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(54) **METHOD OF MANUFACTURING AN OXIDATION-RESISTANT COMPONENT OF A MOLYBDENUM BASE ALLOY**

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(57) **ABSTRACT**

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The present invention relates to a method of producing a component of an Mo base alloy which is protected against high-temperature oxidation, and a correspondingly produced component.

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The method comprises:

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provision of a semifinished part composed of a Mo base alloy,

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provision of an Si-containing slip or of a Si-containing powder,

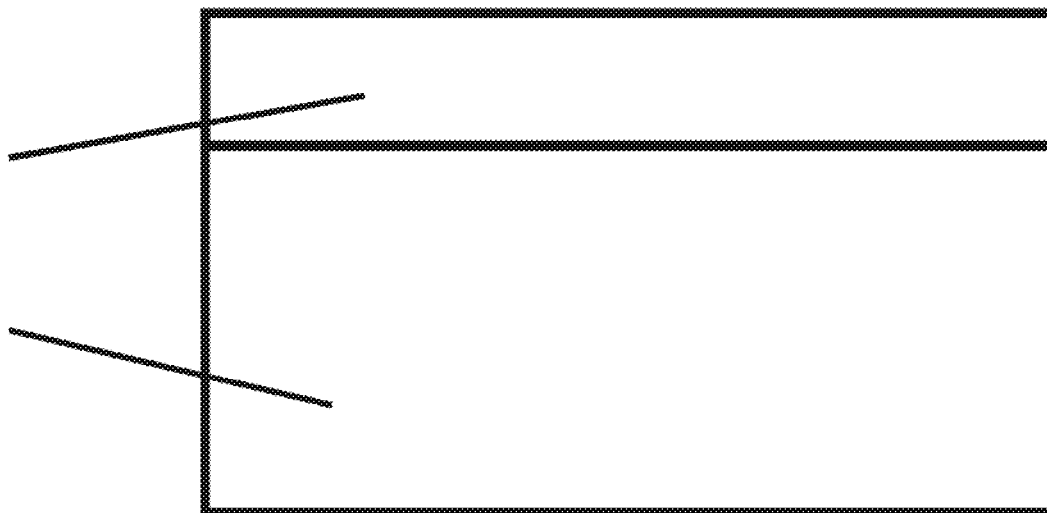
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application of the slip to the semifinished part and diffusion annealing of the semifinished part together with the applied slip to form a Si-containing outer layer or transfer of at least part of the silicon present in the powder via the gas phase to the semifinished part by means of a diffusion heat treatment of the semifinished part together with the Si-containing powder which is arranged at a distance from the semifinished part.

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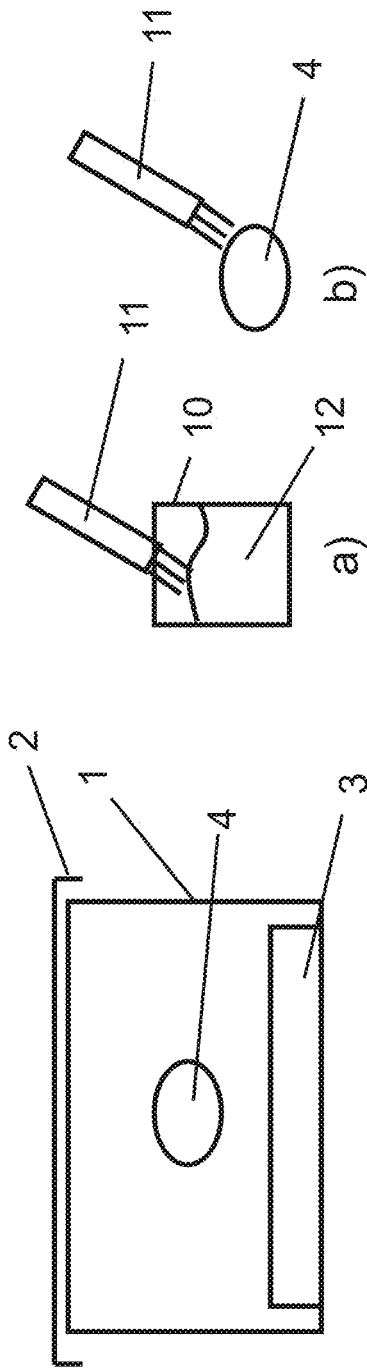


Fig. 1

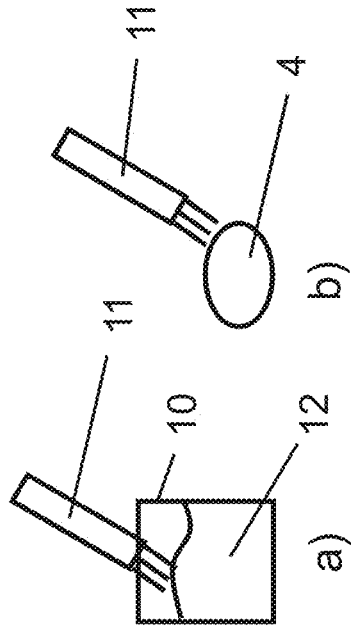


Fig. 2

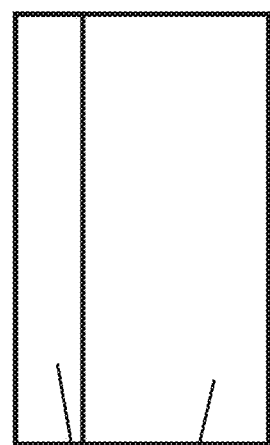


Fig. 3

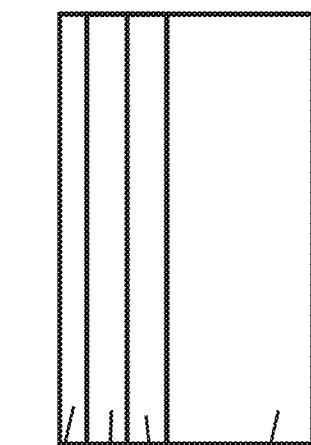


Fig. 4

## METHOD OF MANUFACTURING AN OXIDATION-RESISTANT COMPONENT OF A MOLYBDENUM BASE ALLOY

### CROSS-REFERENCE TO RELATED APPLICATIONS

**[0001]** The present application claims priority under 35 U.S.C. § 119 of German Patent Application No. 102018215313.2, filed Sep. 10, 2018, the entire disclosure of which is expressly incorporated by reference herein.

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

**[0002]** The present invention relates to a method of improving the high-temperature oxidation resistance of molybdenum-based alloys or molybdenum base alloys. In addition, the present invention relates to a correspondingly produced component composed of a molybdenum base alloy which can, in particular, be a component of a turbomachine and in particular an aircraft engine.

#### 2. Discussion of Background Information

**[0003]** Molybdenum and its alloys are interesting materials for high-temperature applications because of the high melting point and the good corrosion resistance. However, in order to avoid high-temperature oxidation it is necessary to enrich at least the surface regions of a corresponding component composed of molybdenum or a molybdenum-based alloy with silicon to such an extent that the silicon together with oxygen forms a slowly growing silicon oxide layer which protects the component against further oxidation.

**[0004]** For this purpose, subjecting components composed of molybdenum-based alloys to a diffusion heat treatment in a powder packing composed of silicon-containing powder, so that the regions of the molybdenum-based component which are close to the surface can be enriched in silicon by diffusion processes, is already known. However, the known powder pack method has the disadvantage that it requires very long processing times. Furthermore, caking of the powder particles which surround the component can occur in the diffusion heat treatment, with the result that the component has to be released from a solid shell after the corresponding diffusion heat treatment, which can lead to damage to the component. In addition, the removal of the caked silicon-containing powder is time-consuming.

**[0005]** It would therefore be advantageous to have available a method by means of which a molybdenum-based component resistant to high-temperature oxidation can be produced in a simpler manner compared to the prior art, with, in particular, improved process efficiency being ensured. However, the component should also be reliably protected against high-temperature oxidation.

### SUMMARY OF THE INVENTION

**[0006]** The present invention provides a method having the features of the independent method claim. A component having the features of the independent product claim is likewise provided by the present invention. Advantageous embodiments are subject matter of the dependent claims.

**[0007]** In order to solve the problems arising in the prior art, the invention proposes applying the silicon via either a liquid or a gaseous phase to an appropriate region to be

protected against high-temperature oxidation on a molybdenum-based semifinished part in order to produce a correspondingly protected component. Accordingly, the method of the invention encompasses not only the provision of a molybdenum-based semifinished part but also the provision of either a silicon-containing slip or a silicon-containing powder.

**[0008]** The silicon-containing slip is applied to the regions of the semifinished part which are to be protected against high-temperature oxidation, with diffusion annealing subsequently being carried out so that silicon can diffuse from the slip into at least the regions close to the surface of the molybdenum-based semifinished part in order to provide silicon there for formation of a silicon oxide layer.

**[0009]** The silicon-containing powder is provided in order to introduce silicon into the region close to the surface of the semifinished part via the gas phase. However, instead of arranging the semifinished part in a powder packing, the silicon-containing powder is arranged at a distance from the semifinished part to be protected, so that the silicon can diffuse into the surface of the semifinished part in a diffusion heat treatment on the semifinished part with the silicon-containing powder.

**[0010]** After the regions close to the surface of the semifinished part have been enriched in silicon, the semifinished part prepared in this way can additionally be conditioned by means of an oxidation treatment, so that a thin, slowly growing silicon oxide layer which protects the component against further oxidation is formed on the component. The conditioning can be carried out by means of an oxidation treatment at a temperature of more than about 900° C., in particular in the temperature range from about 1000° C. to about 1400° C., in particular at about 1380° C., for a time of up to about 2 to 100 hours, preferably from about 10 to 15 hours, in particular about 12 hours.

**[0011]** Heating to the treatment temperature and cooling from the treatment temperature can be carried out slowly, in particular at a heating and/or cooling rate of less than or equal to about 10 K/min.

**[0012]** Conditioning can be carried out in ambient air or under specifically prepared oxygen-containing gases.

**[0013]** As semifinished part, it is possible to use, for example, a semifinished part composed of Mo alloys with Si and/or titanium and/or boron and/or Fe. The proportion of Si can here be in the range from about 5 to about 25 at. %, while Ti can be present in the alloy in an amount in the range from 0 to about 30 at. % and B can be present in an amount in the range from about 5 to about 15 at. %. In addition, such an Mo base alloy can comprise up to about 5 at. % of iron, with any combinations of the alloying elements being possible while the respective balance is formed by Mo.

**[0014]** The enrichment of at least subregions of the surfaces of the semifinished part with silicon via application of a slip or via the gas phase is, in the present invention, carried out in particular directly on the above-described materials of the semifinished parts, so that no additional intermediate layers on the surface of the semifinished part are necessary.

**[0015]** In the diffusion heat treatment for transferring the silicon via the gas phase from the silicon-containing powder into the molybdenum-based semifinished part provided, halogens can be present in the silicon-containing powder in order to improve the diffusion of the silicon into the semifinished part. As halogen-containing compounds, it is possible to use NH<sub>4</sub>F, NH<sub>4</sub>Cl or NaF.

[0016] Furthermore, the silicon-containing powder for transferring the silicon via the gas phase into the semifinished part can contain additional constituents in addition to the silicon powder. In particular, it is possible to use a mixture of silicon powder and aluminum oxide powder. The additional constituents of the powder can serve as filler material and prevent caking of the powder. Furthermore, additional constituents can influence the total amount of silicon and control the gas-phase activity of the silicon. The silicon-containing powder for transferring the silicon via the gas phase into the semifinished part can preferably be arranged in a ceramic vessel underneath the semifinished part during the diffusion heat treatment.

[0017] The diffusion heat treatment of the semifinished part with the silicon-containing powder arranged at a distance can be carried out at a temperature of more than about 900° C., in particular in the temperature range from about 1100° C. to about 1300° C. The hold time at the appropriate heat treatment temperature can be in the range from about 0.5 to 5 hours and preferably in the range from about 1 to 2 hours. For the diffusion heat treatment, the semifinished part can be arranged together with the powder in a protective gas atmosphere, for example an argon atmosphere or a hydrogen atmosphere.

[0018] The slip can comprise silicon-containing powder or silicon powder and a solvent and a binder.

[0019] Possible solvents are, for example, water, alcohols or alcoholic solvents or liquid-organic solvents. As binders, it is possible to use, for example, polyvinyl alcohols or resins. The slip can contain further constituents such as Mo, W, B, Ta, Cr, Fe, Ti and alloys thereof, with these components either being able to be present as alloying constituents in the silicon-containing powder or being able to be added as separate powder particles. For example, constituents for controlling the silicon activity or matching the coefficients of thermal expansion of the layer produced and of the substrate or semifinished part can be added.

[0020] Furthermore, the slip can contain further constituents in the form of oxide, carbide or nitride particles which can be incorporated into a silicon oxide layer on the component in order to reduce the viscosity of the oxide layer and prevent running-off of the oxide layer at high use temperatures of the component. Accordingly, the slip can contain aluminum oxide, zirconium oxide, yttrium oxide, hafnium oxide, neodymium oxide, silicon carbide and/or silicon nitride.

[0021] The powder particles can be present with an average particle size or a maximum particle size of from about 0.5 μm to about 100 μm and in particular about 1-60 μm in the slip.

[0022] The slip can be applied to the semifinished part by dipping, spraying, printing and in particular by screenprinting or template printing.

[0023] The diffusion annealing of the semifinished part with the applied slip can be carried out at temperatures above about 900° C. and in particular at temperatures of from about 1000° C. to about 1400° C. The hold time at the annealing temperature can be in the range from about 1 to 3 hours and in particular up to about 2 hours.

#### Definitions

[0024] When indications of position are given in the present description, for example bottom, top or the like, these indications are based on the usual position during use

in the gravitational system of the Earth, so that top indicates the position remote from the Earth's surface, while bottom is localized in the direction toward the Earth's surface.

[0025] For the purposes of the present invention, a molybdenum-based alloy or molybdenum base alloy is an alloy whose largest constituent is molybdenum. Alloys in which one alloying component is present in an equal or similar proportion to that of molybdenum in the alloy are also intended to be included under the term molybdenum-based alloy or molybdenum base alloy. Accordingly, the term molybdenum-based alloys or molybdenum base alloys refers to alloys which comprise more than 50 percent by weight or atom percent of molybdenum.

[0026] For the purposes of the present invention, high-temperature oxidation is an oxidation at temperatures which are higher than normal ambient temperatures and in particular higher than about 500° C., preferably higher than about 1000° C.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0027] The accompanying drawings schematically show in

[0028] FIG. 1 a depiction of an arrangement for producing an Si-containing outer layer via the gas phase,

[0029] FIG. 2 in subfigures a) and b), a depiction of the application of a slip to a semifinished part,

[0030] FIG. 3 a depiction of a cross section through the outer region of a semifinished part which has been treated as shown in FIG. 1 or FIG. 2, and in

[0031] FIG. 4 a depiction of a cross section through the outer region of the semifinished part of FIG. 2 after conditioning.

#### DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

[0032] The particulars shown herein 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 in combination with the drawings making apparent to those of skill in the art how the several forms of the present invention may be embodied in practice.

[0033] In various working examples, technical-grade molybdenum, a molybdenum alloy comprising 9 at. % of silicon and 8 at. % of boron with molybdenum as balance and also a molybdenum alloy comprising 27 at. % of titanium, 13.5 at. % of silicon, 5.5 at. % of boron and 1 at. % of iron with molybdenum as balance have been used as materials of the treated semifinished parts. In the case of Mo base alloys, oxides such as La<sub>2</sub>O<sub>3</sub> can additionally be added to the material. An overview of alloys from which the semifinished part can be made is given in the following table:

alloy No.	Proportion in at. %										
	Mo	Si	Ti	B	Fe	Nb	Hf	Al	Cr	W	V
1	Balance	9	8								
2	Balance	13.5	27	5.5	1						
3	Balance	9	8			2.7					

[0034] FIG. 1 shows an example of an arrangement for producing an Si-containing outer layer in a semifinished part 4 via the gas phase. For this purpose, a vessel 1, for example made of aluminum oxide, which has a lid 2 and in which a silicon powder containing  $\text{NH}_4\text{F}$  is present is provided. The semifinished part 4 to be treated is located above the silicon powder so that when the vessel 1 is heated to a temperature of about  $1190^\circ\text{C}$ . in an argon atmosphere for a time of 2 hours, silicon can diffuse into the outer layer of the semifinished part 4.

[0035] The diffusion heat treatment results in formation of an outer region of the semifinished part 4 as is shown in cross section in FIG. 3. A silicide layer 6 has been formed on top of the base material 5 by inward diffusion of silicon.

[0036] After the formation of the silicide layer 6 by means of the heat treatment under an argon atmosphere, as has been shown schematically in FIG. 1, the semifinished part 4 is aged in air at a temperature of about  $1400^\circ\text{C}$ . for 8 hours so that a silicate layer 8 is formed on top of the silicide layer 6 by oxidation of the silicon, while an interdiffusion layer 7 which serves as silicon reservoir is formed between the silicide layer 6 and the base material. This structure of the outer region is shown in FIG. 4.

[0037] FIG. 2 shows, in the subfigures a) and b), an alternative working example in which the silicide layer 6 is formed by a slip 12, which is present in a vessel 10, being applied by means of a brush 11 to the semifinished part 4 and drying at about  $50^\circ\text{C}$ . subsequently being carried out. A heat treatment under reduced pressure at  $1400^\circ\text{C}$ . for 1 hour is subsequently carried out so that silicon can once again penetrate into the base material 5 of the semifinished part 4 and a silicide layer 6, as depicted in FIG. 3, is formed. The semifinished part 4 which has been enriched with silicon is appropriately conditioned so that formation of the outer region as depicted in FIG. 4 and as has been described above occurs.

[0038] The enrichment with silicon by means of the slip process can of course be applied to all molybdenum-containing materials in the same way as the silicon gas-phase coating procedure.

[0039] In one working example, the slip is formed by a silicon powder having a particle size of  $45\ \mu\text{m}$  in an aqueous solution, with additional components, for example boron powder having a particle size of  $35\ \mu\text{m}$  or the like, being able to be added to the slip solution.

[0040] Although the present invention has been described in detail with the aid of the working examples, it will be self-evident to a person skilled in the art that the invention is not restricted to these working examples but instead that modifications made by omitting individual features or different combinations of features may be made without going outside the scope of protection of the accompanying claims. In particular, the present disclosure includes all combinations of the individual features indicated in the various working examples, so that individual features which have been described only in connection with one working

example can also be used in other working examples or combinations of individual features which are not explicitly presented.

1.-13. (canceled)

14. A method of producing a component of a Mo base alloy which is protected against high-temperature oxidation, wherein the method comprises:

provision of a semifinished part composed of a Mo base alloy,

provision of a Si-containing slip which comprises powder of at least one of Mo, W, B, Ta, Cr, Fe, Ti and alloys thereof or of a Si-containing powder which comprises a mixture of Si and  $\text{Al}_2\text{O}_3$  powders,

(a) application of the slip to the semifinished part and diffusion annealing of the semifinished part together with the applied slip to form a Si-containing outer layer or

(b) transfer of at least part of the silicon present in the powder via a gas phase to the semifinished part by a diffusion heat treatment of the semifinished part together with the Si-containing powder which is arranged at a distance from the semifinished part but in a vicinity of the semifinished part.

15. The method of claim 14, wherein a molybdenum silicide or molybdenum disilicide layer is formed on at least part of the surface of the component as a result of the diffusion annealing or the diffusion heat treatment.

16. The method of claim 14, wherein after the diffusion annealing or the diffusion heat treatment conditioning of the component by a high-temperature oxidation at a temperature above  $900^\circ\text{C}$ . is carried out.

17. The method of claim 16, wherein the conditioning is carried out at a temperature of from  $1000^\circ\text{C}$ . to  $1400^\circ\text{C}$ . for from 2 hours to 100 hours.

18. The method of claim 14, alternative (b), wherein the powder for transferring the silicon via the gas phase comprises one or more halogens.

19. The method of claim 18, wherein the powder comprises one or more of  $\text{NH}_4\text{F}$ ,  $\text{NH}_4\text{Cl}$ , and  $\text{NaF}$ .

20. The method of claim 14, alternative (b), wherein the powder for transferring the silicon via the gas phase is arranged in a vessel underneath the semifinished part.

21. The method of claim 14, alternative (b), wherein the diffusion heat treatment is carried out at a temperature above  $900^\circ\text{C}$ .

22. The method of claim 21, wherein the diffusion heat treatment is carried out at a temperature of from  $1000^\circ\text{C}$ . to  $1300^\circ\text{C}$ ., with a hold time at the temperature of from 0.5 to 5 hours.

23. The method of claim 21, wherein the diffusion heat treatment is carried out under a protective gas atmosphere.

24. The method of claim 14, alternative (a), wherein the slip comprises Si powder or Si-containing powder, a solvent and a binder.

25. The method of claim 24, wherein the binder comprises a polyvinyl alcohol and/or a resin.

26. The method of claim 14, alternative (a), wherein the slip comprises powder of at least one of aluminum oxide, zirconium oxide, yttrium oxide, hafnium oxide, neodymium oxide, silicon carbide, silicon nitride.

27. The method of claim 14, alternative (a), wherein the slip comprises powder particles having an average or maximum particle size of from 0.5 to  $100\ \mu\text{m}$ .

**28.** The method of claim **14**, alternative (a), wherein the slip is applied by dipping the semifinished part into the slip, spraying the slip onto the semifinished part or printing the slip onto the semifinished part.

**29.** The method of claim **14**, alternative (a), wherein the slip is applied by onto the semifinished part by screen printing or template printing.

**30.** The method of claim **14**, alternative (a), wherein the diffusion annealing is carried out at a temperature above 900° C.

**31.** The method of claim **30**, wherein the diffusion annealing is carried out at a temperature of from 1000° C. and 1400° C., with a hold time at the temperature of from 1 minute to 3 hours.

**32.** A component of a Mo base alloy which is protected against high-temperature oxidation, wherein the component is produced by the method of claim **14**.

**33.** The component of claim **32**, wherein the component is a component of a turbomachine.

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