium must possess a melting point well in excess of 2000° C*, a low vapor pressure, favorable thermal and dielectric properties at elevated temperatures, and good resistance to thermal shock. A review of current information regarding the thermodynamic stability and physical properties of yttrium oxide (yttria) indicates that this material has the potential to resist attack by molten titanium. During the first phase of this program, the feasibility of using yttria as a coating on graphite crucibles was investigated.[12] This investigation revealed a detrimental reaction between yttria and graphite near the melting temperature of titanium which resulted in severe contamination of the titanium due to evolution of gaseous reaction products. Nonetheless, the thermodynamic stability and favorable refractory properties pointed to yttria as a prime candidate crucible material for melting titanium.

BACKGROUND

The molar free energy of dissociation (ΔG_{RO}) for an oxide measures the ability of the compound to resist being reduced or partially dissociated in a particular environment. The greater the value of ΔG_{RO} at a particular temperature and pressure, the more resistant the oxide is to being reduced (losing oxygen) or partially dissociated. Since titanium has an extremely high affinity for oxygen, holding an oxide in contact with titanium is equivalent to subjecting the material to a severe reducing environment.[13] Table 1 lists ΔG_{RO} value for several refractory oxides at 1200° and 2000° K. Examination of these data indicates that at both temperatures, yttrium oxide has the highest ΔG_{RO} value and should be the most difficult oxide to reduce or partially dissociate. The ranking of the oxides at 2000° K, which is above the melting point of titanium, points out that yttrium oxide should be more stable than thorium oxide. In this connection, results of several earlier

*Abbreviations used in this text are from the GPO Style Manual, 1967, unless otherwise noted.

investigations using thorium oxide crucibles revealed that this material is only partially dissociated by molten titanium. The data in table 1 suggest that yttrium oxide is potentially more stable and should be considered more resistant to dissociation by molten titanium.

TABLE 1
MOLAR FREE ENERGY OF DISSOCIATION FOR REFRACTORY OXIDES

Refractory Oxide	Molar Free Energy of Dissociation (ΔG_{RO}) (kcal/gram-atom oxygen)		Reference
	1200° K	2000° K	
Yttrium	+124.7	+106.5	14
Thorium	+120.2	+101.6	15
Beryllium	+116.5	+ 97.6	16
Calcium	+122.8	+ 96.9	16
Zirconium	+102.4	+ 85.4	16

kcal - thousand calories

Although the above analysis points out the relatively high thermodynamic stability of yttrium oxide compared to other refractory oxides, a material must possess other physical properties to be suitable for use as a crucible material for the high melting point metals. Included among these properties are a high melting point, a low vapor pressure, and relatively low coefficients of thermal expansion and thermal conductivity at approximately 2000° K. To further illustrate the potential of yttrium oxide as a crucible material, relevant physical properties of yttrium oxide are compared to those of stabilized zirconium oxide in table 2. The latter is a common crucible material used in the vacuum melting of steels and nickel-base alloys. The data in table 2 indicate that yttrium oxide possesses comparable physical properties and should also be suitable as a crucible material. Therefore, based on the favorable thermodynamic stability and physical properties of yttrium oxide, an investigation was undertaken to determine the feasibility of using yttrium oxide as a crucible material for melting titanium.

TABLE 2
SELECTED PHYSICAL PROPERTIES OF
YTTRIUM AND ZIRCONIUM OXIDES

Property[1]	Yttrium Oxide (Y_2O_3)	Zirconium Oxide[2] (ZrO)
Melting Point, $^{\circ}$ C	2410	2500
Density, grams/cm^3	5.0	5.0
Crystal Structure	Cubic	Cubic
Thermal Conductivity, gram-cal/cm-sec $^{\circ}$ C	0.5	0.5
Coefficient of Thermal Expansion, 1400° - 2200° C, cm/cm $^{\circ}$ C	$9.3X10^{6}$	$16X10^{6}$
Dissociation Pressure @ 1700 $^{\circ}$ C, atmosphere	10^{-9}	10^{-9}

[1] Collected from reference 17.

[2] Stabilized by addition of 1 to 2 volume percent CaO.

OBJECTIVE

The overall task objective is to develop materials and techniques for the induction melting of titanium. This report presents the results of an investigation on the feasibility of using high purity, yttrium oxide as a crucible material for melting titanium.

EXPERIMENTAL PROCEDURE

MATERIALS

All crucibles used in this investigation were manufactured from commercial, 99.99% Rare Earth Oxide (REO) yttrium oxide powder. The oxide was obtained from W. R. Grace and Co., Davison Chemical Division, and had an average particle size of less than 2 microns. All melting experiments were performed with commercial purity titanium sponge which was arc-melted to obtain approximately 10-gram buttons.

CRUCIBLE FABRICATION

Crucibles were fabricated by isostatic compaction of the yttrium oxide powder, followed by sintering at selected temperatures. Initially, 10-gram capacity crucibles were fabricated to obtain a range of densities and establish optimum fabrication parameters. The powder was isostatically compacted into cylinders, $1\frac{1}{4}$ inch in diameter by 3 inches long, using pressures ranging from 30 to 60 ksi.* Crucibles similar to item (a), figure 1, were then machined from the as-pressed cylinders and sintered at 1500° ±15° C for 8 hours, or 1600° ±15° C for 1 hour. Sintering at 1500° C was performed in air using a globar-type furnace, while the 1600° C sintering was conducted in argon using the susceptor furnace depicted in figure 2. To obtain crucible densities greater than 90% of theoretical, several of the 10-gram crucibles were sintered at 1800° ±15° C for times of from 1 to 4 hours in a tungsten mesh vacuum resistance furnace. These crucibles were used to evaluate both a higher density material and the performance of yttrium oxide in an "oxygen deficient" state. It has been reported that vacuum sintering causes the normally white yttrium oxide to turn black and assume an "oxygen deficient" composition of $Y_2O_{2.996}$.[14, 18] Several crucibles were tested in the oxygen deficient condition and others with similar densities were resintered in air at 1500° C to achieve the normal full oxide state.

Density measurements were performed by the standard water displacement method, ASTM-/C 373-56. However, toluene was substituted for water in evaluating the as-pressed, low-density crucibles to prevent the formation of hydroxides, which would affect density measurements. In addition, the hardness of the sintered crucibles was measured by using standard Knoop microhardness tests with a 1.0 kg load.

On the basis of the results with 10-gram crucibles, several 30-gram capacity crucibles and three 400-gram capacity crucibles, illustrated in items (b) and (c), figure 1, were fabricated. These crucibles were formed by isostatically compacting the yttrium oxide powder around wax-coated, aluminum mandrels. The parameters used in fabricating the 30- and 400-gram crucibles are listed on table 3.

*ksi - thousand pounds per square inch.

TABLE 3

FABRICATION PARAMETERS FOR 30- AND 400-GRAM YTTRIUM OXIDE CRUCIBLES

	30-Gram Crucible	400-Gram Crucible
Compaction Pressure, ksi	50	50
Heating Rate, ^{o} C/hr	200 to 400	400
Sintering Temperature, ^{o} C	1500 to 1800	1800
Sintering Time, hr	1 to 8	2.5
Sintering Atmosphere	Air, Argon, or Vacuum	Vacuum

MELTING

Initial melting experiments using the 10-gram capacity crucibles were performed in an argon atmosphere with the molybdenum susceptor furnace shown in figure 2. Temperature measurements in this furnace were obtained with a tungsten-tungsten-26% rhenium thermocouple mounted near the base of the crucible. A continuous flow of high purity argon (99.999%) was maintained in the furnace during the experiments. The melting procedure was as follows:

- A 10-gram button of commercial purity titanium was placed in the crucible.
- After charging the furnace, argon was flowed through the system for 1 hour at 200^{o} C.
- The charge was heated at approximately 100^{o} C/per minute to 1725^{o} ±15^{o} C and held for 5 minutes at that temperature.
- Power was shut off and the titanium was allowed to solidify in the crucible.
- Specimens were removed when the furnace temperature was below 200^{o} C.

The 30-gram crucibles were evaluated in the same susceptor furnace, but the melting experiments were performed in a vacuum melting chamber. The charge was heated at approximately 50° C per minute to 1725° C under a vacuum of 10^{-4} torr. Temperatures for these experiments were measured with an optical pyrometer.

The 400-gram crucibles were fabricated in order to pour actual castings of titanium rather than to evaluate the titanium solidified in the crucible. The crucible was enclosed in a tantalum susceptor and placed in an outer shell of zirconia. The crucible was then charged with 300 grams of commercial purity titanium and placed in a vacuum melting furnace. The charged crucible was then heated at approximately 50° C per minute under a vacuum of 10^{-4} torr. Two 400-gram yttrium oxide crucibles were evaluated in the above manner.

EVALUATION

After the melting experiments, the 10- and 30-gram crucibles containing the solidified titanium were cut in half to examine the cross section of the crucible and the titanium-yttrium oxide interface. Half of each sample was forwarded to Luvak, Inc., Newton, Mass., for chemical analysis of the titanium for oxygen, yttrium, nitrogen, and hydrogen. Gas analyses were performed by vacuum fusion techniques. Atomic absorption methods were used to measure the yttrium content of the titanium. The other half of the sample was subjected to metallographic examination and microhardness testing. It should be noted that microhardness has been found to correlate extremely well with the interstitial oxygen content of titanium.[4, 19] Electron microprobe analyses were also performed on selected samples.

RESULTS AND DISCUSSION

Results of density measurements, expressed as percent of theoretical density, on the 10-gram yttrium oxide crucibles are listed in table 4. These data indicate that crucible densities ranging from 70% to 97% of theoretical density were achieved by varying compaction pressure and sintering temperature. As expected, the crucible density after sintering generally increased with increasing isostatic compaction pressure and increasing sintering temperature. Further, there appeared to be a good correlation between sintered crucible density and Knoop microhardness, as shown by the data in table 5.

It was mentioned earlier that several crucibles were sintered in vacuum at 1800° C to achieve crucible densities on the order of 95% to 97% theoretical density. These crucibles exhibited a noticeable surface darkening which has been identified as an indication of oxygen deficiency in the oxide. Figure 3 illustrates the contrast in the appearance of the crucibles depending upon the sintering atmosphere. Sectioning of the dark, vacuum sintered crucibles revealed that the darkening was not confined to the surface but was apparent throughout the cross section. Microhardness tests on crucibles with similar densities revealed that the oxygen deficiency had no measurable effect on hardness.

TABLE 4
RESULTS OF ISOSTATIC PRESSING AND SINTERING EXPERIMENTS
ON 10-GRAM CAPACITY YTTRIUM OXIDE CRUCIBLES

Isostatic Pressure ksi	Percent of Theoretical Density(1)				
	As-Compacted	1500° C(2) 8 Hours	1600° C(3) 1 Hour	1800° C(4) 1 Hour	1800° C(4) 4 Hours
30	58.5 58.6	70.2 70.0	79.3 79.1	-	-
40	59.6 59.1	74.5 75.5	80.0 81.5	-	-
50	60.6 60.2	75.9 76.1	83.2 83.1	94.8 95.1	97.1 97.3
60	61.8 62.1	77.6 77.3	85.8 86.2	-	-

(1)Density measurements performed in accordance with ASTM-C-373-56.
(2)Sintered in air.
(3)Sintered in argon.
(4)Sintered in vacuum.

TABLE 5
DENSITY AND HARDNESS OF
10-GRAM YTTRIUM OXIDE CRUCIBLES

Density %	Hardness[1] Knoop-1.0 kg
70	190
75	220
76	235
77	280
79	310
81	340
83	365
86	400
95	520
97	570

[1]Average of five readings

The results of the argon melting experiments using the 10-gram yttrium oxide crucibles are summarized in table 6. Examination of the chemical analyses of the titanium melts, which were held at 1725° C for 5 minutes and solidified in the crucible, revealed that substantial levels of oxygen and yttrium contamination were encountered during the melting and solidification cycle.

TABLE 6
RESULTS OF MELTING EXPERIMENTS IN ARGON IN 10-GRAM CAPACITY YTTRIUM OXIDE CRUCIBLES

Crucible Density % of Theoretical	Chemical Analyses of Titanium Melts[1] weight percent				Titanium Hardness[2] Knoop-1.0 kg	
	Oxygen	Yttrium	Nitrogen	Hydrogen	Average	2σ
70	0.2590	0.86	0.0064	0.0037	131	19
75	0.2412	1.06	0.0028	0.0030	121	19
77	0.1753	0.58	0.0046	0.0134	128	19
81	0.1380	0.20	0.0005	0.0018	112	10
83	0.1162	0.43	0.0021	0.0018	107	13
86[3]	0.3023	0.93	0.0010	0.0023	108	13
95	0.1649	0.44	0.0010	0.0013	102	18
95[3]	0.2508	1.03	0.0005	0.0046	115	37
95[3]	0.3158	1.40	0.0015	0.0015	122	14
97[3]	0.3106	1.13	0.0011	0.0014	98	14

(1) Analysis of Starting Material: Oxygen - 0.0500; Yttrium - <0.01; Nitrogen - 0.0005; Hydrogen - 0.0028.
(2) At least 15 determinations.
(3) Surface of specimens was dark indicating apparent oxygen deficiency.

Comparison of the oxygen analyses after melting to that of the starting material which had approximately 500 ppm oxygen indicates that 0.06% to 0.25% oxygen was picked up during melting and solidification. There was no apparent correlation either between crucible density and the oxygen and yttrium content of the titanium, or between the microhardness and composition of the titanium. It was noted, however, that the melts prepared in the dark, oxygen deficient crucibles generally had the highest oxygen and yttrium contents.

Macroscopic examination of the cross sections of the 10-gram melts revealed a darkened zone in the yttrium oxide adjacent to the titanium. This zone, which is illustrated in item (a), figure 4, appears similar to the darkening or oxygen deficiency encountered in the crucibles sintered in vacuum at 1800° C. Upon further examination of the interface between the yttrium oxide and the titanium, it was found that the titanium did not penetrate into the yttrium oxide. The sharp, well-defined interface between the titanium and the oxide is illustrated in item (b), figure 4, which also reveals the cellular network of constituents observed in the microstructures of all the melts. Electron microprobe analyses of this eutectic-like microconstituent revealed that the phase is yttrium-rich, as shown in figure 5. In this connection, it should be noted that yttrium additions to titanium in excess of 0.9 weight percent cause a eutectic reaction.[20] Based on the composition and cellular morphology of these particles, it appears that the yttrium oxide contamination results in the formation of an eutectic in the cast titanium microstructure.

The results of vacuum melting experiments with the larger, 30-gram crucibles are summarized in table 7. Once again there was no significant correlation between crucible density and the oxygen and yttrium contents of the titanium. It was noted, however, that the amount of oxygen and yttrium picked up during melting as well as the microhardness of the titanium were generally higher than the values measured in the 10-gram argon melts.

TABLE 7
RESULTS OF VACUUM MELTING EXPERIMENTS IN 30-GRAM CAPACITY YTTRIUM OXIDE CRUCIBLES

Crucible Density % of Theoretical	Chemical Analyses of Titanium Melts(1) weight percent				Titanium Hardness(2) Knoop-1.0 kg	
	Oxygen	Yttrium	Nitrogen	Hydrogen	Average	2σ
76	0.2024	0.55	0.0014	0.0036	139	10
83	0.2681	0.73	0.0078	0.0011	145	18
85	0.4652	1.52	0.0013	0.0007	159	15
86	0.3712	1.14	0.0012	0.0007	150	17
89	0.3551	1.93	0.0010	0.0008	146	18
89	0.5608	1.92	0.0011	0.0007	160	21

(1) Analyses of Starting Material: Oxygen - 0.0500; Yttrium - <0.01; Nitrogen - 0.0005; Hydrogen - 0.0028.
(2) At least 15 determinations.

The primary reasons for the higher levels of yttrium and oxygen contamination are believed to be the vacuum of 10^{-4} torr used during melting and the slightly higher holding temperatures of approximately 1750° C used in these larger melts. Metallographic examination of the vacuum-melted material revealed that, in addition to the cellular network of particles noted earlier, a larger, flower-type particle, depicted in figure 6, was present in the microstructure. These particles appear to be a massive form of the yttrium-rich eutectic constituent discussed earlier.

Three 400-gram capacity yttrium oxide crucibles were manufactured for use in actual melting and casting experiments. One of the crucibles exhibited severe surface spalling and was not used. The other crucibles were packed in a zirconia outer crucible and subjected to vacuum melting experiments. Both crucibles failed prematurely due to "bridging" of the charge material in the crucible. These mechanical failures precluded evaluation of the 400-gram crucibles. It was noted that the titanium which was melted in the crucible did not wet the yttrium oxide but rather flowed into the outer shell of zirconia. No analyses were performed on the 400-gram crucibles.

Based upon the results of this investigation, several observations can be made relative to the reactivity of yttrium oxide in contact with molten titanium. First, it was noted that there was a dark, oxygen deficient zone in the yttrium oxide adjacent to the titanium. This indicates that yttrium oxide is reduced by or loses oxygen to the molten titanium. Furthermore, it was observed that the oxygen deficient yttrium oxide crucibles generally resulted in higher levels of melt contamination. Second, the oxygen contents of the titanium measured by chemical analyses of the melts were as high as 0.56 weight percent. At these levels of oxygen there should be a marked increase in the titanium hardness. However, as shown on figure 7, which compares the results of this investigation with an established hardness versus oxygen relationship for titanium, there was no noticeable increase in the hardness of the titanium melts. The hardness of all of the melts was relatively constant over the entire range of oxygen contents. This suggests that a majority of the oxygen is concentrated in the yttrium-rich eutectic microconstituent, rather than in the titanium solid solution. Thus, it appears that melting titanium in yttrium oxide crucibles results in a finite amount of crucible dissolution which is accelerated by the presence of an oxygen deficient yttrium oxide at the titanium interface, and in the formation of a titanium-yttrium-oxygen eutectic phase in the cast titanium microstructure.

Table 8 compares the results obtained in this investigation to the results of earlier studies using similar size thorium oxide and beryllium oxide crucibles. These data indicate that the yttrium oxide crucibles displayed lower levels of melt contamination than the other oxides, even though the yttrium oxide melts were superheated to higher temperatures and held for longer times. It should be noted that prior to the present investigation, thorium oxide was generally considered the most stable refractory oxide in contact

with molten titanium. However, the results of this investigation indicate that yttrium oxide is superior to thorium oxide as a crucible material for melting titanium.

TABLE 8
COMPARISON OF CRUCIBLE PERFORMANCE FOR YTTRIUM OXIDE CRUCIBLES OF THIS INVESTIGATION TO THAT OF THORIUM AND BERYLLIUM OXIDE CRUCIBLES OF PREVIOUS INVESTIGATIONS

Crucible Material	Melting Parameters			Titanium Contamination		Average Titanium Hardness DPH
	Atmosphere	Superheat Temperature °C	Holding Time minutes	Oxygen w/o	Calculated Oxide w/o	
Yttrium Oxide	Vacuum	50	5	0.2 to 0.56	0.7 to 2.5 (Y_2O_3)	130(1)
Thorium Oxide(2)	Argon/ Vacuum	25	4	0.4 to 1.2	3.1 to 10.6 (ThO_2)	245
Beryllium Oxide(2)	Argon/ Vacuum	25	1	2.4 to 8.8	3.6 to 13.6 (BeO)	650

(1)Values from Knoop hardness number measurements.
(2)Obtained from Brace[2] and Eisenberg and Stavrolahis.[4]
w/o - weight percent.
DPH - diamond pyramid hardness.

The favorable resistance of yttrium oxide to attack by molten titanium suggest several areas which require additional investigation and also several possible immediate applications for the material. Investigations are required to establish the effect of the eutectic constituent introduced by the limited dissociation of yttrium oxide on the properties of the titanium castings poured from larger crucibles. Furthermore, since yttrium oxide is a rather expensive material (approximately $34 per pound in 1972), the durability of the material in the form of a crucible should be established. In this connection, several 30-gram crucibles were fabricated by combining yttrium oxide powder with approximately 20 weight percent molybdenum to produce a cermet crucible. The cermet crucible was found to have outstanding shock resistance. Thus, the use of yttrium oxide-base cermets may also provide more cost effective crucibles for melting titanium. Finally, there are several immediate applications for yttrium oxide. These include the use of plasma spray coatings of yttrium oxide on ceramic molds and immersion thermocouples

used in the manufacture of titanium alloys and other refractory metals such as nickel- and cobalt-base alloys. Another possible use of yttrium oxide is as a thermal and electrical insulator for titanium welding applications.

SUMMARY

On the basis of results of the melting experiments reported herein, using 10- and 30-gram capacity yttrium oxide crucibles, it is concluded that molten titanium partially dissociates yttrium oxide, resulting in limited interstitial oxygen contamination of the titanium and in the formation of a titanium-yttrium-oxygen eutectic phase in the cast microstructure. Variation in the density of the crucibles over the range of 70% to 97% of theoretical had no measurable effect on the extent of melt contamination. However, it was observed that several melts prepared in oxygen deficient yttrium oxide crucibles generally had the highest levels of melt contamination. Although up to 1.93% yttrium and 0.56% oxygen were picked up from the crucible, comparison of the results of this investigation with previous studies on refractory oxides indicates that yttrium oxide appears to be the best candidate crucible material for melting titanium. The favorable resistance of yttrium oxide to attack by molten titanium suggests several areas requiring additional research and development as well as areas where the material may have immediate industrial applications.

RECOMMENDATIONS

It is recommended that additional investigations be performed to determine the significance of the eutectic constituent introduced by the yttrium oxide contamination on the properties of cast titanium. In addition, experiments designed to establish the durability of yttrium oxide crucibles should be performed. In this connection, it is suggested that yttrium oxide-base cermets or ceramic composites may dispiay improved durability.

FUTURE WORK

No additional investigations are planned under the present program. This report constitutes the final report on this task.

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Item (a)
10-Gram Capacity (1X)

Item (b)
30-Gram Capacity (2X)

Item (c)
400-Gram Capacity (1X)

Figure 1 - Yttrium Oxide Crucibles Used in Melting Experiments

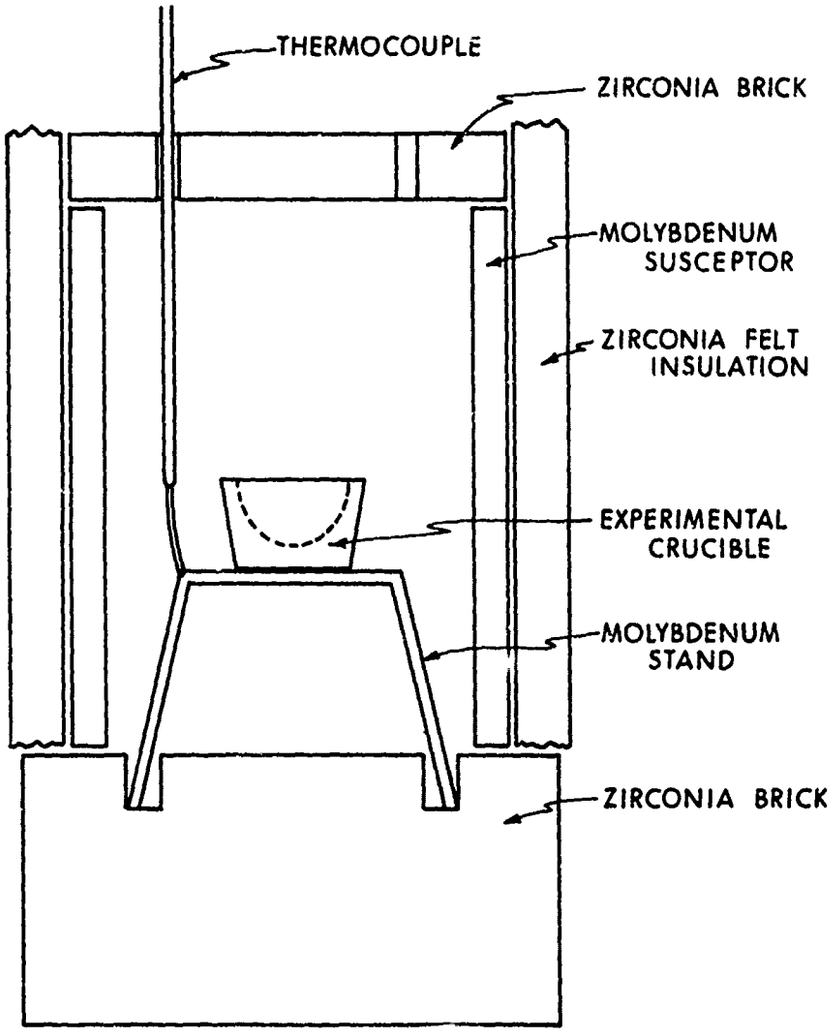
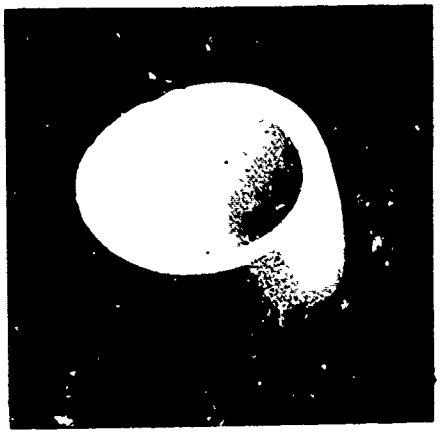
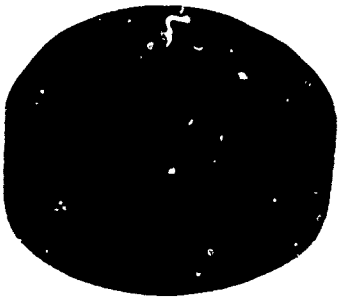


Figure 2 - Molybdenum Susceptor Furnace Used in Sintering and Melting Experiments

Item (a)
Air Sintered - 1500° C
(70% density)

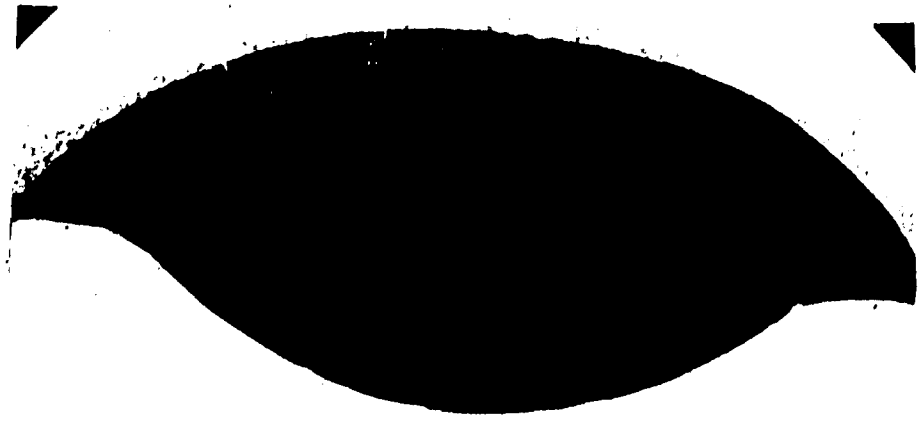




Item (b)
Vacuum Sintered - 1800° C
(95% density)

Figure 3 - Effect of Vacuum Sintering on
Appearance of Yttrium Oxide

Item (a)
Macrophotograph (4X)



Item (b)
Photomicrograph (100X)

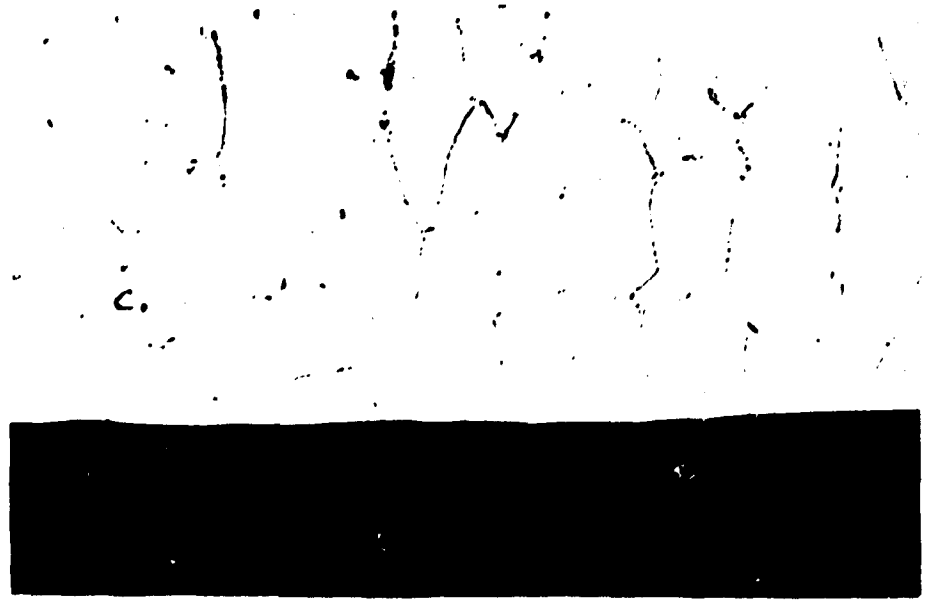


Figure 4 - Interface Between Yttrium Oxide and Titanium Melts

Item (a)
Photomicrograph (500X)

Item (b)
Photomicrograph (1000X)

Item (c)
Electron Micrograph (1000X)

Item (d)
Electron Microprobe Scan
for Yttrium (1000X)

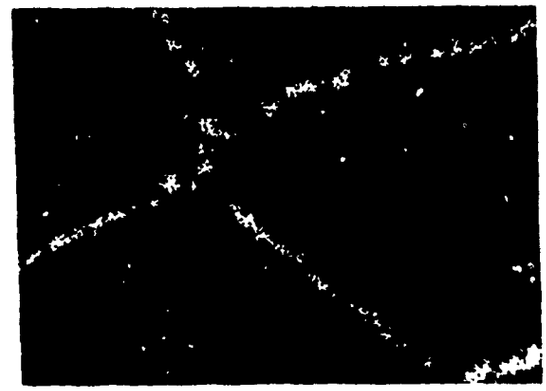
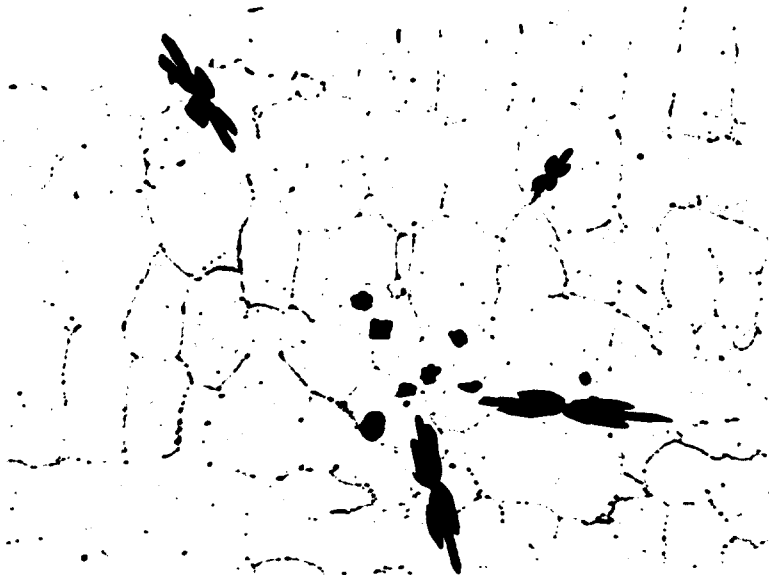
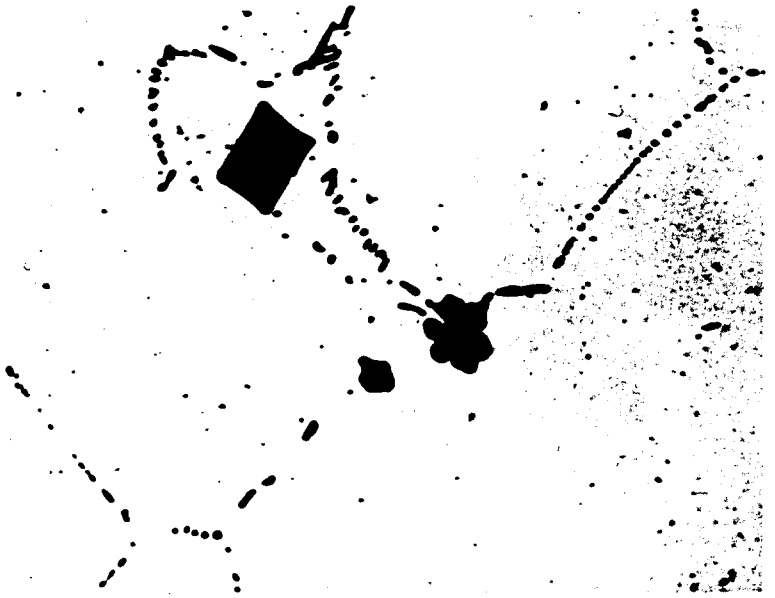


Figure 5 - Results of Electron Microprobe Analyses
on Eutectic Constituents in Titanium Melts

100X



500X



10μ

Figure 6 – Microstructures of Titanium Vacuum Induction Melted in 30-Gram Yttrium Oxide Crucibles Unetched

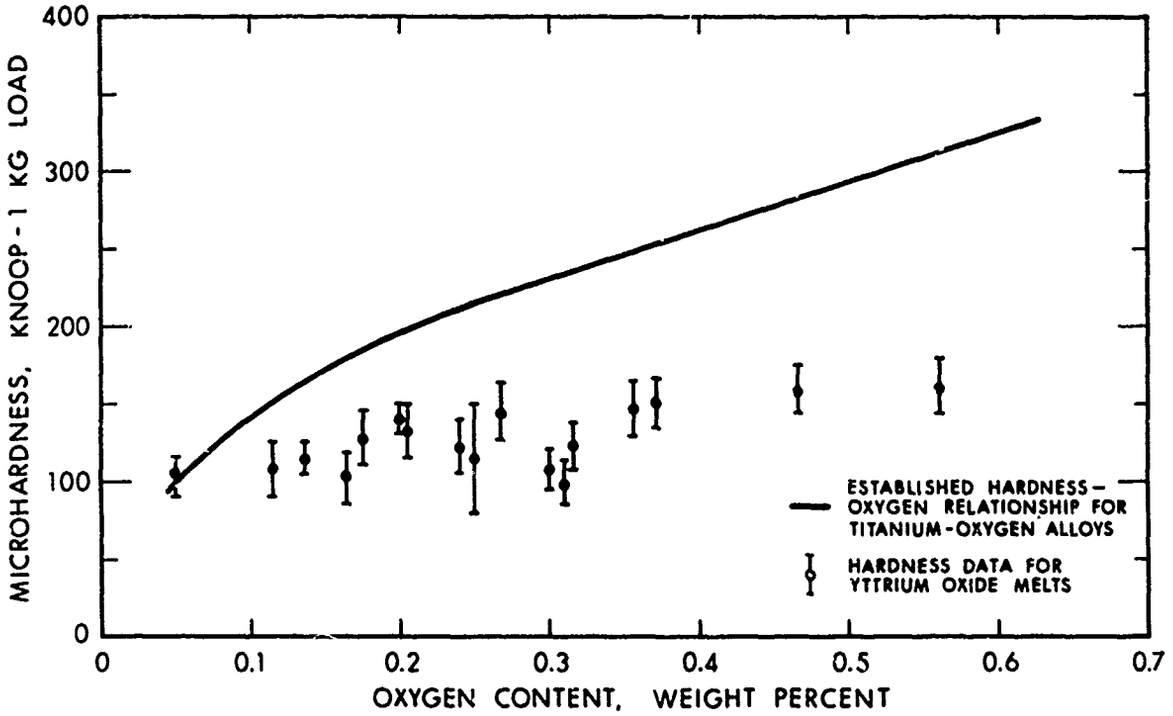


Figure 7 - Comparison of Hardness Data from Yttrium Oxide Melts to Established Hardness-Composition Relationship for Titanium-Oxygen Alloys