



US 20160060734A1

(19) **United States**

(12) **Patent Application Publication**
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(10) **Pub. No.: US 2016/0060734 A1**

(43) **Pub. Date: Mar. 3, 2016**

(54) **CREEP- AND OXIDATION-RESISTANT
MOLYBDENUM SUPERALLOY**

Publication Classification

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(51) **Int. Cl.**
C22C 27/04 (2006.01)

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(52) **U.S. Cl.**
CPC **C22C 27/04** (2013.01)

(21) Appl. No.: **14/835,866**

(57) **ABSTRACT**

(22) Filed: **Aug. 26, 2015**

The present invention relates to a quaternary or multinary molybdenum alloy for the production of structural components, in particular of vanes of a turbomachine having the main constituents molybdenum, silicon, boron and titanium, which, as minor alloying elements, additionally comprises at least one of iron and yttrium.

(30) **Foreign Application Priority Data**

Aug. 28, 2014 (EP) 14182613.1

CREEP- AND OXIDATION-RESISTANT MOLYBDENUM SUPERALLOY

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims priority under 35 U.S.C. § 119 of European Patent Application No. 14182613.1, filed Aug. 28, 2014, the entire disclosure of which is expressly incorporated by reference herein.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to a quaternary or multinary molybdenum alloy for the production of structural components, in particular of components and preferably vanes, of a turbomachine and also corresponding components of a turbomachine, in particular of a gas turbine or of an aero engine, made of a corresponding molybdenum alloy.

[0004] 2. Discussion of Background Information

[0005] In the prior art, ternary molybdenum alloys are already known which have molybdenum, silicon and boron as main alloying constituents. Such alloys, however, when used at high temperatures, that is to say for example, in the temperature range from 900° C. to 1300° C., do not exhibit sufficient creep strength. Also, attempts to increase the creep strength with very finely dispersing particles of titanium, zirconium and carbon, as is described, for example, in WO 85/03953 A1, the entire disclosure of which is incorporated by reference herein, have likewise not yet led to the desired results. Correspondingly, attempts have been made, as described in WO 85/03953 A1, to improve the creep strength using other alloying elements, such as titanium, zirconium, hafnium, boron, carbon, aluminum, thorium, chromium, manganese, niobium, tantalum, rhenium and tungsten.

[0006] However, for use of such an alloy for forming structural components, in particular components such as, preferably vanes, of a turbomachine, which is not considered in WO 85/03953 A1, and which are used at high temperatures, it is not only necessary to have a high creep strength, but such an alloy must also be able to withstand the ambient conditions in such a manner that, inter alia, a good oxidation resistance is required. In WO 2005/022065, the entire disclosure of which is incorporated by reference herein, oxidation protective coatings are described which are said to ensure oxidation resistance, inter alia for molybdenum alloys containing silicon and boron.

[0007] Furthermore, however, it is also necessary that further properties such as, for example, the specific weight and/or the density of the material, are suitable for the intended purpose, since, for example, for the production of rotor vanes which rotate at high speeds, light materials having a low specific gravity are advantageous, since they cause lower centrifugal forces and can be accelerated with less energy expenditure. Ternary molybdenum alloys having the alloying main constituents molybdenum, silicon and boron, however, have a very high density of greater than 9 g/cm³. Although quaternary molybdenum alloys having the main alloying constituents molybdenum, silicon, boron and titanium permit a reduction of the specific gravity or the density owing to the replacement of the heavy molybdenum by the lighter titanium, owing to the formation of titanium oxides, the oxygen diffusion through an edge oxide layer that forms is increased, and so the oxidation resistance is adversely impaired.

[0008] In addition, to achieve adequate tolerance to damage and component life, it is necessary that the molybdenum alloys have a correspondingly high deformability or ductility over the entire temperature usage range, which is frequently not the case with molybdenum alloys known from the prior art.

[0009] The documents Daniel Schliephake et al., High—Temperature Creep and Oxidation Behavior of Mo-Si-B Alloys with High Ti Contents, Metallurgical and Material Transactions A Volume 45A, March 2014 and Ying Yang et al., Effects of Ti, Zr, and Hf on the phase stability of Mo₃Si+Mo₅SiB₂ alloys at 1600° C., Acta Materialia 58 (2010) 541-548 disclose quaternary Mo-Si-B-Ti alloys.

[0010] The documents T. Sossaman et al., Influence of minor Fe addition on the oxidation performance of Mo-Si-B alloys, Scripta Materialia 67 (2012) 891-894, B. Gorr et al., High—temperature oxidation behavior of Mo-Si-B-based and Co-Re-Cr-based alloys, Intermetallics 48 (2014), 34-43, S. Majumdar et al., Effect of Yttrium Alloying on Intermediate to High—Temperature Oxidation Behavior of Mo-Si-B Alloys, Metallurgical and Materials Transactions A, Volume 44A, May 2013, 2243-2257 and U.S. 2014/0141281A1 disclose ternary Mo-Si-B alloys having differing alloying elements. The document U.S. 2004/0219295A1 additionally discloses oxidation protective coatings for Mo-Si-B alloys.

[0011] The entire disclosures of all of the documents mentioned above are incorporated by reference herein.

[0012] In view of the foregoing, it would be desirable to have available a molybdenum alloy which has a balanced property profile and has, especially for high-temperature applications in the field of turbomachines, an adequate static strength, good creep resistance, sufficient ductility and an excellent oxidation resistance in the temperature range from 900° C. to 1300° C.

SUMMARY OF THE INVENTION

[0013] The present invention provides a molybdenum alloy for the production of structural components, in particular of vanes of a turbomachine, comprising the main constituents molybdenum, silicon, boron and titanium. The alloy further comprises, as minor alloying elements, one or both of iron and yttrium.

[0014] In one aspect, the alloy may comprise iron and/or yttrium, each at a fraction of from 0.1 to 5 at. %, in particular from 0.3 to 3 at. %. For example, iron may be present at a fraction of from 0.5 to 3 at. %, e.g., from 0.8 to 1.6 at. %, and/or yttrium may be present at a fraction of from 0.3 to 2 at. %, e.g., from 0.5 to 1.5 at. %.

[0015] In another aspect, the alloy of the present invention may further comprise one or more of zirconium, niobium, tungsten. For example, zirconium may be present at a fraction of less than or equal to 5 at. %, e.g., from 0.3 to 3 at. %, and/or niobium may be present at a fraction of less than or equal to 20 at. %, e.g., from 0.3 to 15 at. %, and/or tungsten may be present at a fraction of less than or equal to 8 at. %, e.g., from 0.3 to 5 at. %.

[0016] In yet another aspect, the alloy of the present invention may comprise silicon at a fraction of from 9 to 15 at. %, e.g., from 13 to 14 at. %, and/or boron in a fraction of from 5 to 9 at. %, e.g., from 5 to 6 at. %, and/or titanium at a fraction of from 25 to 33 at. %, e.g., from 26 to 29 at. %.

[0017] In a still further aspect, the alloy may be formed exclusively of molybdenum, silicon, boron, titanium, iron,

yttrium, niobium, tungsten, zirconium, or may be formed exclusively of molybdenum, silicon, boron, titanium, iron, yttrium.

[0018] In another aspect of the alloy of the present invention, molybdenum may be present at a fraction of from 35 to 66 at. %, e.g., from 40 to 55 at. %, or from 45 to 50 at. %, or at a fraction such that the alloy comprises 100 at. % together with the remaining alloying constituents mentioned.

[0019] In another aspect, the true density of the alloy of the present invention may be less than or equal to 9 g/cm³, e.g., less than or equal to 8.5 g/cm³, or less than or equal to 8 g/cm³.

[0020] In 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)₅Si₃ and/or (Mo,Ti)₅SiB₂. For example, the alloy may comprise from 15 to 35 vol. %, e.g., from 25 to 35 vol. % (Mo,Ti)₅Si₃ and from 15 to 35 vol. %, e.g., from 15 to 25 vol. % (Mo,Ti)₅SiB₂ and from 1 to 20 vol. % minor phases. Also by way of example, the alloy may comprise from 45 to 55 vol. %, e.g., 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. %.

[0021] The present invention also provides a component of a turbomachine. The component is formed of a molybdenum alloy according to the present invention as set forth above (including the various aspects thereof). Further, the component may be a guide vane or a rotor blade of an industrial gas turbine or an aero engine.

[0022] As set forth above, it is proposed according to the invention to develop a molybdenum alloy, in particular a quaternary or multinary molybdenum alloy for the production of structural components, and in particular of components such as vanes of a turbomachine, in such a manner that, as main constituents, molybdenum, silicon, boron and titanium are provided, whereas as minor alloying elements, at least one of the elements iron or yttrium is additionally alloyed. Furthermore, the molybdenum alloy according to the invention can also have further minor alloying elements, namely, in particular, niobium, tungsten and/or zirconium.

[0023] A molybdenum alloy is taken to mean an alloy in which the element molybdenum makes up the greatest alloying fraction in at. % and/or vol. %. In other words, in a molybdenum alloy, there is no other element which has a greater alloying fraction in at. % and/or vol. %.

[0024] Main alloying constituents are taken to mean the alloying elements which are present in any case in the alloy and of the elements which are present in any case in the alloy, have the highest fractions of the alloy. Minor alloying elements are then taken to mean those alloying elements that either do not absolutely need to be in the alloy or, if they are in the alloy, are present in all cases only in a lower fraction.

[0025] The titanium fraction in the alloy according to the invention substantially causes a reduction in density. The addition of at least one of the elements iron and yttrium to a quaternary molybdenum alloy having the main alloying constituents molybdenum, silicon, boron and titanium leads to an improvement in the property profile, since iron, in combination with titanium, stabilizes the fractions of the various phase constituents in the microstructure and thus has the effect that the deformability and good creep resistance are retained in an alloy of low density (Ti fraction) and an adequate oxidation resistance can be achieved. Since yttrium likewise improves the deformability, fracture toughness and oxidation resis-

tance, it can be provided as an alternative to or as a supplement to iron. In particular, an alloy which simultaneously comprises iron and yttrium is advantageous, since the advantages of both alloying constituents can be used additively and synergistically.

[0026] By adding zirconium, the brittleness of the material can be reduced, and therefore the deformability improved. The minor alloying elements iron and yttrium can be present each at a fraction from 0.1 to 5 at. %, e.g., from 0.3 to 3 at. % in the alloy, in order to effect the described property improvements.

[0027] It has proved to be particularly advantageous when iron is present in the alloy at a fraction from 0.5 to 3 at. %, e.g., from 0.8 to 1.6 at. %, and when additionally yttrium is also further present in the alloy at a fraction from 0.3 to 2 at. %, e.g., from 0.5 to 1.5 at. %.

[0028] Zirconium will usually be present in the alloy at a fraction of less than or equal to 5 at. %, e.g., from 0.3 to 3 at. %.

[0029] As further minor alloying constituents, one or both of niobium and tungsten can additionally be present in the alloy. The addition of niobium improves the fracture toughness and therefore the deformability or ductility, whereas tungsten in turn improves the oxidation resistance.

[0030] Niobium may further be added to the alloy at a fraction of less than or equal to 20 at. %, e.g., at from 0.3 to 15 at. %, whereas tungsten may be present at a fraction of less than or equal to 8 at. %, e.g., from 0.3 to 5 at. %.

[0031] The main alloying constituents can vary in differing ranges in the composition, wherein silicon may be present in the alloy at a fraction of 9-15 at. %, e.g., 13-14 at. %. Boron, in turn, may occur in the alloy at a fraction of 5-9 at. %, e.g., 5-6 at. %, whereas titanium may be present at a fraction of 25-33 at. %, e.g., 26-29 at. %.

[0032] Preferably, the alloy is formed exclusively of the elements molybdenum, silicon, boron, titanium, iron, yttrium, niobium, tungsten and zirconium, wherein the fraction of niobium, tungsten 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.

[0033] Molybdenum may be present at a fraction from 35-66 at. %, e.g., 40-55 at. %, or 45-50 at. %, or at a fraction such that the alloy gives 100 at. % together with the remaining alloying constituents mentioned. Furthermore, the data with respect to the chemical composition are not to be taken to mean that for each alloying element the maximum values or minimal values can be selected, but the range figures for the alloy composition merely indicate in which ranges the individual chemical elements can be present in the alloy, wherein the individual alloying elements can mutually replace each other in such a manner that when an alloying element is present in the range of its maximum fraction, other alloying elements are only present in the alloy at smaller fractions. In addition, the alloy comprises unavoidable impurities which are not explicitly stated.

[0034] With the main and minor alloying elements, therefore, alloys can be formed which, in addition to unavoidable impurities, exclusively comprise Mo, Si, B, Ti, Fe, Y, Zr, Nb 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 formed, likewise a Mo-Si-B-Ti-Y

alloy which does not comprise iron, wherein, however, an alloy containing iron is preferred in principle.

[0035] 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/cm³, e.g., less than or equal to 8.5 g/cm³, or less than or equal to 8 g/cm³.

[0036] The corresponding structure of the alloy can be adjusted in such a manner that the structure has a matrix of molybdenum mixed crystal, into which the silicide phases are incorporated, wherein the silicide phases can be formed by (Mo, Ti)₅Si₃ and/or (Mo, Ti)₅SiB₂. In the respective silicides, therefore, molybdenum can be replaced by titanium and vice versa.

[0037] The molybdenum alloy may comprise from 15 to 35 vol. %, e.g., from 25 to 35 vol. % (Mo, Ti)₅Si₃ and from 15 to 35 vol. %, e.g., from 15 to 25 vol. % (Mo, Ti)₅SiB₂ 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.

[0038] The molybdenum alloy may additionally comprise from 45 to 55 vol. %, e.g., 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. %.

[0039] Here also, in a similar manner to the statements on chemical composition, the statements on the ranges of values of the phase constituents are not to be taken to mean the maximum values or minimal values can be selected for every phase, but the range figures for the phase composition merely indicate in which ranges the individual phases can be present in the alloy, wherein the individual phases, depending on the composition and the production conditions, can be mutually exchanged within the stated limits.

[0040] 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.

Exemplary Embodiments

[0041] 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:

Molybdenum	Silicon	Boron	Titanium	Iron	Yttrium	Zirconium	Niobium	Tungsten
49.5	12.5	8.5	27.5	2.0	0	0	0	0
48.5	13.5	8.5	26.5	2.0	0	1.0	0	0
51.0	10.0	8.5	27.5	2.0	0	1.0	0	0
46.5	12.5	8.5	27.5	2.0	2.0	1.0	0	0
46.5	12.5	8.5	27.5	2.0	2.0	0	1.0	0
46.5	12.5	8.5	27.5	2.0	2.0	0	0	1.0
49.3	13.5	5.5	27.5	1.2	0	0	0	1.0

[0042] 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.

What is claimed is:

1. A molybdenum alloy for the production of structural components, wherein the alloy comprises molybdenum, silicon, boron and titanium as main constituents and further comprises one or both of iron and yttrium as minor alloying elements.

2. The molybdenum alloy of claim 1, wherein the alloy further comprises one or more of zirconium, niobium and tungsten as additional minor alloying elements.

3. The molybdenum alloy of claim 1, wherein the alloy comprises from 0.1 to 5 at. % of each of iron and/or yttrium.

4. The molybdenum alloy of claim 1, wherein the alloy comprises from 0.3 to 3 at. % of each of iron and/or yttrium.

5. The molybdenum alloy of claim 1, wherein the alloy comprises from 0.5 to 3 at. % of iron and from 0.3 to 2 at. % of yttrium.

6. The molybdenum alloy of claim 5, wherein the alloy comprises from 0.8 to 1.6 at. % of iron and from 0.5 to 1.5 at. % of yttrium.

7. The molybdenum alloy of claim 2, wherein the alloy comprises less than or equal to 5 at. % of zirconium.

8. The molybdenum alloy of claim 2, wherein the alloy comprises less than or equal to 20 at. % of niobium.

9. The molybdenum alloy of claim 2, wherein the alloy comprises less than or equal to 8 at. % of tungsten.

10. The molybdenum alloy of claim 1, wherein the alloy comprises from 9 to 15 at. % of silicon, from 5 to 9 at. % of boron, and from 25 to 33 at. % of titanium.

11. The molybdenum alloy of claim 10, wherein the alloy comprises from 13 to 14 at. % of silicon, from 5 to 6 at. % of boron, and from 26 to 29 at. % of titanium.

12. The molybdenum alloy of claim 1, wherein the alloy is formed exclusively by molybdenum, silicon, boron, titanium, iron, yttrium, niobium, tungsten, zirconium.

13. The molybdenum alloy of claim 1, wherein the alloy is formed exclusively by molybdenum, silicon, boron, titanium, iron, yttrium.

14. The molybdenum alloy of claim 1, wherein the alloy comprises from 35 to 66 at. % of molybdenum.

15. The molybdenum alloy of claim 1, wherein a true density of the alloy is less than or equal to 9 g/cm³.

16. The molybdenum alloy of claim 1, wherein the alloy comprises a matrix of a molybdenum mixed crystal and one or more silicide phases.

17. The molybdenum alloy of claim 16, wherein the one or more silicide phases comprise (Mo, Ti)₅Si₃ and/or (Mo, Ti)₅SiB₂.

18. The molybdenum alloy of claim **16**, wherein the alloy comprises from 15 to 35 vol. % of $(\text{Mo,Ti})_5\text{Si}_3$, from 15 to 35 vol. % of $(\text{Mo,Ti})_5\text{SiB}_2$, and from 1 to 20 vol. % of one or more minor phases.

19. The molybdenum alloy of claim **16**, wherein the alloy comprises from 45 to 55 vol. % of molybdenum mixed crystal.

20. A component of a turbomachine, wherein the component is formed of the molybdenum alloy of claim **1**.

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