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(54) METHOD OF MAKING A MOLYBDENUM ALLOY HAVING A HIGH TITANIUM CONTENT

(57) The present invention relates to method of making a molybdenum alloy which has a high titanium content and further comprises silicon and/or boron. The method comprises subjecting to pressureless sintering or sintering under pressure in an inert gas atmosphere a mixture of one or more powders (i) of an alloy of Mo and Ti and, optionally, one or more additional metals X and/or (i') powders of Mo and of TiN, and (ii) one or more powders comprising one or more powders of silicides of Mo and/or Ti and/or (iii) one or more powders of nitrides which comprise Si_3N_4 powder and/or BN powder.

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Description

[0001] The present invention relates to a method of making a molybdenum alloy having a high titanium content which is suitable, for example, for the production of structural components, in particular of components, preferably vanes and blades, of turbomachines such as gas turbines and aircraft engines.

[0002] Ternary molybdenum alloys are already known which comprise molybdenum, silicon and boron as main alloying constituents. However, when used at high temperatures, for example in the range from 900°C to 1300°C, such alloys do not exhibit sufficient creep resistance. Attempts to increase the creep resistance with very finely dispersed particles of titanium, zirconium and carbon, as described, for example, in WO 85/03953 A1 have likewise not led to the desired results. Correspondingly, attempts have been made to improve the creep resistance of corresponding alloys using additional alloying elements, such as titanium, zirconium, hafnium, boron, carbon, aluminum, thorium, chromium, manganese, niobium, tantalum, rhenium and tungsten. However, if a corresponding alloy is to be suitable for the production of structural components and in particular, components such as vanes and blades of turbomachines which are used at high temperatures, it must show not only a high creep resistance, but also a good oxidation resistance in the temperature range from 900°C to 1300°C, as well as an adequate static strength and sufficient ductility.

[0003] US 2016/0060734 A1 discloses alloys which are suitable for the production of structural components such as vanes and blades of turbomachines and comprise molybdenum, silicon, boron and titanium as main components. However, due to the high reactivity of titanium metal with *inter alia,* oxygen, nitrogen, carbon and hydrogen and its propensity to form stable non-metallic compounds with these elements corresponding alloys are difficult and expensive to produce. If titanium is consumed by reacting with the above elements it is no longer available for the desired phase formation as Mo-Ti silicide and Mo-Ti mixed crystal. These phases are essential for achieving the properties which are required if the alloy is to be used for manufacturing turbine rotor blades and guide vanes.

[0004] DE 10 2011 013 894 A1 discloses a process for the final shape production of components made of a (titanium-free) material comprising intermetallic phases of trimolybdenum silicide and molybdenum borosilicide homogeneously distributed in a molybdenum matrix, which process comprises subjecting a starting powder mixture that comprises at least molybdenum

[0005] (80 mass) and additionally silicon nitride and boron nitride to a grinding process; producing a suspension with the ground starting powder mixture that comprises at least an organic binder; introducing the resulting suspension into a metal powder injection molding tool or constructing a green body in layers by screen printing; subjecting the placed green body to thermal and/or chemical treatment for expelling the organic components; and performing an unpressurized sintering in a non-oxidizing atmosphere or in high-vacuum conditions at 1600 °C. A similar process is disclosed in US 2009/0011266 A1.

[0006] The problem underlying the present invention is to provide a method for the production of molybdenum alloys which contain high concentrations of titanium and are suitable for the production of structural components which are subjected to high temperatures and high stress in a simple and cost-efficient manner.

[0007] The above problem is solved by a method according to claim 1. Advantageous refinements of the method are set forth in the dependent claims. The problem is also solved by an alloy obtainable by the method and an article made from the alloy.

[0008] The present invention provides a method for making a molybdenum alloy which has a high titanium content and further comprises at least silicon and/or boron. The method comprises subjecting to (pressureless) sintering under vacuum or sintering under pressure in an inert or reducing gas atmosphere (e.g., an Ar/H_2 atmosphere) a mixture of powders which comprise (i) one or more powders of an alloy of Mo and Ti and, optionally, one or more additional metals X and/or (i') powders of Mo and of titanium nitride (hereafter TiN) and at least one of (ii) one or more powders comprising one or more powders of silicides (and preferably also borides) of Mo and/or Ti and (iii) one or more powders of nitrides which comprise silicon nitride (hereafter $Si_3N_{4)}$ powder and/or boron nitride (hereafter BN) powder (in particular, at least silicon nitride powder and preferably both silicon nitride powder and boron nitride powder).

[0009] In advantageous refinements of the method according to the present invention, X, if present in the alloy of Mo and Ti, is selected from one or more (e.g., one, two, three or more) of Fe, Y, Hf, Nb, Zr and W. For example, X may at least be Fe.

[0010] In further advantageous refinements of the method according to the present invention, one or more powders (i) (and preferably no powders (i')) are employed. The one or more powders (i) may be substantially spherical and may have a median particle size d50 (as determined by, e.g., laser diffraction) in the range from 0.001 μm to 50 μm, in particular from 0.001 μm to 40 μm, e.g., from 0.001 to 30 μm.

[0011] In further advantageous refinements of the method according to the present invention, one or more powders (i') (and preferably no powders (i)) are employed. Preferably, the one or more powders (i') are substantially spherical and have a median particle size d50 (as determined by, e.g., laser diffraction) in the range from 0.01 μm to 100 μm, in particular from 0.1 μm to 50 μm, e.g., from 0.01 to 2 μm.

[0012] In further advantageous refinements of the method according to the present invention, one or more powders

(ii) (and preferably no powders (iii)) are be employed. The one or more silicide powders (ii) may comprise powders of $MoTi_5Si_3$, Ti_5Si_3, $MoTi_5SiB_2$, Mo_3Si or combinations of two or more thereof.

[0013] In further advantageous refinements of the method according to the present invention, one or more powders (iii) (and preferably no powders (ii)) are employed. The one or more powders (iii) may comprise one or more powders of silicon nitride and/or one or more powders of boron nitride. For example, the powders (iii) may comprise at least one or more powders of silicon nitride. In a preferred embodiment, both silicon nitride powder(s) and boron nitride powder(s) are employed as powders (iii).

[0014] In further advantageous refinements of the method according to the present invention, the powders (i) and/or (i') and the powders (ii) and/or (iii) are combined in ratios which result in an alloy which comprises at least 35 at.% of molybdenum and/or not more than 66 at.% of molybdenum and/or at least 25 at.% of titanium and/or not more than 33 at.% of titanium and/or at least 9 at.% of silicon and/or not more than 15 at.% of silicon and/or at least 5 at.% of boron and/or not more than 9 at.% of boron. Preferably, the alloy comprises at least 0.1 at.% of Fe and/or not more than 5 at.% of Fe.

[0015] The present invention also provides an alloy which is obtainable by the method set forth above (including the various refinements thereof), as well as an article (e.g. a component of a turbine such as a rotor blade or guide vane) which is made of or comprises this alloy.

[0016] The particulars of the method according to the present invention set forth below are by way of example and for purposes of illustrative discussion of the embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of the present invention. In this regard, no attempt is made to show details of the present invention in more detail than is necessary for the fundamental understanding of the present invention, the description making apparent to those of skill in the art how the several forms of the present invention may be embodied in practice.

[0017] As set forth above, the method according to the present invention comprises subjecting to pressureless sintering or sintering under pressure a mixture of powders which comprise (i) one or more powders of an alloy of Mo and Ti and, optionally, one or more additional metals X (e.g., one or more of Fe, Y, Hf, Nb, Zr, W and preferably at least Fe) and/or (i') powders of Mo and of TiN, and further comprise (ii) one or more powders comprising one or more powders of silicides (and preferably also borides) of Mo and/or Ti and/or (iii) one or more powders of nitrides which comprise Si_3N_4 powder and/or BN powder. Especially in cases where powders (iii) are employed in combination with powders (ii), powders (iii) may not comprise Si_3N_4 powder.

[0018] The powders (i) may either be purchased (e.g. from H. C. Starck, Germany) or may be prepared, for example, by atomization in an inert gas atmosphere (preferably high purity argon) of a block or ingot of an alloy of Mo, Ti and, optionally, X to obtain a powder with particles which will usually be substantially spherical and will have a particle size (longest dimension and/or diameter) of less than 45 μm (particularly less than 10 μm, e.g., less than 1 μm). The alloy can be prepared, for example, by melting together (e.g., by plasma melting or arc melting) powders of metallic Mo, Ti and optionally one or more metals X and/or corresponding pre-alloys such as, e.g., $Mo_{80}Ti_{20}$, $Mo_{70}Ti_{30}$, $Mo_{60}Ti_{40}$, etc. (e.g., in powder form). Powders (i') may be prepared, for example, by reducing molybdenum oxides with e.g., hydrogen and by nitriding Ti powder, respectively. In this regard it is to be noted that the phrase "less than z μm" as used herein is intended to mean that at least 95 % by weight, e.g., at least 98 % by weight, or at least 99 % by weight of the particles have a longest dimension or diameter of z μm. The particle size can be determined by methods well known to those of skill in the art, for example by sieve analysis or optical methods such as laser diffraction.

[0019] The atomization of an ingot or block may, for example, be carried out by an EIGA (Electrode Induction melting Gas Atomization) process or by gas atomization using a Laval nozzle (preferably using high purity argon). The atomization may optionally be preceded by subjecting the alloy obtained by, e.g., arc melting or plasma melting to hot isostatic pressing (HIP), e.g., at a temperature of from 1,300°C to 1,500°C and at a pressure of from 100 to 300 MPa for 5 to 10 hours. Prior to and/or after the hot isostatic pressing a heat treatment may be carried out, e.g., at a temperature of from 1,300°C to 1,600°C for 5 to 50 hours.

[0020] Non-limiting examples of commercially available powders (i) for use in the instant method have a median particle size d50 in the range from 0.01 μm to 50 μm (at a purity of, e.g., from 95 % to 99.9 % by weight) or a d50 of from 0.01 μm to 30 μm (at a purity of, e.g., from 98 % to 99.9 % by weight).

[0021] The alloy of Mo, Ti and, optionally, X for making the one or more powders (i) may, for example, comprise (in % by weight based on the total weight of the alloy):

Mo	from 55 to 95, preferably from 60 to 85
Ti	from 10 to 30, preferably from 15 to 25
Fe	from 0 to 3, preferably from 1 to 2
Nb	from 0 to 30, preferably from 10 to 20
Zr	from 0 to 10, preferably from 2 to 4
W	from 0 to 20, preferably from 4 to 10

Hf	from 0 to 3, preferably from 1 to 2
Y	from 0 to 3, preferably from 1 to 2.

[0022] If present, one, two, three, four, five or all of Fe, Nb, Zr, W, Hf and Y may be present in the alloy.

[0023] The alloy for making the one or more powders (i) preferably does not contain any (or at most only trace amounts) of Si and B because the presence of these elements will cause the alloy to become brittle. The same applies to the one or more powders (i').

[0024] Non-limiting examples of commercially available Mo powders (i') for use in the instant method have a median particle size d50 in the range from 0.1 μm to 50 μm (at a purity of, e.g., from 95 % to 99.9 % by weight) or a d50 of 0.5 μm to 2 μm (at a purity of, e.g., from 98 % to 99.9 % by weight). The same applies to TiN powders.

[0025] The one or more powders (ii) for use in the instant method may comprise powders of one or more of $Mo(Ti)_5Si_3$, Ti_5Si_3, $Mo(Ti)_5SiB_2$, Mo_3Si. The one or more powders (ii) may either be purchased (e.g., from H. C. Starck, Germany) or may be prepared by, for example, arc melting (usually in an argon atmosphere) from elemental Mo, Ti and Si (and preferably B), usually in the form of powders of the elements and/or corresponding pre-alloys. The powders (ii) will usually comprise one or more phases of formula $MoTi_5Si_3$, Ti_5Si_3, MoTi, and $MoTi_5SiB_2$ and/or corresponding substoichiometric or hyperstoichometric phases. For example, these phases may contain more or less Si and/or B than indicated, or may contain Mo and/or Ti, which can activate the sintering process and can result in high sinter densities (e.g., > 95 %).

[0026] The powders (ii) for use in the instant method will usually have a median particle size d50 (as determined by, e.g., laser diffraction) in the range from 0.001 μm to 50 μm, in particular from 0.001 μm to 40 μm, e.g., 0.001 to 30 μm.

[0027] Non-limiting examples of commercially available powders (ii) for use in the instant method may have a median particle size d50 as follows:

Mo_3Si	from about 10 μm to about 30 μm (at a purity of, e.g., from about 98 % to about 99.99 % by weight) or from about 1 μm to about 10 μm (at a purity of, e.g., from about 99 % to about 99.9 % by weight)
Ti_5Si_3	from about 10 μm to about 30 μm (at a purity of, e.g., from about 98 % to about 99.9 % by weight)
$Mo(Ti)_5Si_3$	from about 0.01 μm to about 50 μm (at a purity of, e.g., from about 98 % to about 99.99 % by weight) or from about 0.01 μm to about 30 μm (at a purity of, e.g., from about 99 % to about 99.9 % by weight)
$Mo(Ti)_5SiB_2$	from about 0.01 μm to about 50 μm (at a purity of, e.g., from about 98 % to about 99.99 % by weight) or from about 0.01 μm to about 30 μm (at a purity of, e.g., from about 99 % to about 99.9 % by weight).

The one or more powders (iii) which may be used in combination with or instead of the one or more powders (ii) are readily commercially available (e.g., from H. C. Starck, Germany).

[0028] The powders (iii) for use in the instant method will usually have a median particle size d50 (as determined by, e.g., laser diffraction) in the range from 0.001 μm to 50 μm, e.g., from 0.001 μm to 40 μm, or from 0.001 to 30 μm.

[0029] Non-limiting examples of commercially available powders (iii) for use in the instant method may have a median particle size d50 as follows:

Si_3N_4	from about 0.1 μm to about 5 μm (at a purity of, e.g., from about 95 % to about 99.9 % by weight) or from about 0.5 μm to about 1 μm (at a purity of, e.g., from about 98 % to about 99.9 % by weight)
BN	from about 0.1 μm to about 5 μm (at a purity of, e.g., from about 95 % to about 99.9 % by weight) or from about 0.5 μm to about 1 μm (at a purity of, e.g., from about 98 % to about 99.9 % by weight)

[0030] The powders (i) and/or (i') and the powders (ii) and/or (iii) are mixed and optionally milled, and then subjected to a sintering process (either pressureless or under pressure in a reducing or inert gas atmosphere, e.g., an atmosphere consisting essentially of Ar/H_2 or helium). Corresponding processes are well known to those of skill in the art. Prior to sintering the mixed (and optionally milled) powders will usually be combined with a preferably organic binder (e.g., an organic wax) and then subjected to cold isostatic pressing (CIP) at room temperature, e.g., at a pressure of from 100 to 300 MPa for, e.g., 5 to 60 minutes, to form a green body.

[0031] The one or more powders (i) or (i') are usually mixed with the one or more powders (ii) and/or (iii) in ratios which result in a weight percentage of the one or more powders (i) and/or the one or more powders (i') of at least 85 %, e.g., at least 88 %, at least 90 %, at least 92 %, or at least 94 % by weight, but usually not higher than 97 %, e.g., not higher than 96 % by weight, based on the total weight of the powder mixture (i.e., without optional binder). Merely by way of example, weight percentages of powders (i) and (iii) in a corresponding mixture may be as follows:

Powder (i)	from 85 to 97, preferably from 92 to 96
Si_3N_4	from 2 to 15, preferably from 3 to 7

BN	from 0.5 to 5, preferably from 1 to 3.

[0032] The sintering (or reaction sintering if nitrides are present) is usually carried out in several (e.g., two, three or four) steps at different temperatures. Merely by way of example, the sintering may be carried out, in each case with a holding time of from 1 to 3 hours, (1) at a temperature of from 350°C to 450°C (e.g., at about 400°C) to decompose the optionally present organic binder, (2) at a temperature of from 650°C to 750°C (e.g., at about 700°C) to decompose nitrides, if present, (3) at a temperature of from 1,150°C to 1,250°C (e.g., at about 1,200°C) and (4) at a temperature of from 1,650°C to 1,750°C (e.g., at about 1,700°C).

[0033] The sintered body thus obtained may optionally be subjected to hot isostatic pressing (HIP), e.g., at a temperature of from 1,300°C to 1,500°C and at a pressure of from 100 to 300 MPa for 5 to 10 hours. Prior to and/or after the HIP a heat treatment may be carried out, e.g., at a temperature of from 1,300°C to 1,600°C for 5 to 50 hours.

[0034] The sintered body may also be subjected to forming (optionally preceded by HIP and/or heat treatment(s) as set forth above) such as, e.g., rolling, extrusion, forging (e.g., isothermal or "hot die"), optionally followed by a heat treatment as set forth above.

[0035] It should also be noted that in the case of the absence of nitrides in the powder mixture the sintering (and the CIP) can be replaced by a generative production method, e.g. by using a laser with which a desired structure is built up layer by layer, the laser being used to sinter each deposited layer of powder material before the next layer of powder material is deposited.

[0036] The following embodiments of the instant method are provided for purely illustrative purposes.

Embodiment 1:

[0037] A powder (i) was prepared by arc melting of a powder mixture of elemental Mo (81 % by weight), Ti (18 % by weight) and Fe (1 % by weight) to form an ingot, followed by atomization of the ingot by means of a Laval nozzle. The powder (i) (93 % by weight based on powder mixture) was then mixed with powders (iii) of Si_3N_4 (5 % by weight) and BN (2 % by weight) in a planetary ball mill (mass ratio balls : powder = 10 : 1, 100 rev/min) for 15 minutes and the resultant mixture was combined with an organic binder (e.g., wax) and then subjected to CIP for about 10 minutes at about 300 MPa and thereafter to reaction sintering at about 400°C for about 1 hour in an Ar/H_2 atmosphere, about 700°C for about 1 hour in an Ar/H_2 atmosphere, about 1,200°C for about 1 hour in vacuum and about 1,700°C for about 1 hour in vacuum, followed by a heat treatment at about 1,400°C for about 10 hours and HIP for about 5 hours at about 1,400°C and about 150 MPa. The resultant product showed the following (approximate) concentrations (in at.%):

Mo	57
Ti	25
Fe	1
Si	9
B	8

Embodiment 2:

[0038] A powder (i) is prepared by plasma melting of a powder mixture of elemental Mo, Ti, Fe and Hf to form an ingot, followed by atomization of the ingot by means of a Laval nozzle. The powder (i) is then mixed with powders (iii) of Si_3N_4 and BN and an organic binder and the resultant mixture is subjected to CIP and thereafter to reaction sintering at temperatures of about 400°C, about 700°C, about 1,200°C and about 1,700°C, each for about 1-3 hours in a reducing atmosphere or in vacuum, followed by a heat treatment at about 1,400°C for about 10 hours and HIP for about 5 hours at about 1,400°C and about 150 MPa.

Embodiment 3:

[0039] A powder (i) is prepared by arc melting or plasma melting of a powder mixture of elemental Mo, Ti, Fe, Y, Hf, Nb, Zr and W to form an ingot, followed by an optional heat treatment, optional HIP and atomization of the ingot by means of a Laval nozzle or by means of an EIGA method. The powder (i) is then mixed with powders (iii) of Si_3N_4 and BN and an organic binder and the resultant mixture is subjected to CIP and thereafter to reaction sintering at temperatures of about 400°C, about 700°C, about 1,200°C and about 1,700°C, each for about 1-3 hours in a reducing atmosphere or in vacuum, followed by optional HIP for about 5 to about 10 hours at a temperature of from about 1,300°C to about 1,500°C and a pressure of from about 100 to about 300 MPa, forming by rolling, extrusion or forging at a temperature of higher than 1,600°C and a subsequent heat treatment for about 5 to about 50 hours at a temperature of from about

1,300°C to about 1,600°C.

Embodiment 4:

[0040] A powder (i) is prepared by plasma melting of a powder mixture of elemental Mo, Ti and Fe to form an ingot, followed by atomization of the ingot by means of a Laval nozzle. The powder (i) is then mixed with powders (ii) of $Mo(Ti)_5Si_3$ and $Mo(Ti)_5SiB_2$ and an organic binder and the resultant mixture is subjected to CIP and thereafter to sintering at temperatures of about 400°C, about 1,200°C and about 1,700°C, each for about 1-3 hours in a reducing atmosphere or in vacuum, followed by a heat treatment at about 1,400°C for about 10 hours and HIP for about 5 hours at about 1,400°C and about 150 MPa.

Embodiment 5:

[0041] A powder mixture (i') of elemental Mo and of TiN is mixed with powders (iii) of Si_3N_4 and BN and an organic binder and the resultant mixture is subjected to CIP and thereafter to reaction sintering at temperatures of about 400°C, about 700°C, about 1,200°C and about 1,700°C, each for about 1-3 hours in a reducing atmosphere or in vacuum, followed by a heat treatment at about 1,400°C for about 10 hours and HIP for about 5 hours at about 1,400°C and about 150 MPa.

[0042] As set forth above, the method of the present invention is suitable for making molybdenum alloys which have a high titanium content. The term "molybdenum alloy" as used herein and in the appended claims refers to an alloy in which the element molybdenum makes up the greatest alloying fraction in at.%. In other words, in a molybdenum alloy, there is no other element which has a greater alloying fraction in at.% than Mo. The molybdenum content of the alloy in at.% will usually be at least 30 at.%, preferably at least 35 at.%, and in particular at least 40 at.%, e.g., at least 45 at.% (based on all elements present in the alloy, as in the following).

[0043] "High titanium content" as used herein and in the appended claims refers to a titanium content of at least 15 at.%, preferably at least 20 at.% and particularly at least 25 at.%, e.g., at least 30 at. %.

[0044] In one aspect, the alloy made by the instant method may further comprise iron and/or yttrium, each in a concentration of from 0.1 to 5 at.%, in particular in a concentration of from 0.3 to 3 at.%. For example, iron may be present in a concentration of from 0.5 to 3 at.%, in particular from 0.8 to 2 at.%, and/or yttrium may be present in a concentration of from 0.3 to 3 at.%, in particular from 0.5 to 2 at.%.

[0045] The alloy produced by the method of the present invention may further comprise one or more of zirconium, niobium, hafnium, and tungsten. For example, zirconium may be present in a concentration of not more than 5 at.%, in particular in a concentration of from 0.3 to 3 at.%, and/or niobium may be present in a concentration of not more than 20 at.%, in particular in a concentration of from 0.3 to 10 at.%, and/or tungsten may be present in a concentration of not more than 8 at.%, in particular in a concentration of from 0.3 to 5 at.% and/or hafnium may be present in a concentration of not more than 5 at.%, in particular in a concentration of from 0.3 to 3 at.%.

[0046] The alloy of the present invention may comprise silicon in a concentration of from 9 to 15 at.%, in particular in a concentration of from 12 to 14 at.%, and/or boron in a concentration of from 5 to 9 at.%, in particular in a concentration of from 5 to 6 at.%, and/or titanium in a concentration of from 25 to 33 at.%, in particular in a concentration of from 26 to 29 at.%.

[0047] The alloy may, for example, be formed exclusively of molybdenum, silicon, boron, titanium, iron, yttrium, niobium, tungsten, zirconium, hafnium (and unavoidable impurities), or may be formed exclusively of molybdenum, silicon, boron, titanium, iron, yttrium (or hafnium).

[0048] In another aspect of the alloy, molybdenum may be present in a concentration of from 35 to 66 at.%, in particular in a concentration of from 40 to 60 at.%, e.g., from 45 to 57 at.%, or in a concentration such that the alloy comprises 100 at.% together with the remaining alloying constituents mentioned.

[0049] In another aspect, the true density of the produced alloy may be less than or equal to 9 g/cm^3, in particular less than or equal to 8.5 g/cm^3, or less than or equal to 8 g/cm^3.

[0050] In yet another aspect, the structure of the alloy may comprise a matrix of a molybdenum mixed crystal and silicide phases, the silicide phases being formed in particular by $Mo(Ti)_5Si_3$ and/or $Mo(Ti)_5SiB_2$. For example, the alloy may comprise from 15 to 35 vol.%, in particular from 25 to 35 vol.% $Mo(Ti)_5Si_3$ and from 15 to 35 vol.%, in particular from 15 to 25 vol.% $Mo(Ti)_5SiB_2$ and from 1 to 20 vol.% minor phases. Also by way of example, the alloy may comprise from 45 to 55 vol.%, in particular from 48 to 55 vol.%, molybdenum mixed crystal or a fraction of molybdenum mixed crystal such that the alloy together with the remaining phase constituents comprises 100 vol.%.

[0051] As minor alloying constituents, one or both of niobium and tungsten may additionally be present in the alloy. The addition of niobium improves the fracture toughness and therefore the deformability or ductility, whereas tungsten improves the oxidation resistance of the alloy. Preferably, the alloy is formed exclusively of the elements molybdenum, silicon, boron, titanium, iron, yttrium, niobium, tungsten, hafnium and zirconium, wherein the fraction of niobium, tungsten, hafnium and zirconium may be 0 at.%. As is known to those skilled in the art, an alloy can comprise further elements as unavoidable impurities, wherein, however, none of these further elements should make up more than 1 at.%, preferably more than 0.1 at.%, in the alloy.

[0052] With the main and minor alloying elements, therefore, alloys can be produced by the method of the present invention which, in addition to unavoidable impurities, exclusively comprise Mo, Si, B, Ti, Fe, Y, Zr, Nb, Hf and/or W. In particular, Mo-Si-B-Ti-Fe-, Mo-Si-B-Ti-Fe-Zr-, Mo-Si-B-Ti-Fe-Y-, Mo-Si-B-Ti-Fe-Y-Nb- and Mo-Si-B-Ti-Fe-Y-Nb-W alloys can be produced, likewise a Mo-Si-B-Ti-Y alloy which does not comprise iron, although an alloy containing iron is preferred in principle.

[0053] The alloy composition can in particular also be selected in such a manner that the true density, that is to say the density without any pores or cavities, is adjusted to be less than or equal to 9 g/cm^3, in particular less than or equal to 8.5 g/cm^3, preferably less than or equal to 8 g/cm^3.

[0054] The corresponding structure of the alloy can be adjusted in such a manner that the structure has a matrix of molybdenum mixed crystal (e.g., molybdenum-titanium mixed crystal), into which the silicide phases are incorporated, wherein the silicide phases can be formed by $Mo(Ti)_5Si_3$ and/or $Mo(Ti)_5SiB_2$. In the respective silicides, therefore, molybdenum can be replaced by titanium and *vice versa.*

[0055] The molybdenum alloy made by the method of the present invention may comprise from 15 to 35 vol.%, e.g., from 25 to 35 vol.% $Mo(Ti)_5Si_3$ and from 15 to 35 vol.%, e.g., from 15 to 25 vol.% $Mo(Ti)_5SiB_2$ and from 1 to 20 vol.%, e.g., from 1 to 5 vol.%, minor phases. Minor phases can comprise various phases, in particular various mixed phases or mixed crystals of the alloying elements present in the alloy.

[0056] The molybdenum alloy may additionally comprise from 45 to 55 vol.%, in particular from 48 to 55 vol.%, molybdenum mixed crystal or a fraction of molybdenum mixed crystal such that the alloy together with the remaining phase constituents comprises 100 vol.%.

[0057] With a corresponding molybdenum alloy, in particular components of turbomachines, preferably of gas turbines or aero engines can be manufactured, wherein the components can be, in particular, rotor blades or guide vanes of the turbomachine, and in particular guide vanes or rotor vanes of rapidly running uncooled low-pressure turbines.

[0058] Advantageous properties having a balanced property profile with respect to creep resistance, static strength, fracture toughness, ductility, oxidation resistance and low specific gravity have been achieved with the following exemplary alloy compositions (figures in each case in at.%), which can also comprise small amounts of further elements as unavoidable impurities:

Mo	Si	B	Ti	Fe	Y	Zr	Nb	W	Hf
49.5	12.5	8.5	27.5	2.0	0	0	0	0	0
48.5	13.5	8.5	26.5	2.0	0	1.0	0	0	0
51.0	10.0	8.5	27.5	2.0	0	1.0	0	0	0
46.5	12.5	8.5	27.5	2.0	2.0	1.0	0	0	0
46.5	12.5	8.5	27.5	2.0	2.0	0	1.0	0	0
46.5	12.5	8.5	27.5	2.0	2.0	0	0	1.0	0
49.3	13.5	5.5	27.5	1.2	0	0	0	1.0	0
50.5	13.5	5.5	27.5	2.0	0	0	0	0	1.0
53.0	13.5	5.5	27.0	1.0	0	0	0	0	0
51.0	13.5	5.5	27.0	1.0	0	0	0	0	2.0
46.0	13.5	5.5	27.0	1.0	0	0	5.0	0	2.0

[0059] Although the present invention has been described herein with reference to particular means, materials and embodiments, the present invention is not intended to be limited to the particulars disclosed herein; rather, the present invention extends to all functionally equivalent structures, methods and uses, such as are within the scope of the appended claims.

Claims

1. Method of making a molybdenum alloy having a high titanium content and further comprising one or both of silicon

and boron, **characterized in that** the method comprises subjecting to pressureless sintering or sintering under pressure a mixture of powders which comprise (i) one or more powders of an alloy of Mo and Ti and, optionally, one or more additional metals X and/or (i') powders of Mo and of titanium nitride, and at least one of (ii) one or more powders comprising one or more powders of silicides of Mo and/or Ti and (iii) one or more powders of nitrides which comprise at least silicon nitride and/or boron nitride.

2. Method according to claim 1, **characterized in that** X is present and selected from one or more of Fe, Y, Hf, Nb, Zr, W and in particular comprises at least Fe.

3. Method according to any one of claims 1 and 2, **characterized in that** one or more powders (i) are employed.

4. Method according to claim 3, **characterized in that** the one or more powders (i) have a median particle size d50 of from 0.001 μm to 50 μm and/or the particles of (i) are substantially spherical.

5. Method according to any one of the preceding claims, **characterized in that** one or more powders (ii) are employed.

6. Method according to claim 5, **characterized in that** the one or more powders (ii) comprise powders of $MoTi_5Si_3$, Ti_5Si_3, $MoTi_5SiB_2$, Mo_3Si or a combination of two or more thereof.

7. Method according to any one of the preceding claims, **characterized in that** one or more powders (iii) are employed.

8. Method according to claim 7, **characterized in that** the one or more powders (iii) comprise at least silicon nitride powder.

9. Method according to any one of the preceding claims, **characterized in that** one or more powders (i') are employed.

10. Method according to claim 9, **characterized in that** the one or more powders (i') have a median particle size d50 of from 0.001 μm to 50 μm.

11. Method according to any one of the preceding claims, **characterized in that** the powders (i) and/or (i') and the powders (ii) and/or (iii) are combined in ratios which result in an alloy which comprises at least 35 at.% of molybdenum and preferably not more than 66 at.% of molybdenum.

12. Method according to any one of the preceding claims, **characterized in that** the powders (i) and/or (i') and the powders (ii) and/or (iii) are combined in ratios which result in an alloy which comprises at least 25 at.% of titanium and preferably not more than 33 at.% of titanium.

13. Method according to any one of the preceding claims, **characterized in that** the powders (i) and/or (i') and the powders (ii) and/or (iii) are combined in ratios which result in an alloy which comprises at least 9 at.% of silicon and preferably not more than 15 at.% of silicon.

14. Alloy which is obtainable by the method according to any one of claims 1 to 13.

15. Article which is made of or comprises the alloy according to claim 14.

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EUROPEAN SEARCH REPORT

Application Number
EP 16 19 3634

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	18 April 2017	Fodor, Anna

CATEGORY OF CITED DOCUMENTS

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2

EPO FORM 1503 03.82 (P04C01)

page 1 of 2

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EUROPEAN SEARCH REPORT

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2

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page 2 of 2

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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