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An Overview of Titanium Alloys Modified with Boron

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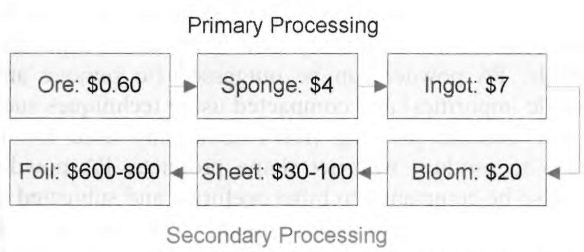
Titanium alloys continue to be vital structural materials for various aerospace as well as non-aerospace applications. There is a strong motivation to develop titanium technologies that can reduce the processing costs and increase the performance of conventional titanium alloys to enhance the affordability and expand their usage. Research work performed in several countries in the past two decades revealed that small boron additions to titanium alloys show significant promise in this direction. The potential of boron-modified titanium (Ti-B) alloys for fracture-sensitive applications is being critically assessed via focused projects at the US Air Force Research Laboratory (AFRL), which will form the basis for this paper. The physical metallurgy of the material system will be briefly described, including compositions, phases, processing, microstructures, and properties. Distinction will be made between Ti-B alloys modified with trace and modest boron levels. Trace (~0.1 wt.%) boron addition significantly refines the cast grain size by an order magnitude, which provides important opportunities for as-cast products. The grain refinement could also lead to reduction/elimination of processing steps that could lead to novel and affordable processing paths. Addition of boron of the order of 1 wt%, on the other hand, significantly (25-30%) increases the strength and stiffness of conventional Ti alloys at room as well as elevated temperatures while retaining good fracture related properties. Better understanding of the processing-microstructure-property-performance relationships has been found to be the key in the development of Ti-B alloys for aerospace applications where fatigue and damage tolerance are critical factors. Research and development programs currently underway at the AFRL, aimed at exploring and establishing the effects of boron addition to Ti alloys will be reviewed.

Keywords: titanium, boron, processing, microstructure, properties, performance

1. Introduction

Accelerating usage of titanium (Ti) alloys is attributable to their remarkable and distinctive combination of physical and metallurgical properties. Increased strength-to-weight ratio is the primary incentive for selection and design of aerospace applications including engine and airframe components. Although, the cost of titanium ore is significantly higher than other competing structural metals (e.g. aluminum, steel), titanium products are rather expensive primarily due to significant processing costs. The approximate costs of producing various titanium products[1)] starting from ore to foil are shown in Figure 1. Secondary processing of titanium from ingot to bloom (or plate) accounts for 47% of the total cost of the material[2)]. Sheets and foils produced from plate are much more expensive due to high price of the starting plate and extensive processing steps. In addition to the cost of extraction, the data show that much of the cost of titanium is in fabrication, which needs to be reduced if titanium use is to be justified and the industrial base is to be expanded significantly.



igure 1. Approximate costs in US$/lb of various titanium product orms (from Reference 1).

A typical processing sequence adopted for the anufacture of titanium products along with icrostructural changes are illustrated in Figure 2, which volves ingot breakdown, billet conversion, and finishing. The grain sizes of cast titanium alloys produced via melt processing (e.g. vacuum arc remelting, plasma arc melting), are rather coarse (from several millimeters to centimeters depending on cast billet size, Figure 2b) due to rapid grain coarsening in the high temperature β phase, and the grain size typically increases with increase in section thickness (i.e. decrease in cooling rate). Microstructural parameters such as coarse grain size, columnar morphology, and thick platelike grain boundary α are responsible for very poor workability of the as-cast condition[3)]. Extensive thermo-mechanical processing is essential to breakdown the cast structure and texture in order to improve the workability and obtain a good balance of static and dynamic properties. Ingot breakdown is typically performed above the beta transus (temperature at which α+β to β phase transformation occurs) to obtain a goal microstructure of lamellar α+β in coarse prior 3 grains of 200-300 µm (Fig. 2c). Conversion involves production of semi-products (e.g. blooms, billets, plates) with a concurrent breakdown of lamellar microstructure into equiaxed α+β of 3-5 µm grain size (Figure 2d). Equiaxed microstructure possesses excellent hot workability and enables processes such as superplastic forming. Ingot breakdown and conversion are expensive steps and add significant lead-time (many months) to produce high-quality titanium mill products. Finish processing is performed either above or below the β transus depending on the desired microstructure in the final component. Improvements in titanium processing are highly desirable to enhance affordability of titanium components and reduce lead-time. Small boron additions to Ti alloys have been found to provide significant benefits in terms of processibility and performance, both of which lead to dramatic improvements in affordability. In this paper, we introduce this new class of titanium alloys and describe unique formability benefits obtained via engineering microstructures.

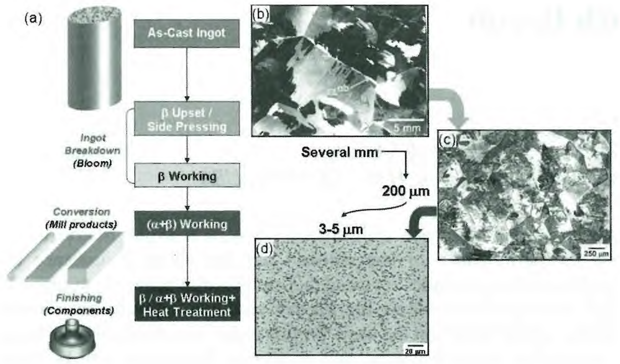


Figure 2. (a) Typical Ti alloy processing sequence and (b-d) corresponding microstructural changes. Micrograph (b) is courtesy of Dr. M. Glavicic.

2. Background

2.1 Ti-B Material System

Boron is completely soluble in the liquid phase of Ti but is essentially insoluble in the solid Ti phases (high temperature β or room temperature α)[4]. Negligible solid solubility of B in Ti eliminates the embrittlement problem commonly caused by other interstitial elements such as H, C, or O. The Ti-rich end of the binary Ti-B phase diagram [5] is shown in Figure 3. The B added to Ti precipitates in the form of intermetallic TiB phase for additions below 18.4 wt.% (50 at.%). TiB formation occurs via an eutectic reaction L⟶β+TiB with the binary eutectic composition of ~2 wt.% B. The TiB phase offers several unique advantages. The density of TiB is comparable to that of Ti but the stiffness is about five times that of Ti. Therefore, the TiB phase provides significant increases in strength and stiffness of Ti alloys without density increase. The crystal structure of TiB is orthorhombic and particles grow as short whiskers which are efficient strengtheners. TiB has excellent crystallographic compatibility with Ti providing atomically sharp interfaces and chemical compatibility. The coefficient of thermal expansion of TiB is comparable to Ti, which eliminates residual stresses at the interfaces. Ti-B materials can be considered as boron-modified Ti alloys at B levels below the eutectic limit (1.55 wt.%B for the most widely used Ti alloy Ti-6Al-4V)[6] since the microstructures, processing, and property combinations are similar to alloys without boron. Above the eutectic limit, the TiB phase is in equilibrium with liquid and rapid growth occurs leading to the formation of coarse primary TiB particles. Although, higher volume fraction of TiB significantly increases stiffness, strength, and wear resistance, the fracture behavior changes from ductile to brittle with increase in B level and results in significant debit in damage tolerance. The microstructures and properties of hypereutectic Ti-B compositions are best classified as discontinuously reinforced titanium metal-matrix composites. A value of 7% tensile elongation is often required by structural designers for fracture-critical applications. Therefore, Ti-B alloys with low-to-modest B concentrations (<1 wt.%) are relevant to aerospace applications and we focus on these alloys in this paper.

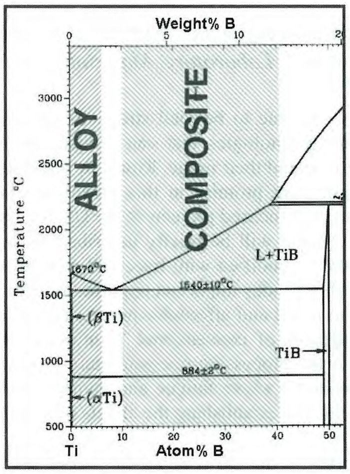
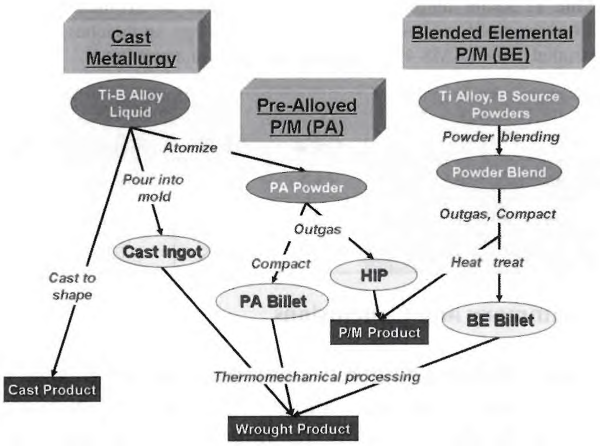


Figure 3. Titanium-rich section of the binary Ti-B phase diagram (from Reference 5).

2.2 Ti-B Alloy Processing

Ti-B alloys can be produced using traditional processing techniques including liquid metallurgy and powder metallurgy. Various Ti-B alloy processing routes and product forms are illustrated in Figure 4. In the conventional cast metallurgy approach, a boron source (TiB_2, elemental B, AlB_{12}, or a boron-containing master alloy) is added to Ti alloy charge mix, which completely dissolves and forms a Ti-B alloy melt. Additional Ti is added to compensate for the Ti scavenged from the alloy to transform the B source to TiB. The liquid Ti-B melt can be directly poured into a shaped mold using conventional casting techniques (e.g. investment casting) to produce Ti-B alloy casting or into an ingot mold to produce a Ti-B alloy cast ingot. The TiB phase precipitates during solidification via the eutectic reaction in the cast product. The cast ingot can be subjected to any conventional metalworking process such as forging, rolling, or extrusion to produce a wrought product.

Alternatively, the Ti-B alloy melt can be subjected to rapid solidification to produce pre-alloyed (PA) Ti-B powder using conventional powder making processes (e.g. inert gas atomization). The TiB phase forms in the solid state, and is uniformly distributed in each powder particle. PA powder can be outgassed (to remove an volatile impurities) and compacted using techniques sucl as hot isostatic pressing (HIP) commonly used for T alloys to produce near-net shape products. PA powde can also be compacted to billet preforms and subjected t conventional thermo-mechanical processing t manufacture wrought products. Isotropic properties al obtained when TiB whiskers are randomly oriented bi intentional alignment of the TiB through processes suc as extrusion or rolling can further increase the properti along the direction of TiB. The PA approach has t advantage of producing finer length scale microstructu- features due to shorter times for growth during raj solidification. In addition, the PA approach also offers 1 advantage of producing supersaturated boron due to non-equilibrium cooling conditions. The supersaturated boron can be precipitated in a controlled fashion via subsequent thermal exposure in the solid state to form nanometer-sized TiB precipitates that may provide additional strengthening and improve isotropy. Typical microstructures of Ti-6Al-4V (Ti-64) containing 1%B produced via cast and PA approach are compared in Figure 5. Both cast and PA approaches, however, are limited to hypoeutectic compositions as coarse primary TiB particles form in hypereutectic compositions.



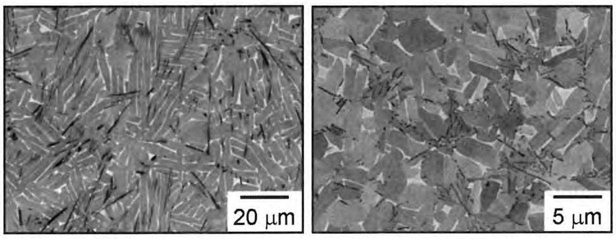


Figure 5. Backscattered electron images of Ti-6A1-4V-1B produced via cast approach (left) and pre-alloyed powder compaction approach (right). The dark phase is TiB, the bright phase is (3 and the gray background is a.

Ti-B products can also be manufactured using a blended-elemental (BE) powder metallurgy process which is conducted completely in the solid state (Figure 4). In the BE process, powders of Ti alloy and boron source are intermixed using an appropriate blending process (wet/dry). The powder blend is outgassed and consolidated to prepare a compact. The BE compact is then subjected to a reaction heat treatment to convert the boron source into TiB. Like the PA process, the BE process can also be used to produce either near-net shapes via compaction or net shapes via compaction plus metalworking. The BE approach offers the ability to introduce higher amounts of TiB without the formation of coarse primary TiB since processing is conducted completely in the solid state and is well suited for producing Ti-B composites. The BE process has been successfully used to produce several commercial products (e.g. automobile engine valves[7]). However, the BE approach results in coarser microstructural features than other approaches due to the high temperatures and long times required for TiB conversion and limited options to control this reaction.

3. Affordable Titanium Alloys

3.1 Grain Refinement

Solidification is a dominant processing route for metallic materials, and grain refinement is of significant industrial importance. Fine grain size improves many mechanical properties such as strength, ductility, and damage tolerance, and enhances subsequent mechanical working response. Addition of inoculants to many molten metal alloys (e.g. trace B to Al alloys) is the most commonly used commercial practice to achieve grain refinement but no such grain refinement mechanism is used commercially for Ti alloys. A systematic study evaluating the effect of trace boron addition to Ti alloys on the grain refinement was performed[8] and the results are summarized in Figure 6. Macrographs recorded on transverse sections of Ti-64 and Ti-64-0.06B ingots are shown in Figure 6a and 6b, which illustrate the dramatic grain refinement produced by the trace boron addition. The variation of grain size of Ti-64 and Ti-6242S alloys with boron concentration is shown in Figure 6c. Addition of 0.1% boron refines the Ti-64 average grain size from 1700 µm to 200 µm and the Ti-62425 average grain size from 550 µm to 50 µm. The grain size vs. boron concentration curves possess a knee in the range 0.06-0.1%B, which indicates that there exists a critical level of boron required for obtaining dramatic grain refinement beyond which only a small additional reduction in grain size is obtained.

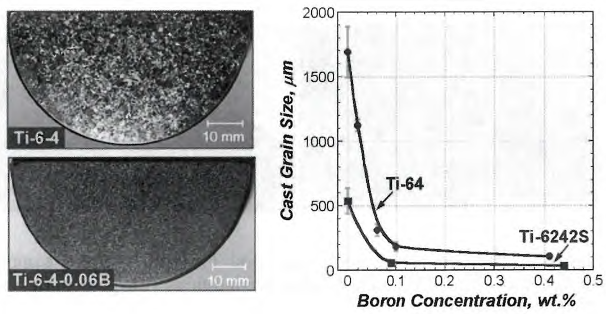


Figure 6. Grain refinement via trace boron addition: macrographs of Ti-64 castings (a) without boron and (b) with trace boron, and (c) variation of cast grain size with boron concentration in Ti-64 and Ti-6242S.

Trace B addition also reduces the thickness of brittle grain boundary a phase (Figure 7), which improves the workability. In addition, TiB forms a necklace structure at the lowest B levels, which helps in restricting the grain growth during subsequent heat treatment/hot forming operations. More uniform distribution of TiB is obtained at higher B concentrations. The refined microstructure and improved properties of cast Ti-B alloys may enable replacement of more expensive machined components from cast and wrought product with more affordable cast-to-shape components.

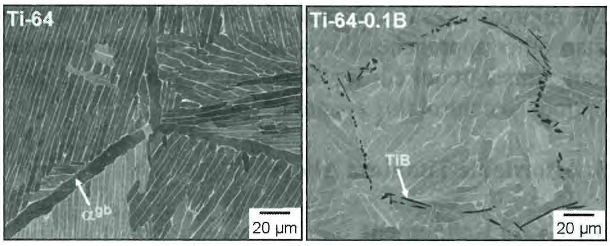


Figure 7. Backscattered electron images of cast Ti-64 (left) and Ti-640.1B (right).

3.2 Processibility Enhancement

Grain refinement via trace boron addition may provide ability to reduce/eliminate thermo-mechanical processing steps necessary to produce high-quality products. For example, Figure 8 illustrates the influence of boron addition on the rolling response of conventional and boron-modified Ti-64. Both the alloys were produced by the same casting method and subjected to rolling under identical conditions. The alloy without boron exhibited poor workability manifested in the form of severe edge and surface cracks (indicated with arrows in Figure 8) that are attributed to coarse grain size. The alloy containing trace boron, on the other hand, could be successfully rolled without any cracks and the rolled product exhibited good surface finish. Similar observations have been made in forging and extrusion processes. Therefore, boron addition offers the advantage of eliminating expensive and time consuming ingot breakdown steps conventionally practiced to improve the workability of cast microstructure. The presence of TiB also restricts grain growth during hot working and facilitates retention of fine-grained microstructures even after processing at high temperatures.

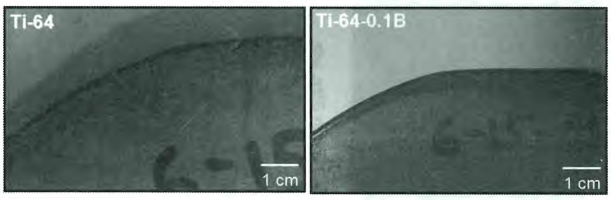


Figure 8. Photographs of Ti-64 (left) and Ti-64-0.1B (right) samples subjected to hot rolling under identical conditions (images courtesy of Dr. R. Srinivasan) .

3.3 Performance Improvement

The requirement for higher structural efficiency (a combination of stiffness and strength normalized by density) provides a significant motivation for the development of improved aerospace materials and processes. Structurally efficient materials provide a direct path for reducing mass via substitutions with thinner and lighter components, thus improving performance and affordability. A number of advanced aerospace missions, such as hypersonic flight and low-cost access to space, require dramatic reductions in flight mass. Materials with higher structural efficiency can provide enabling capabilities in these applications. Small boron addition to Ti alloys result in important improvements in strength and stiffness. For example, room temperature tensile properties of boron-modified Ti-64 produced via cast and PA approaches are presented in Table 1. Compared to Ti-64, addition of 1%B produces 20-30% improvements in modulus and strength with no debit in ductility. Alloy produced via the PA approach gives larger improvements than the cast approach due to refined microstructural features. These property improvements are found to be maintained at elevated temperatures, thus providing enhanced temperature capability.

Table 1. Room temperature tensile properties of extruded Ti-64-1B alloys produced via cast and powder metallurgy approaches. Data on extruded Ti-64 (AMS 4935 A-basis[9]) is used for comparison.

Alloy	*E* GPa	YS MPa	UTS Mpa	*e* %
Ti-64 Cast+Extrude	115	827	896	10
Ti-64-1B Cast+Extr.	134	1045	1138	10
Ti-64-1B PA Extr.	142	1079	1224	13

4. Summary and Conclusions

Trace boron addition refines the cast grain size of conventional titanium alloys by roughly an order magnitude. Refined grain size improves properties in the cast condition and significantly improves the hot workability. Opportunities exist to design thermo-mechanical processing sequences with minimal processing steps to produce high-quality titanium components. Boron addition of the order of 1% improves strength and stiffness by 20-30% while maintaining good ductility. The new class of Ti-B alloys offers significant potential for affordable aerospace applications via reduction in processing costs and lead-time, and enhanced performance.

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