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

VERFAHREN ZUR HERSTELLUNG VON TITANLEGIERUNGSDRAHT MIT VERBESSERTEN
EIGENSCHAFTEN

PROCEDE DE FABRICATION DE FIL EN ALLIAGE DE TITANE PRESENTANT DES PROPRIETES
AMELIOREES

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Description

Field of the Invention

[0001] 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 TiB reinforcement material, possibly also 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

[0002] [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 (see US-A-4 731 115). 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.

[0003] 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 fabrication process and is apparently inherent in such processes. This limitation seriously inhibits the full capability of the discontinuously reinforced titanium potential.

[0004] 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.

[0005] The document US-A-5 141 566 discloses a method for producing a titanium alloy wire.

Summary of the Invention

[0006] The method of the present invention, which is defined in claim 1, 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 5.08 mm (0.2 inches) in diameter; and cold drawing to wire, e.g., of about 0.127 mm (.005 inches) in diameter.

[0007] 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 34.5 MPa to 310.3 MPa (5,000 to 45,000 psi), e.g., 103.4 MPa (15,000 psi), and a temperature of 898.9°C to 954.4°C (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 815.5°C to 1148.9°C (1500°F to 2100°F), e.g., 954.4°C (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

[0008] 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 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 5.08 mm (0.2 inches) in diameter, and cold drawing to wire of about .005 inches in diameter. Intermediate annealing operations are necessary during the cold 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.

[0009] 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 size.

[0010] 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 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 wire forming equipment. The bar is hot rolled into rod or coil with a diameter of about 5.08 mm (0.2 inches), and the rod or coil is then transferred to the cold drawing operations.

[0011] 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 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 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 when the largest TiB grains are present, and the processing window expands as the TiB grain size is reduced.

[0012] 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 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 pe-

riods 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 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.

[0013] 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-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, 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 34.5 MPa to 310.3 MPa (5000 psi to 45,000 psi), e.g., 103.4 MPa (15,000 psi), and a temperature of 898.9°C to 954.4°C (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 815.5°C to 1148.9°C (1500°F to 2100°F), e.g., 954.4°C (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 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 5.08 mm (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 648.9°C to 1093.3°C (1200°F to 2000°F), e.g., 954.4°C (1750°F) for 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 50 percent.

[0014] 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. 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.

Claims

1. A method for producing reinforced titanium alloy wire, comprising:
 - forming a powder of titanium alloy by gas atomization from a Boron rich melt;
 - consolidating the titanium alloy powder under heat and pressure into a billet having grains of precipitated discontinuous TiB reinforcement, wherein said consolidating is by hot isostatic pressing at a pressure of 34.5 MPa to 310.3 MPa (5,000 to 45,000 psi) and a temperature of 898.9°C to 954.4°C (1650°F to 1750°F);
 - hot forming the billet at a temperature of 815.5°C to 1148.9°C (1500°F to 2100°F), producing a 50:1 hot reduction in section area, to reduce the billet to rod or coil form and to break up and reduce the size of the TiB grains;
 - cold drawing the rod or coil in successive operations to wire of reduced diameter;
 - annealing the wire periodically at intervals corresponding to an accumulated reduction of section area of 50% for one hour in inert gas with forced inert gas cooling, to relieve work hardening and to recrystallize the TiB grains to reduce the size thereof.
2. The method of claim 1, wherein said powder is gas atomized powder with a composition of Ti-6Al-4V-1.7B in a size range of minus 35 mesh to plus 270 mesh, with an interstitial content of oxygen less than 1500 ppm.
3. The method of Claim 1, wherein said hot isostatic pressing is at a pressure of 103.4 MPa (15,000 psi).
4. The method of claim 1 wherein said hot forming is at a temperature of 954.4°C (1750°F).
5. The method of claim 1 wherein said cold drawing is

performed periodically to reduce the size of the wire at a rate of approximately 10 percent for each drawing operation during the first half of accumulated reduction of the desired diameter reduction.

6. The method of claim 5 wherein the rate of diameter reduction is increased to 15 percent for each drawing operation at the midpoint of accumulated reduction of the diameter reduction and to 20 percent prior to the end of the diameter reduction.

Patentansprüche

1. Verfahren zur Herstellung von verstärktem Titanlegierungsdraht, umfassend:
 - Bilden eines Pulvers aus Titanlegierung durch Gasatomisierung aus einer borreichen Schmelze,
 - Konsolidieren des Titanlegierungspulvers unter Hitze und Druck zu einem Knüppel, der Körner aus ausgefällter diskontinuierlicher TiB-Verstärkung aufweist, wobei das Konsolidieren durch isostatisches Heißpressen bei einem Druck von 34,5 MPa bis 310,3 MPa (5.000 bis 45.000 psi) und bei einer Temperatur von 898,9 °C bis 954,4 °C (1650 °F bis 1750 °F) erfolgt,
 - Heißformen des Knüppels bei einer Temperatur von 815,5 °C bis 1148,9 °C (1500 °F bis 2100 °F), was zu einer Abschnittsbereich-Heißreduktion von 50:1 führt, um den Knüppel zu einer Stab- oder Spulenform zu reduzieren und die Größe der TiB-Körner aufzubrechen und zu reduzieren,
 - Kaltziehen des Stabs oder der Spule in aufeinanderfolgenden Arbeitsgängen zu Draht von reduziertem Durchmesser,
 - periodisches Ausglühen des Drahts in Zeitabständen entsprechend einer akkumulierten Abschnittsbereichreduktion von 50 % für eine Stunde in inertem Gas unter Zwangskühlung mit inertem Gas, um die Kaltumformung zu erleichtern und die TiB-Körner umzukristallisieren, um die Größe derselben zu reduzieren.
2. Verfahren nach Anspruch 1, wobei das Pulver gasatomisiertes Pulver mit einer Zusammensetzung von Ti-6Al-4V-1.7B in einem Größenbereich von minus 35 Maschen bis plus 270 Maschen mit einem interstitiellen Sauerstoffgehalt von weniger als 1500 ppm ist.
3. Verfahren nach Anspruch 1, wobei das isostatische Heißpressen bei einem Druck von 103,4 MPa (15.000 psi) erfolgt.
4. Verfahren nach Anspruch 1, wobei das Heißformen

bei einer Temperatur von 954,4 °C (1750 °F) erfolgt.

5. Verfahren nach Anspruch 1, wobei das Kaltziehen periodisch durchgeführt wird, um die Größe des Drahts mit einer Rate von etwa 10 Prozent bei jedem Zieharbeitgang während der ersten Hälfte akkumulierter Reduktion der erwünschten Durchmesserreduktion zu reduzieren.
6. Verfahren nach Anspruch 5, wobei die Rate der Durchmesserreduktion bei jedem Zieharbeitgang bei der Hälfte der akkumulierten Reduktion der Durchmesserreduktion auf 15 Prozent und vor dem Ende der Durchmesserreduktion auf 20 Prozent erhöht wird.

Revendications

1. Procédé de fabrication de fil en alliage de titane renforcé, comprenant :
 - formation d'une poudre en alliage de titane par atomisation de gaz à partir d'une fonte riche en bore,
 - consolidation de la poudre en alliage de titane, sous chaleur et pression, en une billette présentant des grains de renforcement de TiB précipité discontinu, ladite consolidation étant réalisée par compaction isostatique à chaud, à une pression comprise entre 34,5 MPa et 310,3 MPa (5.000 et 45.000 psi) et à une température allant de 898,9 °C à 954,4 °C (de 1650 °F à 1750 °F), formage à chaud de ladite billette à une température comprise entre 815,5 °C et 1148,9 °C (1500 °F et 2100 °F) entraînant une réduction à chaud en zone de section de 50 : 1, afin de réduire ladite billette en une forme de barre ou de bobine et afin de rompre et de réduire la taille des grains de TiB,
 - étirage à froid de ladite barre ou bobine dans des opérations successives de manière à obtenir un fil de diamètre réduit,
 - recuit périodique dudit fil à des intervalles correspondant à une réduction accumulée de zone de section de 50 %, pour une heure dans du gaz inerte, avec refroidissement forcé à gaz inerte, afin de faciliter l'écrouissage et de recristalliser les grains de TiB pour réduire la taille de ceux-ci.
2. Procédé selon la revendication 1, dans lequel ladite poudre est une poudre atomisée au gaz ayant une composition de Ti-6Al-4V-1.7B dans une gamme de dimensions de moins 35 mailles à plus 270 mailles, avec une teneur en oxygène interstitielle inférieure à 1500 ppm.
3. Procédé selon la revendication 1, dans lequel la

compaction isostatique à chaud est réalisée à une pression de 103,4 MPa (15.000 psi).

4. Procédé selon la revendication 1, dans lequel le formage à chaud est réalisé à une température de 954,4 °C (1750 °F).
5. Procédé selon la revendication 1, dans lequel ledit étirage à froid est réalisé périodiquement afin de réduire la dimension du fil, à un taux d'approximativement 10 % pour chaque opération d'étirage durant la première moitié de réduction accumulée de la réduction de diamètre souhaitée.
6. Procédé selon la revendication 5, dans lequel on augmente le taux de la réduction de diamètre, pour chaque opération d'étirage, à 15 % à mi-réduction accumulée de la réduction de diamètre et à 20 % avant la fin de la réduction de diamètre.

REFERENCES CITED IN THE DESCRIPTION

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