ADVANCED TITANIUM PROCESSING

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ABSTRACT

The Albany Research Center of the U.S. Department of Energy has been investigating a means to form useful wrought products by direct and continuous casting of titanium bars using cold-wall induction melting rather than current batch practices such as vacuum arc remelting. Continuous ingots produced by cold-wall induction melting, utilizing a bottomless water-cooled copper crucible, without slag (CaF_2) additions had minor defects in the surface such as “hot tears”. Slag additions as low as 0.5 weight percent were used to improve the surface finish. Therefore, a slag melted experimental Ti-6Al-4V alloy ingot was compared to a commercial Ti-6Al-4V alloy ingot in the areas of physical, chemical, mechanical, and corrosion attributes to address the question, “Are any detrimental effects caused by slag addition?”.

INTRODUCTION

Direct and continuous casting of titanium bars using cold-wall induction melting, rather than current batch practices such as vacuum arc remelting (VAR), has been investigated at the Albany Research Center. The induction melting technology allows for the use of various forms of charge materials such as loose titanium sponge, powder, scrap, and turning alloys to be consolidated into continuous ingots. This technology is envisioned to produce starting ingots from inexpensive charge material for further refinement to non-aerospace applications. Ingots produced by cold-wall induction melting at the Albany Research Center had minor defects in the surface (Fig. 1) therefore, calcium fluoride slag additions were used to facilitate melting and improve the surface finish (Fig. 2). Results are presented that show no detrimental effects were discernible from slag additions. Also, a transition gas seal was developed to allow continuously melted ingots to pass from an argon atmosphere into air. A patent application has been filed for the transition gas seal.

Fig. 1 Ingot surface tear without slag additions.

Fig. 2 Smooth ingot surface melted with 0.5 weight percent slag.

EQUIPMENT AND PROCESSING

Cold-wall induction melted ingots were produced with the equipment shown in Fig. 3. This equipment has slight modifications from the original equipment described in U.S. Patent 3,775,091 (ref. 1). The crucible was a 24 segment, approximate 10 cm (4 in.) round, bottomless water-cooled copper crucible. The crucible was surrounded by an induction coil within a vacuum chamber. A solid titanium bar (starting stub) of approximately 17.8 cm (7 in.) length and a slightly undersized diameter was drilled and tapped to allow attachment of a water-cooled copper shaft. This starting stub was positioned within the center of the crucible while the attached shaft extended through the bottom withdraw chamber via a vacuum gland.

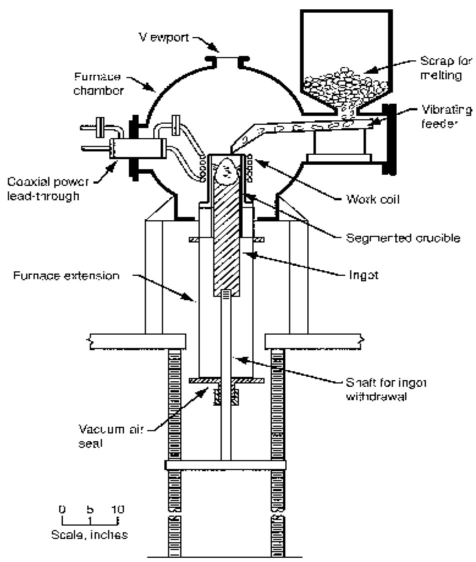

Fig. 3 Cold-wall induction furnace schematic.

The vacuum-tight aluminum furnace chamber was approximately 76 cm (30 in.) diameter by 76 cm long with a 76 cm diameter hinged door. The crucible was mounted in the bottom of the chamber with an additional approximate 18 cm (7 in.) diameter by 76 cm long extension chamber for ingot withdrawal. Two approximate 15 cm (6 in.) diameter view ports were located in the chamber, one directly above the crucible and one in the door. All flanges were sealed with o-rings and water-cooled. The furnace was installed on an elevated deck to facilitate ingot withdrawal. The power supply was a 100 kW, 9600 Hz motor generator rated at 440 VAC and 228 AAC. The vacuum system consisted of a rotary blower backed by a mechanical pump.

Charge material preparation consisted of hand screening Ti-6Al-4V chips to eliminate foreign material and fines. Next, the chips were washed with acetic acid and rinsed with hot water to remove any residue such as cutting fluids. Then the chips were dried at 177°C. Charge material mixed with 0.5 weight percent CaF_2 slag was placed in an approximate 50 cm (20 in.) diameter by 50 cm high chamber mounted on a 25 cm (10 in.) diameter extension to the right side of the furnace chamber. The furnace chamber was evacuated to less than 50 millitorr and then backfilled with 1/5 atmosphere of an inert gas, typically argon. The charge composition was gravity fed through the bottom of the chamber via a funnel-shaped opening onto an electric vibratory feeder. The vibratory feeder delivered the charge into the crucible by a chute extended over the edge of the crucible.

The CaF_2 slag has a lower melting point (1330°C) than the titanium charge (~1660°C). This allowed the slag to melt and migrate to the outer edge of the melt to solidify on the surface and outer diameter of the ingot. This slag boundary layer facilitated withdrawal of the semi-solid ingot from the crucible.

As the charge material melted, an equivalent amount of solidified bar was withdrawn continuously from the coil area and into an unheated water-cooled portion of the crucible for further cooling before entering the withdraw chamber. The withdraw mechanism consisted of an initial starting stub of ingot material of similar composition as the charge material, and was positioned inside the crucible within the coil. The bottom of the stub was drilled and tapped to allow attachment of a water-cooled copper shaft. This shaft extended through the bottom of the withdraw chamber via a vacuum gland. Withdraw was accomplished by an electric motor and worm drive screw mechanisms.

The CaF_2 slag layer on the outer diameter of the resulting experimental alloy bar was easily chipped off and removed by a hammer. The resulting experimental alloy bar surface was machined before x-ray and ultrasonic determination of defects. Ultrasonic defects were detected at a length of 8.89 to 12.70 cm (3.5 to 5 in.) and a depth of 2.54 cm (1.0 in.) and 27.94 to 31.12 cm (11.0 to 12.25 in.) length, 1.27 cm (0.5 in.) deep in the ingot. Cutting and machining the ingot at the defect locations revealed a CaF_2 (slag) inclusion in one location and a WC (tungsten carbide) defect location in the other. The probable WC source was a cutting tool chip in the scrap charge.

Further processing of the experimental alloy included step forging two pieces at 1066°C from 8.73 cm (3 7/16 in.) diameter to 3.81 cm (1.5 in.) plate. The pieces were then reheated at 954°C for 30 minutes and crossed and straight-away rolled to a final thickness of 1.59 cm (0.625 in.) The final step was to anneal for 30 minutes at 788°C. The final dimensions of the plates were approximately 14.6 × 38.10 cm (5 3/4 × 15 in.) and 13.34 × 26.21 cm (5 1/4 × 11 1/2 in.). Samples were cut from these for corrosion and mechanical testing. A commercial alloy Ti-6Al-4V ingot was similarly step forged and rolled in preparation for comparison samples.

RESULTS

CHEMISTRY

Table 1 shows the chemical analysis of typical reported literature values, the slag melted experimental alloy, and the commercial alloy composition. The experimental alloy, which was produced from Ti-6Al-4V scrap chips, had elevated oxygen levels.

Table 1. Chemistry percent comparison of Ti-6Al-4V alloy titanium castings

Source	MIL T-9046J literature values[2]	Slag melted experimental alloy	Commercial alloy
Al	5.5–6.75	6.42	6.81
C	0.08	0.05	0.03
Fe	0.30	0.22	0.20
H	0.0125	Not analyzed	Not analyzed
N	0.05	0.06	0.06
O	0.20	0.24	0.18
V	3.5–4.5	4.17	4.46
Others Total	0.40	0.16	0.07
Balance	Ti	Ti	Ti

MECHANICAL TESTING

Test blanks were cut from the forged and rolled plates for determination of mechanical properties. The room temperature mechanical properties of the two Ti-6Al-4V alloys were determined from specimens sectioned parallel to the rolling direction, so that the load axis of the tensile samples was aligned in the longitudinal direction. The Charpy specimens were notched transverse to the rolling direction. Impact specimens were standard Charpy V-notch specimens conforming to ASTM specification E23-91 (ref. 3). Tensile specimens were sub-size specimens proportional to the standard in ASTM E8-91 (ref. 4). Because of the notch sensitivity of titanium, the end of the tensile bar was designed to fit into a 12.7 mm collet grip. The dimensions of the tensile test specimen are shown in Fig. 4.

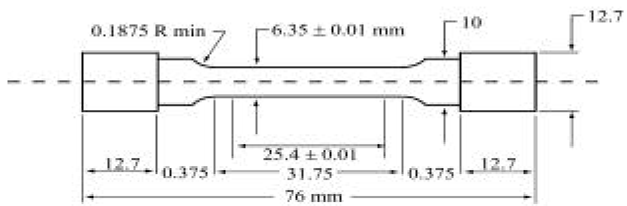

Fig. 4 Tensile test specimen dimensions

Tensile specimens were tested on a servo hydraulic machine with a load capacity of 220 kN. The specimens were loaded into hydraulic collet grips. Strain was collected by an extensometer until 5% extension, after which the extensometer was removed. The tensile test was performed by loading at a strain rate of 0.02 mm/mm*min^{-1}.

Charpy V-notch specimens were tested on a Dynatup Model 8250 drop weight impact tester with data analysis by Dynatup 830-I software. The drop weight fixture was designed in accordance with ASTM E23-91. The velocity of the calibrated tup was 3.05 m/sec with an impact energy of 210 J. The temperature of the test was 20°C.

A total of five impact samples were tested for the experimental alloy that was melted with slag additions and the commercial Ti-6Al-4V alloy. A total of four samples were tensile tested for each alloy. The mean results are shown in Table 2.

Table 2. Mechanical testing results

Material	Ultimate tensile strength (MPa)	Yield strength (0.2% offset) (MPa)	Elongation (percent)	Reduction in area (percent)	Charpy (J)
Slag melted Ti-6Al-4V experimental alloy	1047	1004	15	38	15.7
Ti-6Al-4V commercial alloy	1010	957	17	42	18.2
Minimum SAE specifications[5]	896	827	10	25	N/A
Typical properties of annealed wrought bar[6]	1000	925	16	34	22

In comparison to the commercial values, the experimental alloy had slightly higher strengths and lower ductilities. Both the experimental and commercial alloys exceeded the SAE specifications for titanium alloy bars and forgings and are similar to typical properties for an annealed wrought bar of Ti-6Al-4V, with the exception of low values for the impact energy. Prior to sectioning, the forgings received a mill anneal, so the slightly lower impact values may be due to the differences in thermomechanical processing, testing direction, or impurity levels. Overall, slag additions do not appear to detrimentally affect the mechanical properties of Ti-6Al-4V ingots prepared in a cold-wall induction furnace.

CORROSION

Titanium and its alloys exhibit excellent corrosion resistance in a wide variety of environments. The corrosion resistance results from the formation of a very stable, continuous, and highly adherent oxide film. This film can break down under reducing and acidic conditions when TiO_2 reduces to Ti^{2+} or Ti^{3+}. Increasing temperature favors this reduction.

Titanium castings can result in alloys with higher oxygen (O), nitrogen (N), and iron (Fe) contents. Table 1 shows that the slag melted Ti-6Al-4V experimental alloy ingot had more O and about the same N and Fe contents as compared to the commercial alloy. However, the nature of the oxide film is basically unaltered by the presence of most minor alloying (<2 to 3%) additions.[7] For example, despite small differences in O, N, and Fe contents in the various grades of unalloyed titanium, they all have about the same corrosion resistance under low corrosion rate conditions (below 0.13 mm/y) (ref. 8,9). It is under more extreme conditions that O, N, and Fe may increase corrosion rates.[8,9] Minor variations in alloy chemistry are only a concern under conditions where passivity of titanium is borderline or non-existent.[7]

Boiling HCl, an aggressive reducing acid, was chosen for initial corrosion testing at HCl concentrations of 2%, 0.2%, and 0.02%. The corrosion rate of Ti-6Al-4V in boiling 2% HCl is reported to be 260 mils/y (6.6 mm/y) (ref. 10), which is too aggressive for useful service, but well into the active range where minor variations in alloy chemistry may result in corrosion rate differences.

Corrosion samples were cut from the slag melted experimental alloy (nominal dimensions of 2.8 by 1.5 by 0.2 cm with a 0.24 cm diameter hole) and ground to 400 grit, pickled to remove approximately 2 mils, cleaned, dried, and weighed. Pickling was done in a bath containing 35 volume percent stock nitric acid (HNO_3, 70%), 5 volume percent stock hydrofluoric acid (HF, 60%), and the balance deionized water for 38 minutes at 40°C (ref. 11). The samples, in groups of two slag melted Ti-6Al-4V samples and two commercial samples, were individually suspended by teflon thread into deaerated HCl solutions and placed in autoclaves. There was an additional group of four slag melted samples exposed to 2% HCl. The samples were heated to 103°C (the boiling temperature) after three cycles of gas evacuation with a vacuum pump and backfilling with argon. The samples were removed after five days. After five days, the samples were cleaned, dried, and weighed.

The samples exposed in 0.02% HCl were scale-free and not etched. The samples exposed in 2% were scale-free and lightly etched. However in 0.2% HCl, a gray surface layer appeared on three of the four slag melted experimental samples (Fig. 5). No such layer appeared on the commercial alloys. Both alloys were lightly etched. Based on other results in hot, strong reducing acids,[11] the gray layer is probably a thin layer of hydrided titanium that deposited onto the sample from Ti^{3+} ions in solution. Typically this gray hydrided surface does not have significant effects on weight-loss measurements.[11]

The corrosion rates were found to be strongly dependent upon the HCl concentration. The individual sample results and linear fit with HCl concentration and are shown in Fig. 6, while average values are listed in Table 3. The average value of 6.6 mm/y for the slag melted experimental alloy in the 2% HCl

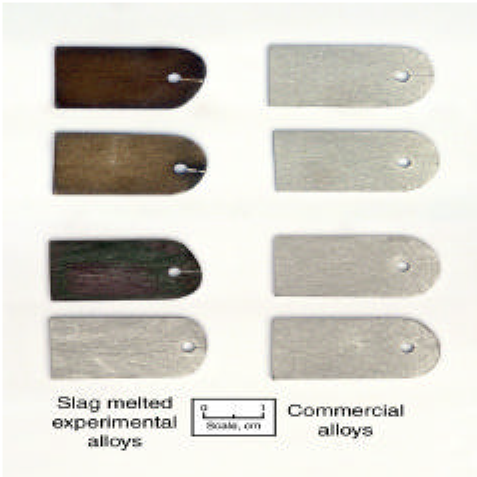

Fig. 5. Ti-6Al-4V alloy samples after 5 days in boiling 0.2% HCl solution.

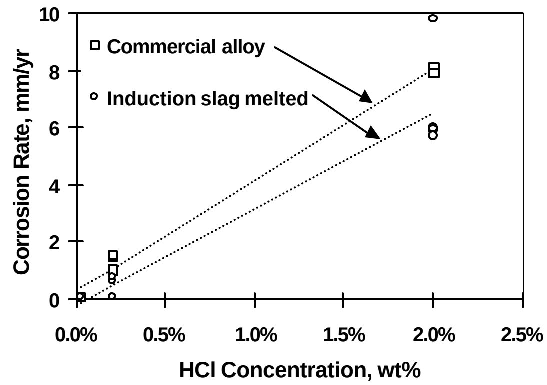

Fig. 6. Individual samples and linear fit (dashed lines) corrosion results after 5 days in boiling HCl solutions.

Table 3. Averaged corrosion rates in mm/y for boiling HCl solutions

HCl concentration	Slag melted Ti-6Al-4V experimental alloy	Ti-6Al-4V commercial alloy	Ti-6Al-4V literature value[(10)]
0.02 %	<0.1	<0.1	–
0.2 %	0.4	1.5	–
2.0 %	6.6	8.0	6.6

exposure agrees with the literature value of 6.6 mm/y (ref. 10). However, as Fig. 6 shows, there was one slag melted sample with a corrosion rate close to 10 mm/y, while the rest were close to 6 mm/y. Initial corrosion results in aggressive reducing acids (where active corrosion occurs) indicates no increased corrosion rates for the slag melted experimental alloy as compared with either the literature value, or the commercial alloy.

FATIGUE

Fatigue test specimens were tested in the elastic regime (<1000 MPa) for comparison of the slag melted alloy with the commercial alloy. The white circles in Fig. 7 are the slag melted alloy and it appears that the slag melted alloy has lower fatigue life and more scatter in the data than the commercial alloy.

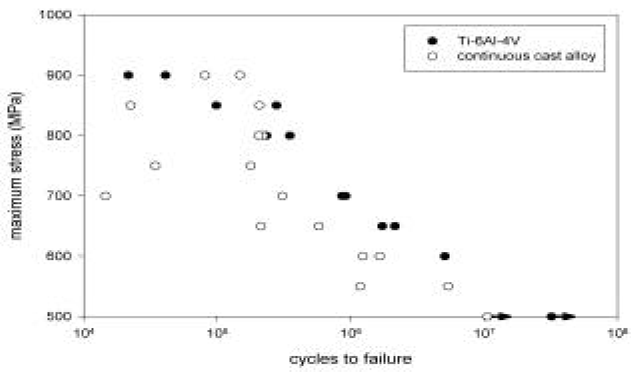

Fig. 7 Fatigue comparison of slag melted (white circles) and commercial (black circles) Ti-6Al-4V alloys.

CONCLUSIONS

The bottomless cold-wall copper crucible induction furnace provides the capability to consolidate many forms of charge materials such as titanium sponge, scrap and turning alloys, and powder into a continuous ingot with and without slag additions. The produced ingot could be used as stock material for casting furnaces or be processed further for other products such as bar and wire. Although a slag defect was identified in the resulting ingot the following specific results can be drawn from this research:

- Slag additions as low as 0.5 weight percent enhance melting by providing a “lubricated” surface between the ingot and the copper crucible. This slag layer facilitates ingot withdrawal resulting in the elimination of surface tears and providing better surface finishes.
- The experimental alloy chemistry produced with slag additions is in agreement with chemical specifications cited in literature for Ti-6Al-4V alloys.
- Slag additions do not appear to detrimentally affect the mechanical properties of Ti-6Al-4V ingots prepared in a cold-wall induction slag furnace.
- No increased corrosion rates for the slag melted experimental alloy were noted from corrosion testing in an aggressive reducing acid.

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