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(54)	Benevnelse	**METHOD FOR PRODUCING COMPONENTS FROM TITANIUM OR TITANIUM ALLOYS WITH POWDER METALLURGY**
(56)	Anførte publikasjoner	WO-A1-2012/148471, US-A- 5 441 695, GB-A- 818 827

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Process for powder metallurgical production of titanium or titanium alloy components

The present invention relates to a process for powder metallurgical production of a titanium or titanium alloy component, wherein first, a green part is formed using metal powder formed from titanium or titanium alloy and then this is compacted and solidified in a subsequent sintering step.

There are various powder metallurgical processes for producing true-to-scale titanium components (with "titanium component" here and hereinafter reference is drawn simply components that are made of titanium (pure titanium) or one or several titanium alloys), wherein in all processes first a green part is formed and then it is compacted and solidified in a sintering process. The production of the green part can take place in different ways, in particular by means of additive manufacturing processes, metal powder injection moulding, extrusion processes and pressureless powder metallurgical production processes.

The powder metallurgical production of titanium components is gaining in importance due to the excellent properties of the titanium material paired with the economic and commercial production method. The good biocompatibility and the high specific strength of titanium material play an important role, especially in the application areas of medical technology and in the aerospace industry. The most economically important alloy, with sales of more than 50% of the total titanium market, is Ti6Al4V.

To produce a powder-metallurgically processed titanium component, the following steps must be generally carried out:

a) Shaping
b) Debinding
c) Sintering

The aim of shaping is to bring the titanium powder particles in near dense packing close to the final shape. In this step, depending on the method used, additives are used, which must be removed in one or more subsequent debinding step(s). In the subsequent, often final, process step, sintering, the powder particles are consolidated by material transport.

Due to the high reactivity of titanium, all processing steps have to take place under specially adapted process conditions. In the EP 1 119 429 B1 [1] patent, Gerling et al. describe the necessary process conditions for sintering titanium components. The combined implementation of debinding and sintering in a common furnace concept is described by Bluem in EP 1 496 325 A2 [2].

Titanium has two crystal modifications. The hexagonal α-phase, which is present in pure titanium and atmospheric pressure at a temperature of up to 882.5°C, and the cubic body-centred ß-phase, which occurs in pure titanium and at normal pressure above the temperature described above. The presence of different phases at ambient temperature is used to classify titanium alloys in α-Ti, (α + ß) -Ti and ß-Ti alloys. For example, Ti6Al4V is an (α + ß) alloy, i.e. that at ambient temperature both phases are stable in the microstructure. In order to produce components with a traditionally desired density of > 97% in a sintering process of titanium and titanium alloys, sintering temperatures of approximately 1100 - 1400°C with a sintering duration of approximately 2 – 5 hours are usually required. For pure titanium and Ti6Al4V, this means that the materials are processed in the β-phase region, which leads to a massive ß-grain growth.

In EP 1 119 429 B1 [1], Gerling et al. describe that the microstructure that results has a ß-grain size of approx. 150 μm. To describe the sizes of the various structures in the lamella (α + β)-microstructure, the nomenclature according to Sieniawski et al. [3] depicted in Fig. 1 is used. Therein denoted:

D: the primary β-phase grain size

d: the size of a parallel α-lamella colony

t: the width of α-lamella

In contrast to forming processes, shaping takes place on the powder metallurgical route as the first process step. In the subsequent process step, sintering, the previously formed, dense titanium component is created. In contrast to classical processing approaches, due to the inverse sequence of the process steps (1. forming, 2. material consolidation) the powder metallurgical approach does not have the ability to refine or optimise the metal structure and thus, its material properties by thermal/mechanical processing prior to the forming step. For powder metallurgical processes for producing titanium and/or titanium alloy components, especially the process-related inverse sequence combined with very limited influence on the microstructure that arises in known sintering process is a limiting factor. By way of illustration, a standard microstructure of a Ti6Al4V sample sintered with titanium powder particles commonly used in the state of the art (with powder particles of sizes 45 μm) and sintered under conditions typically used in the state of the art in sintering process is shown in Figure 2. Evident there is the formed mixed microstructure, typical lamella of α-phase and ß-phase for known powder metallurgically produced and sintered titanium components; the (α + ß) microstructure, with a mean primary ß-phase grain size (D) of approx.190 μm.

The production of powder metallurgically processed titanium and titanium alloys with small grain sizes is described in US Pat. No. 4,601,874 [4] by Marty et al. Due to the targeted admixture of S, P, B, As, Se, Te, Y and lanthanoids, a material is produced with grain sizes that are two orders of magnitude smaller than the titanium powder particles used in the consolidation process. Disadvantage of this approach is that the use of titanium and titanium alloys is common in strictly regulated market segments. For these applications, the chemical compositions of the material and its mechanical properties are regulated by standards. For example, in the standards ASTM F2885 and ASTM F2889, the material compositions and mechanical properties of Ti6Al4V or pure titanium are established.

In WO 2012/148471 A1 [7] a process for the powder metallurgical production of components made of titanium or titanium alloys is described, in which moulded body of customary particle size and with at usual sintering temperatures of 1100°C and higher, especially at 1200°C, is sintered. The thus obtained microstructure with comparatively large grains is then cooled under a hydrogen atmosphere in order to achieve a conversion of the grain structure.

An objective generally pursued by the invention for powder-metallurgically produced and sintered titanium components is now to provide a possibility of manipulating the microstructure and optimising the material properties. In particular, it should be possible to adjust material properties adapted to the specific application directly in the sintering process and/or in the sintering process to create an optimum starting point for further thermal treatment steps after sintering. Thus, it should be possible, e.g. to produce a predominantly globular microstructure, which features high ductility, by targeted setting of the sintering conditions.

To solve the problem, a method according to claim 1 is proposed. Advantageous embodiments of the method are specified in claims 2 to 14.

A crucial prerequisite for the implementation of the method according to the invention and for the creation of the possibility of influencing the material properties in the sintering process is the use of metal powder formed from titanium or titanium alloys with an average particle size < 25 μm, so-called fine powder. In such fine powder used for the process according to the invention, the maximum particle size may be in particular < 30 μm. Thus, maximum particle size will be specified as limit by the manufacturers of such fine powder. Nevertheless, a small proportion of particles in such a charge may still have particle sizes above this limit. Such a proportion is usually specified with a maximum of 1 to a maximum of 5% by weight.

The mean particle size can advantageously be even lower, in particular at < 20 μm, with advantage < 10 μm and particularly preferred < 5 μm. The smaller the particle size of the metal powder, the sooner the high-end densities can be achieved even at significantly reduced sintering temperatures compared to the comparatively high sintering temperatures used hitherto.

The measurement of the particle sizes essential for the invention and their distribution is carried out by means of a particle size analysis by means of laser beam scattering according to ASTM B822.

The particle size distribution is determined by weight-% and according to D10/D50/D90, wherein D50 is the mean particle size. Specifically, the particle sizes cited here were determined in applicant's comparative experiments by measurement with particle size analysing devices COULTER® LS of the manufacturer Beckman Coulter and evaluation using the Fraunhofer theory according to ASTM B822.

The particle size in the sense of the invention in the case of spherical particles is determined by the particle diameter. For non-spherical particles, the particle size corresponds to the projected maximum particle dimension.

Due to the reduced particle size, in non-consolidated component, the surface available for the sintering process increases and thus surface energy stored. Since the reduction of this energy is the driving force in the sintering process, the sintering process can then continue using less thermal energy.

A further advantage of using fine powder sizes as described above for moulding the green parts is that more powder particles can be introduced per unit volume. This leads, in addition to the increased surface area, to a higher number of contact points of the particles per unit volume, as illustrated in Figure 3. There, the influence of halving the particle size (on the example of spherical particles) on the number of particles for filling a defined volume is illustrated in a schematic representation.

The contact points of the particles are in turn starting point and a necessary condition for the sintering process, which is driven by diffusion processes. The increase in the number of such contact points per unit volume thus provides an improvement in the starting conditions for the sintering process.

By using fine powder having mean particle sizes of < 25 μm according to the invention, the ideal packing density, in addition to the stated advantages, also leads to a reduced volume enclosed by the powder particles, as illustrated in Figure 4 in an idealised manner. Figure 4 illustrates, in a schematic representation, the reduction of the cavity between adjoining particles by halving the particle size (using spherical particles as an example). Since this cavity must be closed by material transport during the sintering process in order to achieve the high density of material desired for the component obtained after the sintering process, a smaller volume to be bridged represents a further decisive reason for improving the process result.

The sintering step typically takes place in an atmosphere with reduced pressure. This can be a vacuum with a pressure of $\leq 10^{-3}$ mbar, in particular $\leq 10^{-5}$ mbar. However, it can also be an inert gas atmosphere with reduced pressure of e.g. ≤ 300 mbar. In particular, argon may be considered as inert gas.

The sintering temperatures are inventively below 1100°C. In particular, they can be at maximum of 1050°C, at a maximum of 1000°C, even at a maximum of only 950°C. The sintering temperature should advantageously not be chosen below 860°C to achieve a good sintering result. The sintering temperature can be maintained evenly. In particular, however, it is also possible and within the meaning of the invention to vary the temperature during the sintering process. As the sintering temperature here, it is the temperature that the workpiece to be sintered is exposed to. Depending on the sintering plant, an adapted process temperature will have to be selected at its control point, since it may happen that the process temperature measured as process temperature remotely from the workpiece differs from the sintering temperature experienced by the workpiece.

The sintering duration can be in particular ≤ 3.5 hours, often even ≤ 3 hours or even ≤ 2.5 hours. However, it has been found that, as a rule, to achieve good results, the sintering duration should be at least 1 hour, preferably at least 2 hours.

After the sintering step, titanium or titanium alloy components produced by the method according to the invention generally have a final density > 97%. It can also happen that final densities above 98% and even ≥ 99% are attained.

To obtain a globular microstructure, titanium components were sintered below the β-transus temperature (e.g., at a temperature 30°C below the β-transus temperature).

Thus, in the first experiments at a sintering temperature of 950°C below the ß-transus temperature and with a sintering duration of less than three hours components with a final density > 97% were produced. These had a globular microstructure with an average α-grain size of 10.1 μm and a max. size of 29 μm. The microstructure of this material is shown in Figure 5. These grain sizes are in the order of magnitude of the used powder particles.

According to the literature, the ß-transus temperature of Ti6Al4V is in the range of 985°C to 1015°C [3; 5]. This comparatively wide range stated in the literature is due, on the one hand, to the distribution of the alloy elements in the titanium alloys. On the other hand, the ambient pressure is another influencing factor. Thus, Huang et al. describe that due to increased process pressures (1500 bar) in the alloy Ti46A18Nb lead to a reduction in the α-transus temperature [6].

The inventors currently assume that, depending on the process conditions, shifts in the ß-transus temperature of only 20°C at maximum will be observable due to pressure variations.

For the creation of a bimodal microstructure, the components were sintered near the ß-transus temperature, but still below it.

Thus, in order to also produce the lamella microstructure with reduced primary β-phase grain size of the Ti6Al4V alloy, which is advantageous for many applications, first samples were produced by sintering the titanium components at a sintering temperature of 1000°C (Fig. 6). This sintering temperature was still below the ß-transus temperature, although only slightly, as investigations of the obtained samples with respect to the microstructure formed in the sintered alloy showed. The emerging bimodal microstructure consists of a globular α-microstructure and small proportions of lamella (α + ß) microstructure, wherein the mean ß-grain size is 81 μm.

The density was measured according to ASTM B962 and ASTM B311 specifications. The grain size was determined in accordance with the provisions of ASTM E112.

To produce a lamella microstructure with the smallest possible grain size of the primary β-phase grains, the components were largely sintered, i.e. for most of the time below the ß-transus temperature, but with a minimum hold time, which remained below 30 min, preferably below 20 min, in particular less than 10 min, phase-wise even above the ß-transus temperature, so that the ß-phase was fully present, so as to produce just the lamella microstructure, but the primary ß-phase grain did not exceed the size range mentioned in claim 16. The sintering above the β-transus temperature with minimum hold time was carried out at any rate at a temperature above 1015°C. Thereby, this temperature was kept below 1080°C, was advantageously below 1040°C and was chosen in particular ≤ 1020°C.

In the above-mentioned possibilities of influencing the phase composition in the sintered material by selective adjustment of the sintering conditions at sintering temperatures below 1100°C, in particular predominantly below the β-transus temperature is a particular advantage of the procedure according to the invention. The prerequisite for this variability is that sufficiently dense titanium components can be produced below the ß-transus temperature, which, as the inventors have realized, becomes possible due to the invention-essential use of fine powder with particle sizes < 30 μm.

Thus, it has been demonstrated that, according to the process of the invention, powder metallurgically shaped bodies of titanium and titanium alloys are sintered below the sintering temperatures usually above 1100°C and above, generally below 1200°C and above, advantageously below the ß-transus temperature, components with good structural and other material properties can be obtained. Thereby, it could be shown that at sintering temperatures that are much lower in comparison with the sintering temperatures set in the state of the art, components with high-end densities > 97% can be obtained - unexpectedly. In particular, it has been shown that the method according to the invention allows the microstructure of titanium components to be varied in the sintering process and the grain size to be drastically reduced, whereby the mechanical properties of the components, for example tensile strength, ductility and fatigue strength, can be optimised.

Within the scope of the invention, e.g. also a particularly low temperature for sintering may be chosen, e.g. a temperature below 950°C, and it can, if in such a sintering step the desired material density in the finished component (usually > 97%) is not reached, undergo further compression of the material in a subsequently performed pressing step in which the material is subjected to pressure and optionally a temperature, in particular by cold isostatic pressing (CIP) or by hot isostatic pressing (HIP). Here, e.g. the material density after sintering is < 97% and are compressed by the pressing step carried out after sintering compacted to > 97%.

Furthermore, components produced by the process according to the invention may be subjected to further thermal post-treatments subsequent to the sintering step in order to influence the properties of the material even more. Such further thermal post treatments may, e.g. be one or several of the following processes: Hot Isostatic Pressing (HIP), chilling (Quench), uniform rapid chilling - Uniform Rapid Quench (URQ).

Due to the sintering temperatures reduced according to the invention compared with the sintering temperatures used in the state of the art, give rise to further ecological/economic and process engineering advantages. On the one hand, less thermal energy is required in the sintering process, which leads to lower costs but also shorter process durations. On the other hand, the process carried out according to the invention with reduced sintering temperature makes it possible to use hot-wall oven concepts, which in turn are more cost-effective than ovens designed for process temperatures

> 1100°C, which are classically cold-wall furnaces.

The targeted combination of fine powders with average particle size < 25 μm, preferably also with maximum particle sizes < 30 μm, and reduced sintering temperatures to be classified as low compared to the state of the art, allows unique manipulation of microstructure and thus of the material properties.

In the figures already referred to above:

Fig. 1 a representation of a lamella (α + ß) microstructure of a Ti6Al4V sample with description of the microstructure fractions according to Sieniawski et al. [3];

Fig. 2 a microscopically magnified image of a Ti6Al4V sample, by using powder particles < 45 μm, powder-metallurgically produced and standard sintering, and proves for this a lamella (α + β) microstructure;

Fig. 3 a schematic representation of the influence of halving the particle size (for example using spherical particles) on the number of particles needed to fill a definite volume;

Fig. 4 a schematic representation of the reduction of the cavity between adjacent particles by halving the particle size (for example, spherical particles);

Fig. 5 a microscopically magnified micrograph of a powder metallurgically produced and sintered Ti6Al4V sample using powder particles < 20 μm, which proves the formation of a globularly pronounced α-microstructure

Fig. 6 a microscopically magnified micrograph of a powder metallurgically produced and sintered Ti6Al4V sample using powder particles < 20 μm, which proves the formation of a bimodal microstructure with a globular α-microstructure and lamella pronounced (α + β) microstructure.

<u>References:</u>

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Patentkrav

1. Fremgangsmåte for pulvermetallurgisk fremstilling av en komponent fra titan eller en titanlegering, hvor en grønn del først dannes ved anvendelse av metallpulver dannet av titan eller titanlegeringen og dette komprimeres og stivnes i et etterfølgende sintringstrinn, **karakterisert ved at** for fremstillingen av den grønne delen anvendes metallpulver av titan eller titanlegeringen, med en gjennomsnittlig partikkelstørrelse <25 µm, målt ved laserstrålespredning i henhold til ASTM B822, og at sintringstrinnet utføres ved en sintringstemperatur opp til max. 1100°C, ved en sintringstid på ≤ 5 timer i en atmosfære med redusert trykk sammenlignet med normaltrykk.

2. Fremgangsmåte ifølge krav 1, **karakterisert ved at** den maksimale partikkelstørrelsen av metallpulveret av titan eller titanlegering er <30 µm.

3. Fremgangsmåte ifølge et av de foregående krav, **karakterisert ved at** sintringstrinnet utføres i et vakuum med et trykk ≤ 10^{-3} mbar, spesielt ved et trykk ≤ 10^{-5} mbar.

4. Fremgangsmåte ifølge et av kravene 1 eller 2, **karakterisert ved at** sintringstrinnet utføres i en inertgassatmosfære, spesielt i en argonatmosfære, ved et trykk ≤ 300 mbar.

5. Fremgangsmåte ifølge et av de foregående krav, **karakterisert ved at** for fremstillingen av den grønne delen anvendes metallpulver av titan eller titanlegering med en gjennomsnittlig partikkelstørrelse <20 µm, spesielt <10 µm, fortrinnsvis <5 µm.

6. Fremgangsmåte ifølge et av de foregående krav, **karakterisert ved at** sintringstiden er ≤ 3,5 timer, spesielt ≤ 3 timer, fortrinnsvis ≤ 2,5 timer.

7. Fremgangsmåte ifølge et av de foregående krav, **karakterisert ved at** sintringstiden er minst 1 time, fortrinnsvis minst 2 timer.

8. Fremgangsmåte ifølge et av de foregående krav, **karakterisert ved at** sintringstemperaturen er maksimalt 1050°C, fortrinnsvis maksimalt 1000°C, spesielt maksimalt 950°C.

9. Fremgangsmåte ifølge et av de foregående krav, **karakterisert ved at** sintringstemperaturen er minst 860°C.

10. Fremgangsmåte ifølge et av de foregående krav, **karakterisert ved at** i sintringstrinnet justeres sintringstemperaturen ved en temperatur under en p-transus-temperatur av titan- eller titanlegeringsmaterialet.

11. Fremgangsmåte ifølge et av de foregående krav, **karakterisert ved at** komponenten etter sintringstrinnet har en materialtetthet > 97%, spesielt > 98%, fortrinnsvis ≥ 99%.

12. Fremgangsmåte ifølge et av kravene 1 til 11, **karakterisert ved at** i sintringstrinnet velges en sintringstemperatur under 950°C og at for å oppnå en materialtetthet av komponenten > 97% underkastes komponenten i et ytterligere trinn for trykk og eventuelt for en temperatur, for eksempel et trinn med kaldisostatisk pressing (CIP) og/eller varmisostatisk pressing (HIP).

13. Fremgangsmåte ifølge et av de foregående krav, **karakterisert ved at** komponenten blir utsatt for en etterfølgende termisk behandling etter sintringstrinnet.

14. Fremgangsmåte ifølge krav 13, **karakterisert ved at** den termiske etterbehandlingen utføres i form av en eller flere av følgende behandlingsmetoder: varmisostatisk pressing (HIP), bråkjøling (quench), ensartet hurtig bråkjøling (Uniform Rapid Quench, URQ).

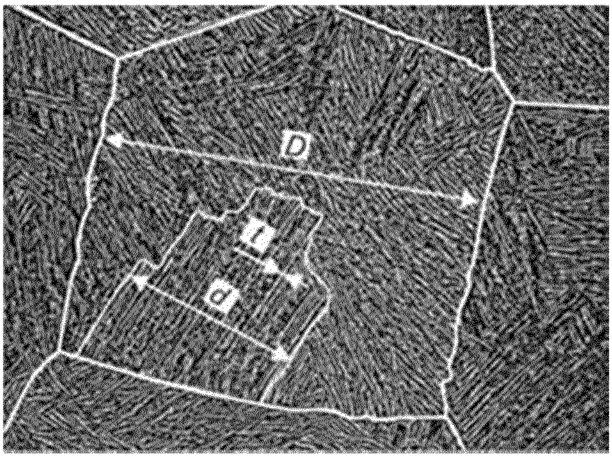

Fig. 1

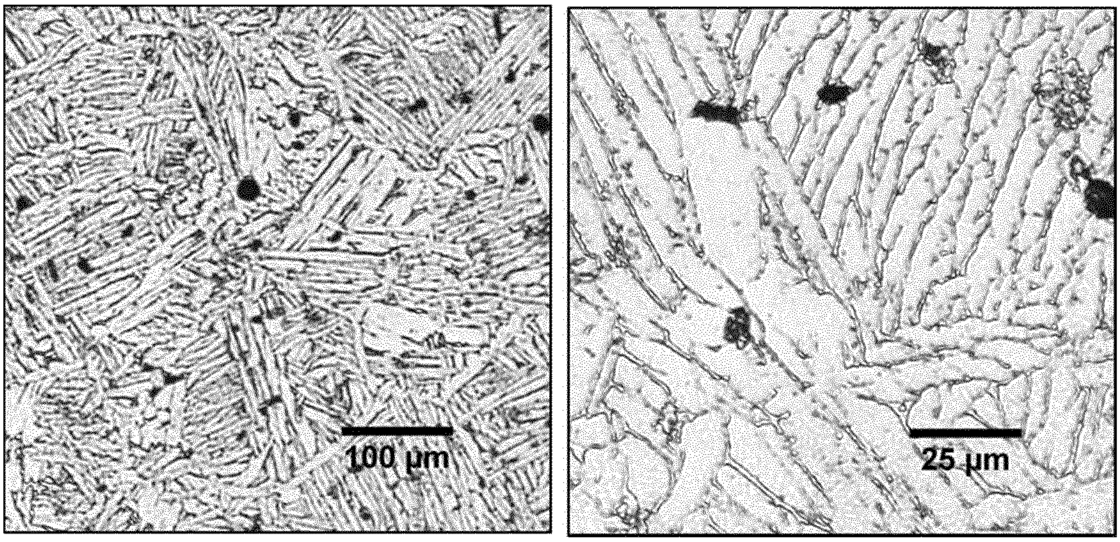

Fig. 2

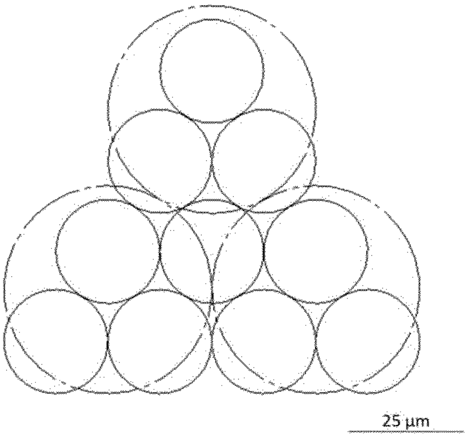

Fig. 3

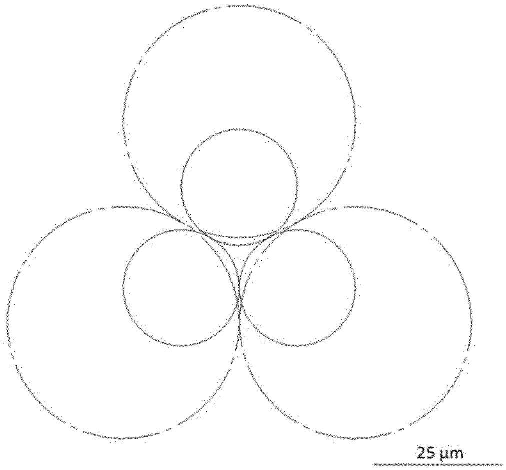

Fig. 4

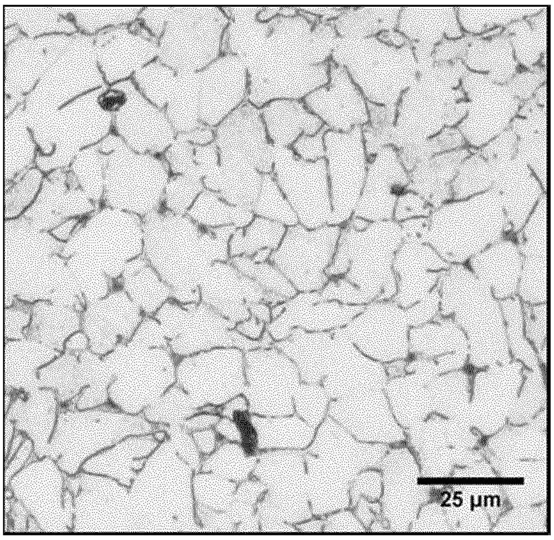

Fig. 5

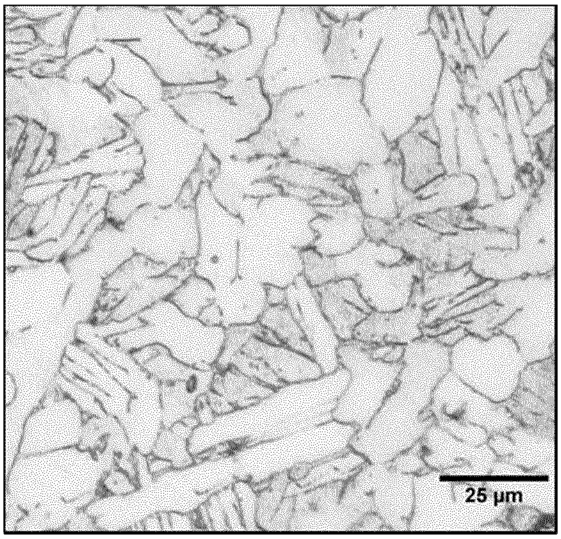

Fig. 6