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(54) **METHOD OF PRODUCING TITANIUM COMPOSITE PARTS BY MEANS OF CASTING**

VERFAHREN ZUR HERSTELLUNG VON TITANVERBUNDWERKSTOFFTEILEN MITTELS
GIESSEN

PROCEDE D OBTENTION DE PIECES DE COMPOSITE DE TITANE PAR FUSION

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Description

OBJECT OF THE INVENTION

[0001] The method of the invention enables reinforced titanium composite parts, by means of casting, to be produced with a reduced production cost.

[0002] The method also allows us to produce reinforced titanium composite parts whose percentage of reinforcement can be controlled.

[0003] The reinforced titanium composite parts produced by this method are also the object of the invention.

BACKGROUND OF THE INVENTION

[0004] Titanium has many properties that make it an attractive material for high-performance applications, such as for instance one of the highest strength-weight ratios and its high resistance to corrosion due to the layer of oxide that forms on it.

[0005] However, despite the advantages offered by titanium alloys over other materials in such sectors as aeronautics, the search is continuing for new alloys and materials that offer a higher performance both from the standpoint of properties and of recycling and which may be used therefore in a wider range of applications. Specifically, the aeronautical companies are seeking cost-competitive, high-performance materials lighter than conventional titanium alloys and recyclable, which may improve performance and reduce consumption by means of reducing the weight of the aircraft.

[0006] Amongst the materials currently being investigated are titanium composites that make it possible to enhance some of the physical and mechanical properties in comparison with the non-reinforced starting material by means of reinforcing titanium alloys.

[0007] Over the last few decades this search has focused mainly on reinforcing titanium alloys with one-way continuous reinforcements, such as titanium composites reinforced with continuous silicon carbide (SiC) fibres.

[0008] In this respect, materials have been developed with an excellent performance in terms of reinforcement, but these materials have considerable limitations, such as:

- High production cost of the composite, as they are composed of a material with a reinforcement alien to the matrix introduced by means of a complex manufacturing process.
- They show chemical instability at the fibre-matrix interface, which affects the end performance of the material.
- They have a limitation of the improvement of the properties to the direction of reinforcement, as in the transverse direction to reinforcement they have properties even lower than non-reinforced alloys.

[0009] The latest studies have shown that the best way

of preventing chemical reaction at the fibre-matrix interface is by means of the natural formation of the reinforcement within the matrix by means of the "in-situ" precipitating of reinforcement. The advantage of in-situ reinforcement precipitation is the balance between this and the matrix, preventing the chemical instability that may be presented by the reinforcement-matrix interface. Another of the advantages of in-situ precipitation is that the reinforcement formed has no pre-defined direction, thereby endowing the material with isotropic properties.

[0010] Nonetheless, since the volumetric fraction and the composition of the reinforcement phase are hard to adjust, use may be made practically only of titanium borides and carbides, which improve the resistance, strength and friction of the resultant composite by means of the formation of TiB and TiC type precipitates

[0011] Although in-situ reinforcement precipitation may take place in the solid or liquid state of the matrix, titanium matrix composite has mainly been manufactured by means of the powder metallurgy process. This process has the disadvantage that it is necessary to machine the piece down to the final dimensions, which means that the cost of producing pieces by this method is high.

[0012] US patent 5897830 describes the production of titanium composite parts with titanium carbide and boride reinforcements, by means of industrial casting processes. For this purpose we melt an ingot of titanium composite containing reinforcement particles in a proportion similar to that required for the pieces to be produced, said reinforced ingot being obtained by means of powder metallurgy techniques.

[0013] This patent US 5897830, therefore, is centred on producing an ingot of titanium composite by means of powder metallurgy techniques.

[0014] The process described in this Patent US 5897830 has two drawbacks:

- It is necessary to make the whole consumable ingot by means of powder metallurgy, which, being an expensive process, increases the end cost of the parts obtained.
- The proportion of end reinforcement in the parts obtained by casting is predetermined by the percentage of reinforcement available in the ingot, which requires the manufacture of a specific ingot for each casting in accordance with the percentage reinforcement we want to obtain in the end parts.

DETAILED DESCRIPTION OF THE INVENTION

[0015] The present invention refers to a method that overcomes the aforementioned drawbacks, enabling reinforced composite parts, obtained by means of casting, to be produced at a low manufacturing cost and with a percentage reinforcement that is simple to control.

[0016] First of all, the present invention is based on obtaining a reinforcement material formed of titanium bo-

rides (TiB) and/or titanium carbides (TiC) distributed in a titanium matrix. In accordance with the method of the invention, the reinforcement material will be produced by means of a process based on the self-propagated high-temperature synthesis (SHS) reactions of strongly exothermic composites, as is the case of titanium carbides and titanium borides.

[0017] This process is based on the highly exothermic nature of the formation reactions of titanium carbides and titanium borides. This means that the formation of TiC from its constituent elements is highly favourable from the thermodynamic standpoint, the same as TiB, since, once the reaction is initiated, the temperature rises quickly due to the heat given off, so that it encourages and facilitates the formation of titanium borides or carbides. Due to the very high formation enthalpy both of titanium carbide and of titanium boride, the method that is proposed for producing them is simple, economic and perfectly applicable at an industrial scale.

[0018] This method makes it possible to produce a reinforcement material with a high proportion (30-70% by weight) of TiB and/or TiC, and, in addition, it presents a series of advantages over conventional powder metallurgy processes, such as for instance:

- The starting materials are titanium, carbon and boron powders.
- No sophisticated equipment is needed for its production, such as high-temperature furnaces, high-vacuum equipment, etc. The process takes place in a metal mould and a press.
- The external energy used in the process is minimal. The reaction is initiated on the surface with an isolated heat supply and it is propagated by means of the self-combustion of the actual material.
- It is an extremely fast process that lasts seconds, which provides high productivity.
- A pure product is obtained as the impurities are evaporated in the actual process.
- It is a safe, clean process, as it generates few residues and is not at all hazardous.

[0019] In an independent manufacturing process, a consumable ingot of titanium or conventional titanium alloy is produced, i.e. a ingot with no reinforcement particles and preferably a cp-Ti grade 1, cp-Ti grade 2, cp-Ti grade 3, cp-Ti grade 4, Ti-0.05Pd, Ti-6Al-4V, Ti-5Al-2.5Fe, Ti-5Al-2.5Sn, Ti-6Al-2Sn-4Zr-2Mo-0.1Si, Ti-5.8Al-4Sn-3.5Zr-0.5Mo-0.7Nb-0.35Si-0.06C, Ti₃Al, Ti-14Al-11Nb, Ti₂AlNb, γ TiAl, or Ti(22-23)Al-(25-26)Nb (at%) alloy.

[0020] The reinforcement material produced is then melted in an industrial casting process, together with the consumable ingot of titanium or conventional titanium alloy.

[0021] The reinforcement material is melted with the consumable ingot, without there being any physical or chemical union between them or, sometimes, the rein-

forcement material, either in a single piece or divided up, may be united with consumable ingot before melting using mechanical means, welding or any other method. It is also envisaged that holes or openings may be drilled or made in the surface of the ingot in which the reinforcement material is inserted, so that it may be distributed suitably.

[0022] Melting may be produced by means of the vacuum electric arc and/or vacuum induction melting method and the mould casting is carried out by means of a centrifuging or gravity filling process.

[0023] During the melting and mould filling in the industrial process, the reinforcement material that has been used along with the consumable ingot is diluted in the liquid titanium, so that end composite parts are produced with variable percentages of reinforcing TiB and/or TiC, which may achieve values ranging from 0% by weight and under 70% by weight.

[0024] In this way, by controlling the amount of TiB and/or TiC in the reinforcement material produced by means of the self-propagated high-temperature synthesis method, we can control the percentage of TiB and/or TiC reinforcement that we want to obtain in the end parts, thereby reducing the cost of having to produce a whole ingot of composite with the necessary percentage of reinforcement in accordance with the characteristics required for the end composite part.

[0025] With this method we obtain reinforced titanium melting parts that have a percentage of titanium boride and/or titanium carbide between 0% and 70% by weight, dispersed in titanium or titanium alloy, the castings being made from a consumable ingot of non-reinforced titanium or titanium alloy and a titanium composite reinforcement material, formed of titanium borides and/or carbides in a proportion of 30% or 70% by weight, dispersed in titanium or titanium alloy, produced by SHS techniques.

DESCRIPTION OF THE DRAWINGS

[0026] To supplement the description being given and in order to assist a clearer appreciation of the features of the invention, in accordance with a preferred example of practical embodiment of the same, a set of drawings is attached as an integral part of this description wherein there is represented, on an informative and non-restrictive basis, the following:

Figure 1.- It shows a micrograph (x1000) of the reinforcing material (Ti/TiB) produced by the SHS process. The reinforcement is TiB with a proportion of 60% by weight distributed in a pure Ti matrix.

Figure 2.- It shows a micrograph (x2000) of the end melting parts of titanium composite. The end TiB reinforcement distributed in the Ti6Al4V matrix is 2% by weight.

PREFERRED EMBODIMENT OF THE INVENTION

[0027] We will now go on to describe an example of manufacture in accordance with the object of the invention.

EXAMPLE

[0028] In this example we describe the production of reinforced titanium parts.

1. Production of a titanium composite reinforcement material.

[0029] Using the self-propagated high-temperature synthesis method we prepare a titanium composite reinforcement material, Ti/TiB (60% by weight). The process consists of mixing the powders, pressing the powders and self-propagated synthesis accompanied by compacting.

Mix:

[0030] The materials making up the mix are:

800 gr of Ti
65 gr of B

The mix is prepared in a dry medium, using tubular equipment with Al_2O_3 as the grinding medium for 12 hours.

Sample pressing:

[0031] The powder mix is densified using a 5t load.

Self-propagated synthesis + compaction:

[0032] For carrying out the synthesis we use a steel mould resistant to high pressures and temperatures. This mould consists of three parts: the mould base, the mould ventilation portion and the mould cover.

Base of the mould, where the sample to be reacted is placed.

Ventilation part of the mould, the part where we place the resistance with which the reaction is initiated. It consists of holes that permit the ventilation of the system. They are necessary so that the gas which is formed during the reaction can escape and thereby be able to produce a dense piece without pores.

[0033] Cover of the mould, it closes the whole system and is where the pressure is applied.

When the green piece has been prepared, it is inserted in the mould, this mould is then placed in a 100t press and the reaction + compaction is carried out.

[0034] Figure 1 is a micrograph (x1000) of the reinforcement material obtained by means of the self-propagated high temperature synthesis process described above. The reinforcement is TiB in a proportion of 60%

by weight distributed in a pure Ti matrix.

2. Use of a consumable ingot of Ti6Al4V alloy

5 [0035] A consumable ingot of Ti6Al4V alloy is used.

3. Simultaneous melting of the consumable ingot and the reinforcement material

10 [0036] A hole is made in the Ti6Al4V ingot and the reinforcement material obtained by means of the self-propagated high-temperature synthesis method is introduced into the hole.

[0037] The assemblage of reinforcement material (Ti/TiB 60% by weight) and the consumable ingot (Ti6Al4V) is melted by the vacuum induction melting method.

4. Casting of the melted composite and production of parts in their final shape and dimensions.

[0038] The lost-waxed process is the technique used for the manufacture of ceramic moulds where the melted composite is cast.

25 The casting in moulds is carried out by means of the centrifuged casting technique.

Figure 2 shows us the microstructure obtained in the end part.

Claims

1. Method for producing titanium composite parts, by means of casting, which comprises the following operational stages:

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- Obtaining a titanium composite reinforcement material by means of the self-propagated high-temperature synthesis method,
- Obtaining a consumable ingot of titanium or non-reinforced titanium alloy,
- Simultaneous melting of the reinforcement material and of the consumable ingot,
- Casting of the melted composite in the corresponding mould in order to produce the composite piece in its final shape and dimensions.

2. Method for producing titanium composite parts, by means of casting, according to claim 1, **characterised in that** the reinforcement material is a composite with titanium borides and/or carbides distributed in a titanium or titanium alloy matrix.

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3. Method for producing titanium composite parts, by means of casting, according to claim 1, **characterised in that** the titanium composite which constitutes the reinforcement material has between 30-70% by weight of titanium boride and/or carbide, dispersed

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in titanium or titanium alloy.

4. Method for producing titanium composite parts, by means of casting, according to claim 1, **characterised in that** the consumable ingot is of titanium or titanium alloy. 5
5. Method for producing titanium composite parts, by means of casting, according to claim 1, **characterised in that** the consumable ingot is a cp-Ti grade 1, cp-Ti grade 2, cp-Ti grade 3, cp-Ti grade 4, Ti-0.05Pd, Ti-6Al-4V, Ti-5Al-2.5Fe, Ti-5Al-2.5Se, Ti-6Al-2Sn-4Zr-2Mo-0.1Si, Ti-5.8Al-4Sn-3.5Zr-0.5Mo-0.7Nb-0.35Si-0.06C, Ti₃Al, Ti-14Al-11Nb, Ti₂AlNb, γ TiAl, or Ti(22-23)Al-(25-26)Nb(at%) alloy. 10 15
6. Method for producing titanium composite parts, by means of casting, according to claim 1, **characterised in that** the reinforcement material, which may be a single piece or divided up, and the consumable ingot are united prior to melting by a welding procedure. 20
7. Method for producing titanium composite parts, by means of casting, according to claim 1, **characterised in that** the reinforcement material, which may be a single piece or be divided up, and the consumable ingot are united prior to melting by mechanical means. 25 30
8. Method for producing titanium composite parts, by means of casting, according to claim 1, **characterised in that** the reinforcement material, which may be a single piece or be divided up, is inserted in one or more holes made in the consumable ingot. 35
9. Method for producing titanium composite parts, by means of casting, according to claim 1, **characterised in that** the melting is done by the vacuum electric arc and/or vacuum induction melting method. 40
10. Method for producing titanium composite parts, by means of casting, according to claim 1, **characterised in that** the casting in moulds is done by means of a centrifuging or gravity filling process. 45

Patentansprüche

1. Verfahren zum Herstellen von Teilen aus Titan-Verbundstoff mittels Gießen, das die folgenden Arbeitsschritte umfasst: 50
 - Gewinnen von Titan-Verbundstoff-Verstärkungsmaterial mittels des SHS-Verfahrens (self-propagated high-temperature synthesis method), 55
 - Gewinnen eines schmelzbaren Blocks aus Ti-

tan oder nicht verstärkter Titanlegierung,
 - gleichzeitiges Schmelzen des Verstärkungsmaterials und des schmelzbaren Blocks,
 - Gießen des geschmolzenen Verbundstoffs in die entsprechende Form, um das Verbundteil in seiner abschließenden Form und seinen abschließenden Abmessungen herzustellen.

2. Verfahren zum Herstellen von Teilen aus Titan-Verbundstoff mittels Gießen nach Anspruch 1, **dadurch gekennzeichnet, dass** das Verstärkungsmaterial ein Verbundstoff mit Titanboriden und/oder -karbiden ist, die in einer Titan- oder Titanlegierungs-Matrix verteilt sind.
3. Verfahren zum Herstellen von Teilen aus Titan-Verbundstoff mittels Gießen nach Anspruch 1, **dadurch gekennzeichnet, dass** der Titan-Verbundstoff, der das Verstärkungsmaterial bildet, zwischen 30-70 Gew.-% Titanborid und/oder -karbid enthält, das in Titan oder Titanlegierung dispergiert ist.
4. Verfahren zum Herstellen von Teilen aus Titan-Verbundstoff mittels Gießen nach Anspruch 1, **dadurch gekennzeichnet, dass** der schmelzbare Block aus Titan oder Titanlegierung besteht.
5. Verfahren zum Herstellen von Teilen aus Titan-Verbundstoff mittels Gießen nach Anspruch 1, **dadurch gekennzeichnet, dass** der schmelzbare Block eine cp-Ti-grade-1-, cp-Ti-grade-2-, cp-Ti-grade-3-, cp-Ti-grade-4-, Ti-0,05Pd-, Ti-6Al-4V-, Ti-5Al-2,5Fe-, Ti-5Al-2,5Se-, Ti-6Al-2Sn-4Zr-2Mo-0,1Si-, Ti-5,8Al-4Sn-3,5Zr-0,5Mo-0,7Nb-0,35Si-0,06C-, Ti₃Al-, Ti-14Al-11Nb-, Ti₂AlNb-, γ -TiAl- oder Ti(22-23)Al-(25-26)Nb(at%)-Legierung ist.
6. Verfahren zum Herstellen von Teilen aus Titan-Verbundstoff mittels Gießen nach Anspruch 1, **dadurch gekennzeichnet, dass** das Verstärkungsmaterial, das aus einem Stück bestehen oder geteilt sein kann, und der schmelzbare Block vor dem Schmelzen mit einem Schweißvorgang verbunden werden.
7. Verfahren zum Herstellen von Teilen aus Titan-Verbundstoff mittels Gießen nach Anspruch 1, **dadurch gekennzeichnet, dass** das Verstärkungsmaterial, das aus einem Stück bestehen oder geteilt sein kann, und der schmelzbare Block vor dem Schmelzen mit mechanischen Mitteln verbunden werden.
8. Verfahren zum Herstellen von Teilen aus Titan-Verbundstoff mittels Gießen nach Anspruch 1, **dadurch gekennzeichnet, dass** das Verstärkungsmaterial, das aus einem Stück bestehen oder geteilt sein kann, in ein Loch oder mehrere Löcher eingeführt wird, die in dem schmelzbaren Block vorhanden sind.

9. Verfahren zum Herstellen von Teilen aus Titan-Verbundstoff mittels Gießen nach Anspruch 1, **dadurch gekennzeichnet, dass** das Schmelzen mit dem Vakuumlichtbogenschmelz- und/oder dem Vakuuminduktionsschmelz-Verfahren durchgeführt wird.

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10. Verfahren zum Herstellen von Teilen aus Titan-Verbundstoff mittels Gießen nach Anspruch 1, **dadurch gekennzeichnet, dass** das Gießen in Formen mittels eines Zentrifugier- oder eines Gravitations-Füllverfahrens durchgeführt wird.

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Revendications

1. Procédé d'obtention de pièces composites à base de titane par moulage comprenant les étapes opérationnelles consistant à :

- se procurer un matériau de renfort composite à base de titane par la méthode de synthèse autopropagée à haute température,
- se procurer un lingot fusible en titane ou en un alliage de titane non renforcé,
- faire fondre simultanément le matériau de renfort et le lingot fusible,
- mouler le composite fondu dans un moule correspondant pour obtenir la pièce composite ayant sa forme et ses dimensions finales.

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2. Procédé d'obtention de pièces composites à base de titane par moulage conforme à la revendication 1, **caractérisé en ce que** le matériau de renfort est un matériau composite renfermant des borures et/ou des carbures de titane répartis dans une matrice en titane ou en alliage de titane.

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3. Procédé d'obtention de pièces composites à base de titane par moulage conforme à la revendication 1, **caractérisé en ce que** le matériau composite à base de titane qui constitue le matériau de renfort, renferme entre 30 et 70 % en poids de borure et/ou de carbure de titane réparti dans du titane ou dans un alliage de titane.

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4. Procédé d'obtention de pièces composites à base de titane par moulage conforme à la revendication 1, **caractérisé en ce que** le lingot fusible est un lingot en titane ou en un alliage de titane.

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5. Procédé d'obtention de pièces composites à base de titane par moulage conforme à la revendication 1, **caractérisé en ce que** le lingot fusible est en un titane commercialement pur de grade 1, en un titane commercialement pur de grade 2, en un titane commercialement pur de

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grade 3, en un titane commercialement pur de grade 4, ou en un alliage Ti-0,05Pd, Ti-6Al-4V, Ti-5Al-2,5Fe, Ti-5Al-2,5Se, Ti-6Al-2Sn-4Zr-Mo-O,1Si, Ti-5,8Al-4Sn-3,5Zr-0,5Mo-0,7Nb-0,35Si-0,06C, Ti₃Al, Ti-14Al-11Nb, Ti₂AlNb, γ TiAl, ou Ti(22-23)Al-(25-26)Nb (at%).

6. Procédé d'obtention de pièces composites à base de titane par moulage conforme à la revendication 1, **caractérisé en ce que** le matériau de renfort qui peut être une pièce unique ou divisée et le lingot fusible sont réunis avant la fusion par un procédé de soudage.

7. Procédé d'obtention de pièces composites à base de titane par moulage conforme à la revendication 1, **caractérisé en ce que** le matériau de renfort qui peut être une pièce unique ou divisée et le lingot fusible, sont réunis avant la fusion par des moyens mécaniques.

8. Procédé d'obtention de pièces composites à base de titane par moulage conforme à la revendication 1, **caractérisé en ce que** le matériau de renfort qui peut être une pièce unique ou divisée est inséré dans un ou plusieurs trous réalisés dans le lingot fusible.

9. Procédé d'obtention de pièces composites à base de titane par moulage conforme à la revendication 1, **caractérisé en ce que** la fusion est effectuée par un procédé de fusion à arc électrique sous vide et/ou par un procédé de fusion à induction sous vide.

10. Procédé d'obtention de pièces composites à base de titane par moulage conforme à la revendication 1, **caractérisé en ce que** le moulage dans les moules est effectué par un procédé de centrifugation ou de remplissage par gravité.

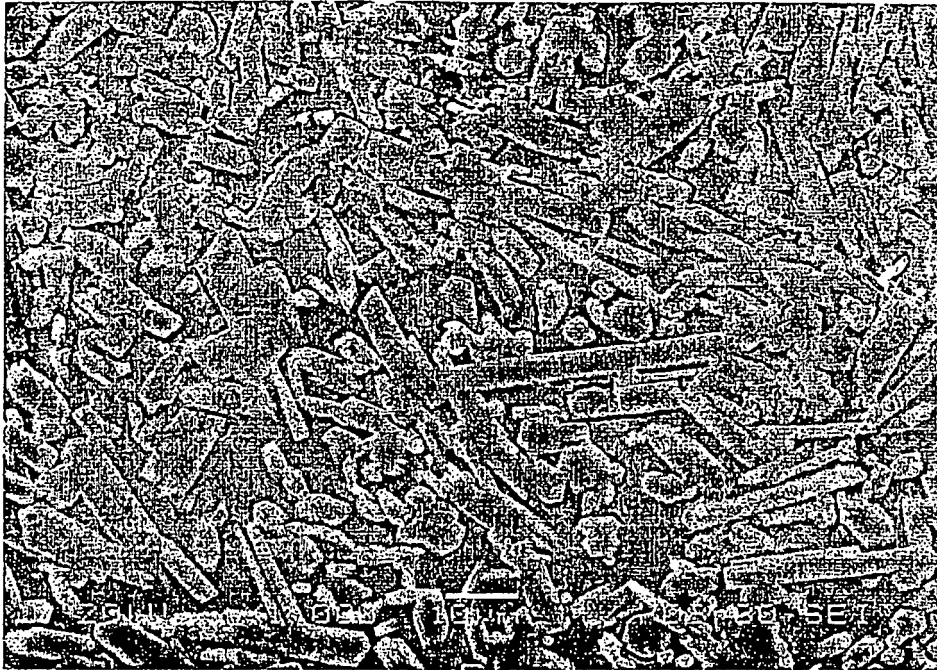


FIG.1

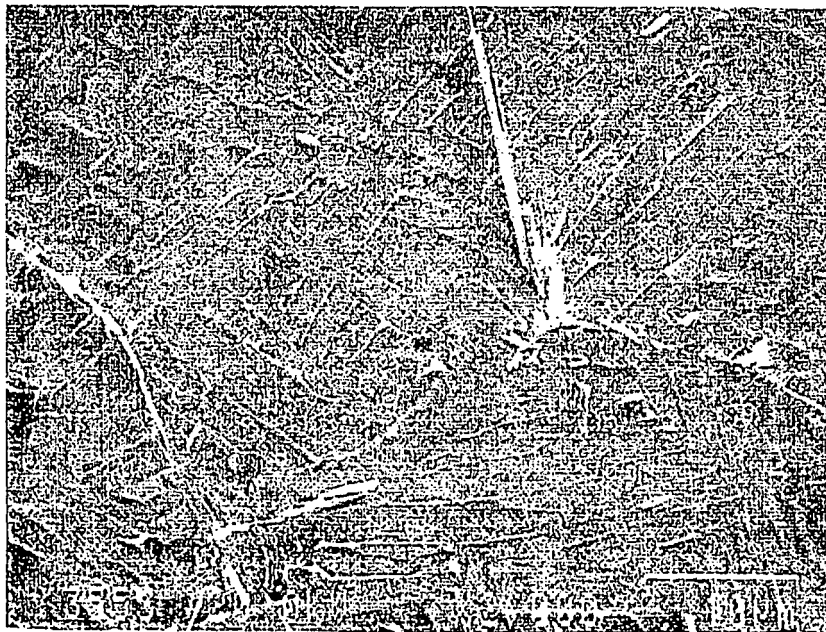


FIG.2

REFERENCES CITED IN THE DESCRIPTION

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