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(54) Title: METHOD FOR MANUFACTURING TITANIUM ALLOY WIRE WITH ENHANCED PROPERTIES

(57) Abstract: A method for producing reinforced titanium alloy wire, comprising forming a billet of titanium alloy with grains of a precipitated discontinuous reinforcement material such as TiB and/or TiC. The billet may be formed by the hot consolidation of a titanium alloy powder formed by gas atomization. The billet is then hot formed to reduce it to rod or coil form. The rod or coil is then subjected to successive cold drawing operations to form a reinforced titanium alloy wire of reduced diameter. The cold drawing includes periodic annealing operations under low oxygen conditions to relieve work hardening and to recrystallize the reinforcement material grains to reduce the size thereof.



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METHOD FOR MANUFACTURING TITANIUM ALLOY WIRE WITH ENHANCED PROPERTIES

Field of the Invention

The present invention relates to a method of manufacturing titanium alloy wire and, more particularly, to such a method wherein precipitated discontinuous particulates of a reinforcement material such as TiB and/or TiC are added to the alloy and it is processed in accordance with a new and improved method wherein the reinforcement thereof by the particulates is enhanced.

Background of the Invention

Processes have been reported in the literature in which a common alloy of titanium, Ti-6Al-4V, has been reinforced and enhanced by the addition of TiB and/or TiC particulates. This is significant in that the Ti-6Al-4V alloy is utilized extensively in aerospace applications and is one of the most affordable. Enhancements that enable the extension of the useful application range of such alloys without significant cost impact are of great interest to the aerospace design community. In the reported processes, a Ti-6Al-4V casting was produced with TiB and/or TiC additions being added to the melt before casting. These additions dissolve in the melt and recrystallize during cooling to form discontinuous reinforcement in a variety of sizes. Articles compacted by hot isostatic pressing (HIP) and extrusion have demonstrated improved tensile strength and tensile modulus depending on the concentrations of TiB and/or TiC additions.

The results indicate that improvements in properties are related to the amount of discontinuous reinforcement created and to the size of the resulting reinforcement crystals. That is, it is desirable to have the reinforcement content as high as 40% by volume and the reinforcement size to be in the ultra fine size range. In the known processes, however, reinforcement content above a few percent is predominately in the largest size fraction with wide variability in size distribution and the shift to larger sized reinforcement is exaggerated as the reinforcement content increases toward the most desirable levels between 20 to 40% by volume. This is the result of large grains scavenging smaller grains during the casting or

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fabrication process and is apparently inherent in such processes. This limitation seriously inhibits the full capability of the discontinuously reinforced titanium potential.

The new and improved method of the present invention is not subject to these disadvantages and possesses advantages not possible with the use of previously used or known methods.

Summary of the Invention

The method of the present invention is directed to the manufacturing of titanium alloy wire suitable for application to wire/fiber composites, generally comprising the steps of forming the desired alloy via casting a billet or gas atomization; hot forging to create a uniform chemistry and microstructure; conforming to rod or coil, e.g., of about 0.2 inches in diameter; and cold drawing to wire, e.g., of about .005 inches in diameter.

More specifically, a preferred method comprises the formation of titanium alloy powder by gas atomization from a boron rich melt; consolidating the powder metal to bar form using hot isostatic pressing (HIP) with a pressure of about 5,000 to 45,000 psi, e.g., 15,000 psi, and a temperature of about 1,650°F to 1,750°F until full consolidation, yet remaining below the beta transus to avoid grain growth and grain boundary segregation; hot reduction at approximately 1500°F to 2100°F, e.g., 1,750°F, to reduce the bar to rod or coil form and perform the initial break-up of the larger TiB grains; and cold drawing and annealing at approximately a 10 to 20 percent reduction per pass to avoid cracking. In accordance with the method of the present invention, an increased frequency of annealing steps under very low oxygen conditions serves to relieve work hardening and also recrystallizes the TiB grains to a refined size with alignment with the wire axis. This new and improved method enables the fabrication of fine titanium alloy wire with simultaneous achievement of high TiB reinforcement content and small reinforcement grain size. Other reinforcement materials may be used such as TiC, alone or in combination with TiB.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The method of the present invention has been developed to achieve predominately fine grained reinforcement even at high reinforcement content through the combination of precipitation of reinforcement and a new and improved wire fabrication method. Typical fine wire processing practice suitable for application to wire/fiber composites, such as described in

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U.S. Patent No. 5,763,079, consists of four principal operations, namely, formation of the desired alloy via casting a billet, hot forging to create a uniform chemistry and microstructure, hot forming to rod (or coil) of about 0.2 inches in diameter, and cold drawing to wire of about .005 inches in diameter. Intermediate annealing operations are necessary during the cold
5 drawing to relieve residual stresses and restore ductility for further drawing. This basic wire forming process is designed to achieve area reduction through hot forming, hot extrusion and finally cold drawing in the fewest operations and the fewest breaks that would affect continuous lengths.

10 In accordance with the present invention, it has been discovered that the wire drawing process can be designed or modified to control microstructural evolution in addition to the base purpose of area reduction. The wire drawing method of the present invention can achieve improved microstructures in difficult alloys that cannot be achieved by any other known method, and was developed for the purpose of producing a discontinuously reinforced Ti-6Al-4V alloy with the simultaneous achievement of high TiB content and small reinforcement grain
15 size.

The present wire forming method can start with a casting of Ti-6Al-4V alloy from a Boron rich melt. The TiB will precipitate during cooling, but the cooling rate will allow for larger TiB grain growth which is undesirable. In order to start with the best microstructure, a powder metal formed by gas atomization from a Boron rich melt preferably is used rather than
20 a casting. The powder forming process employs more rapid cooling than casting and is less likely to produce large TiB grains. In this method, a compositionally uniform billet is prepared using powder metallurgy techniques to avoid the grain growth and potential for chemical segregation inherent in the casting process. The metal alloy powder produced from Boron rich Ti-6Al-4V alloy is first hot formed into a bar compatible in size with the available industrial
25 wire forming equipment. The bar is hot rolled into rod or coil with a diameter of about 0.2 inches, and the rod or coil is then transferred to the cold drawing operations.

It has been discovered that selection of correct cold drawing processing conditions results in ductile small diameter fine wire and a successful evolution of the desired wire microstructure, that is, high concentrations and fine grains. Execution of this improved process
30 requires consideration of critical processing conditions in each operation. Cold drawing area reduction must be sufficient to cold work the small diameter rods to the core on each pass in order to maintain micro-structural uniformity throughout the cross section. The reduction in area must not be excessive, however, to avoid fracture, microcracking or void formation within

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the rod or coil as it is reduced in diameter. The presence of the large TiB grains in the initial stages of cold drawing make the material susceptible to microcracking and void formation in the region of the large TiB grains. This balance between area reduction and avoidance of microcracking and void formation is more difficult in the beginning of the reduction sequence
5 when the largest TiB grains are present, and the processing window expands as the TiB grain size is reduced.

The cold drawing process of the present invention serves to break up the large TiB grains without deleterious microcracking or void formation. It has been discovered that the addition of frequent annealing steps to relieve work hardening will also recrystallize the TiB
10 grains to a refined size with alignment with the wire axis. Annealing steps have been utilized in the known wire drawing process, but less frequently and for shorter periods of time. The increased frequency of anneals in accordance with the present invention increases the requirement for annealing under very low oxygen conditions to avoid excessive surface material loss due to oxygen contamination and oxygen interstitial pick up by the wire
15 metallurgy that may interfere with the TiB refinement process. Accordingly, the present method enables the fabrication of fine titanium alloy wire with simultaneous achievement of high reinforcement content and small reinforcement grain size.

In accordance with a preferred embodiment of the method of the present invention, an acceptable alloy powder is gas atomized spherical powder with a composition of Ti-6Al-4V-
20 1.7B in a size range of minus 35 mesh to plus 270 mesh. An acceptable interstitial content was found to be oxygen less than 1500 ppm. This quality powder has been used to fabricate composite panels and is known to yield uniform chemistry and microstructure. Consolidation of the powder metal to bar form is based on methods found successful for composite panels. For example, it has been determined that non-contaminating consolidation tooling is needed,
25 such as vacuum degassed mild steel or conventional titanium alloys. Consolidation to a bar is achieved using hot isostatic pressing (HIP) with a pressure of approximately 5000 psi to 45,000 psi, e.g., 15,000 psi, and a temperature of about 1650°F to 1750°F. These conditions serve to achieve full consolidation and yet remain safely below the beta transus to avoid grain growth and grain boundary segregation. The hot reduction operation at about 1500°F to
30 2100°F, e.g., 1750°F, serves to reduce the bar to coil or rod form and performs the initial breakup to the larger TiB grains. It has been determined that about 50:1 hot reduction in section area is effective to breakup of the primary large TiB grains. The subsequent cold drawing must impart sufficient cold work through the thickness of the rod or coil, and the

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annealing must relieve the work hardening without grain growth. It has been determined that about a 10 percent reduction per pass is necessary to assure sufficient uniformity of cold working and avoid microcracking and void formation during the initial cold drawing steps from the nominal 0.2 inch diameter condition. Reductions in area can increase to about 15 percent per pass by the mid-point in the sectional area reduction process, and about 20 percent area reductions are possible by the end of the area reduction process. Annealing at about 1200°F to 2000°F, e.g., 1750°F for about 1 hour in inert gas with forced inert gas cooling is sufficient to remove work hardening, recrystallize the TiB and avoid grain growth. Annealing is performed at intervals corresponding to an accumulated reduction in section area of about 50 percent.

The above-described method of the present invention produces Ti-6Al-4V alloy with fine grained TiB reinforcement in concentrations ranging from 1 to 50 percent by volume with reinforcement alignment along the wire axis. It has been found that this process is effective with a wide variety of titanium alloys, such as Ti-6Al-2Sn-4Zr-2Mo alloy, Ti-6Al-4Sn-4Zr-1Nb-1Mo-0.2Si alloy, Ti-3Al-2.5V alloy, Ti-10V-2Fe-3Al alloy, Ti-5Al-2.5 Sn alloy and Ti-8Al-1Mo-1V alloy. Also, it is effective with other precipitated discontinuous reinforcements such as TiC, or mixtures of TiB and TiC. The method may utilize a billet cast from a Boron rich melt, but the inherent risks of microcracking and void formation would be greater owing to the larger TiB grain growth that results from a slow cooled casting. The extremely high area reductions inherent in the wire forming process combined with properly controlled reduction and annealing conditions in the present method produces high performance titanium alloy wire that cannot be produced by any other known metallurgical process.

While the invention has been described in connection with what is presently considered to be the most practical and preferred embodiment, it is to be understood that the invention is not to be limited to the disclosed embodiment, but on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims.

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WHAT IS CLAIMED IS:

- 1 1. |A method for producing reinforced titanium alloy wire, comprising:
2 forming a billet of titanium alloy with grains of a precipitated discontinuous
3 reinforcement material;
4 hot forming the billet to reduce it to rod or coil form; and
5 cold drawing the rod or coil in successive operations to wire of reduced
6 diameter, said cold drawing including the periodic annealing of the wire under low
7 oxygen conditions to relieve work hardening and to recrystallize the reinforcement
8 material grains to reduce the size thereof.
- 1 2. |The method of claim 1 wherein said billet is hot forged to create a uniform
2 chemistry and microstructure before it is hot formed.
- 1 3. |The method of claim 1 wherein said reinforcement material is TiB.
- 1 4. |The method of claim 3 wherein said billet is cast from a Boron rich melt.
- 1 5. |The method of claim 3 wherein said billet is formed by consolidating titanium
2 alloy powder formed by gas atomization from a Boron rich melt.
- 1 6. |The method of claim 5 wherein said powder is gas atomized powder with a
2 composition of Ti-6Al-4V-1.7B in a size range of minus 35 mesh to plus 270 mesh, with an
3 interstitial content of oxygen less than 1500 ppm.
- 1 7. |The method of claim 1 wherein said reinforcement material is TiC.
- 1 8. |The method of claim 1 wherein said reinforcement material is TiB and TiC.
- 1 9. |The method of claim 5 wherein said consolidating is by hot isostatic pressing at
2 a pressure of approximately 15,000 psi and a temperature of approximately 1650°F to 1750°F.

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1 10. |The method of claim 1 wherein said titanium alloy is Ti-6Al-4V.

1 11. |The method of claim 1 wherein said titanium alloy is Ti-6Al-2Sn-4Zr-2Mo.

1 12. |The method of claim 1 wherein said hot forming is at a temperature of
2 approximately 1750°F.

1 13. |The method of claim 12 wherein said hot forming results in about a 50:1 hot
2 reduction in section area to break up and reduce the size of the reinforcement material grains.

1 14. |The method of claim 1 wherein said cold drawing is performed periodically to
2 reduce the size of the wire at a rate of approximately 10 percent for each drawing operation
3 during the first half of the desired diameter reduction.

1 15. |The method of claim 14 wherein the rate of reduction is increased to
2 approximately 15 percent at the midpoint of diameter reduction and to approximately 20
3 percent near the end of the diameter reduction.

1 16. |The method of claim 1 wherein said annealing is performed at intervals
2 corresponding to an accumulated reduction of wire diameter of about 50 percent for about 1
3 hour in inert gas with forced inert gas cooling.

1 17. |A method for producing reinforced titanium alloy wire, comprising:
2 forming a powder of titanium alloy by gas atomization from a Boron rich melt;
3 consolidating the titanium alloy powder under heat and pressure into a billet
4 having grains of precipitated discontinuous TiB reinforcement;
5 hot forming the billet to reduce it to rod or coil form and to break up and reduce
6 the size of the TiB grains;
7 cold drawing the rod or coil in successive operations to wire of reduced
8 diameter, said cold drawing including the periodic annealing of the wire under low oxygen
9 conditions to relieve work hardening and to recrystallize the TiB grains to reduce the size
10 thereof.

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1 18. |The method of claim 17 wherein said powder is gas atomized powder with a
2 composition of Ti-6Al-4V-1.7B in a size range of minus 35 mesh to plus 270 mesh, with an
3 interstitial content of oxygen less than 1500 ppm.

1 19. |The method of claim 17 wherein said titanium alloy is Ti-6Al-4V.

1 20. |The method of claim 17 wherein said titanium alloy is Ti-6Al-2Sn-4Zr-2Mo.

1 21. |The method of claim 17 wherein said consolidating is by hot isostatic pressing
2 at a pressure of approximately 15,000 psi and a temperature of approximately 1650°F to
3 1750°F.

1 22. |The method of claim 17 wherein said hot forming is at a temperature of
2 approximately 1750°F.

1 23. |The method of claim 22 wherein said hot forming results in about a 50:1 hot
2 reduction in section area to break up and reduce the size of the reinforcement material grains.

1 24. |The method of claim 17 wherein said cold drawing is performed periodically to
2 reduce the size of the wire at a rate of approximately 10 percent for each drawing operation
3 during the first half of the desired diameter reduction.

1 25. |The method of claim 24 wherein the rate of reduction is increased to
2 approximately 15 percent at the midpoint of diameter reduction and to approximately 20
3 percent near the end of the diameter reduction.

1 26. |The method of claim 17 wherein said annealing is performed at intervals
2 corresponding to an accumulated reduction of wire diameter of about 50 percent for about 1
3 hour in inert gas with forced inert gas cooling.