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(54) **PRODUCTION OF ALLOYS BASED ON
TITANIUM ALUMINIDES**

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(57) **ABSTRACT**

In an alloy based on titanium aluminides, metal droplets are obtained from a titanium aluminide metal melt. The metal droplets are enriched with halogens resulting in halogen-enriched titanium aluminide metal droplets. The alloy is molded from the halogen-enriched titanium aluminide metal droplets by, preferably hot isostatic, pressing. Titanium aluminide powder can be heated in a container, for a predetermined period of time, wherein an atmosphere, enriched with halogens, is or will be provided in the container, so that a halogen-enriched titanium aluminide metal powder is formed, or metal droplets are formed from a titanium aluminide metal melt. The metal droplets are enriched with halogens so that halogen-enriched titanium aluminide metal droplets result. Subsequently, the alloy is molded from the halogen-enriched titanium aluminide metal droplets.

PRODUCTION OF ALLOYS BASED ON TITANIUM ALUMINIDES

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application is a continuation of and claims priority to International Patent Application No. PCT/EP2008/003173 filed on Apr. 21, 2008, which claims priority to German Patent Application No. 10 2007 032 406.7 filed on Jul. 10, 2007, subject matter of these patent documents is incorporated by reference herein in its entirety.

FIELD OF THE INVENTION

[0002] The invention relates to a method for the production of an alloy based on titanium aluminides.

BACKGROUND OF THE INVENTION

[0003] Alloys, based on titanium aluminides, prepared using melt metallurgical and powder metallurgical techniques, with a specified alloy composition of titanium and aluminum and, optionally, further components such as niobium, boron, chromium, molybdenum, manganese and vanadium etc., as well as carbon in different compositions are known in the prior art.

[0004] Titanium aluminide alloys have properties, which are particularly advantageous for use as a light-weight construction material, in particular for high temperature applications. Because of their strength and creep properties at high temperatures, these light-weight construction materials based on titanium aluminides open up possibilities for manufacturing mechanically stressed components in high temperature technology, such as turbine blades in aircraft construction, final stage impellers, engine valves, etc. Moreover, because of their low density (approximately 3.8 to 4.3 g/cm³), their use as a replacement for nickel-based super alloys, which typically have a density of 8.5 g/cm³, suggests itself.

[0005] The formulation of titanium aluminide alloys is limited by their limited resistance to oxidation to temperatures below about 750° C. Moreover, it is known that the oxidation behavior is improved clearly by a slight amount of halogens in the surface of the titanium aluminide material because of the so-called halogen effect, by means of which the areas of use of the materials can be extended to temperatures above about 1000° C.

[0006] For example, the DE-A-103 51 946 discloses a method for the treatment of the surface of a component, consisting of a titanium aluminide alloy, for improving its oxidation resistance. Furthermore, the DE-C-196 27 605 discloses a method for increasing the corrosion resistance of alloys based on titanium aluminide, wherein halogens are transferred by the process of ion implantation into the surface of the material.

[0007] Furthermore, products of an intermetallic compound of a Ti—Al system with a high resistance to oxidation and wear, and a method for the production of these products are described in DE-T-693 09 167.

[0008] It is an object of the present invention to provide titanium aluminide alloys with a high oxidation resistance, wherein, when the alloys are used or employed, any damage to the alloy in the surface will not have an effect on the oxidation resistance. Moreover, it is an object of the invention to provide a component of a corresponding titanium aluminide alloy.

SUMMARY OF THE INVENTION

[0009] The present invention resides in one aspect in a method for producing an alloy based on titanium aluminides, wherein metal droplets are obtained from a titanium aluminide metal melt, in particular by using the gas atomization method, the metal droplets being enriched with halogen by exposure to a halogen-containing gas, so that halogen-enriched titanium aluminide metal droplets or halogen-enriched TiAl metal powder are formed and subsequently the alloy is molded from the halogen-enriched titanium aluminide metal droplets or the TiAl metal powder by, preferably hot isostatic, pressing.

[0010] Halogens were alloyed with the titanium aluminide alloy, by using the halogen-containing gas in order to enrich the metal droplets with halogens, whereby a fine or homogeneous distribution of the halogens in the material and in each partial volume of the material or of the alloy and not only at the surface of the material or the alloy is achieved.

[0011] According to the invention, halogens are present also in layers, which are lower than the previously known oxidation layers of titanium aluminide alloys and which are larger or lie deeper, for example, at depths of more than about 100, 200, 300, 400, 500 μm and more below the surface of the alloy or in the whole of the alloy, whereby the resistance to oxidation is present and retained even after the surface of a component, produced from the titanium aluminide alloy, is damaged, since the resistance to oxidation of the whole of the alloy is maintained even at a great depth by the halogens, introduced and, in particular, distributed particularly homogeneously or randomly uniformly in the alloy or in the material.

[0012] The metal powder or the metal droplets are passivated by the intensive contact of the halogens with the titanium aluminide metal droplets.

[0013] Preferably, chlorine and/or fluorine are introduced as halogen into the bulk material produced from titanium aluminide. Within the scope of the invention, the use of other halogens, such as iodine and/or bromine is also possible.

[0014] Moreover, by the hot isostatic pressing (HIP), an alloy with a high isotropy and a uniform consolidation of the material is achieved. Typically, the process of hot isostatic pressing takes place at very high pressures, such as 100 Mpa, and at high temperatures, for example, at temperatures between 1000° C. and 2000° C.

[0015] Moreover, provisions are made so that the metal melt and/or the metal droplets are treated with a carrier gas, preferably with an inert gas, wherein in particular the carrier gas will be or is mixed with the halogen-containing gas.

[0016] Argon or helium or other inert gases have proven their value as a carrier gas, so that, by mixing with a halogen-containing gas, the metal melt is treated selectively in order to obtain metal droplets, which are enriched with halogens.

[0017] Furthermore, in an embodiment of the invention, a titanium aluminide metal powder is formed from the halogen-enriched metal droplets and molded into the alloy. Usually, this takes place by hot isostatic pressing. In particular, a component, which has a high resistance to oxidation even when the surface of the component is damaged, is produced from the molded alloy. The component may, for example, be from the automobile, space, aircraft and industrial machine tool sector.

[0018] Moreover, the object of the invention is solved by a method for producing an alloy based on titanium aluminides, wherein titanium-containing powder and aluminum-contain-

ing powder or titanium powder and aluminum powder and/or powdery titanium aluminide, particularly titanium aluminide metal powder is milled by means of or in a mill, preferably by means of or in a ball mill, wherein a halogen enriched atmosphere will be or is provided during the milling process in the mill, particularly the ball mill, so that a halogen enriched titanium aluminide metal powder is formed during the milling process and subsequently the powdery titanium aluminide, enriched with halogens, is molded into an alloy by, preferably hot isostatic, pressing.

[0019] Owing to the fact that the metal powder, while being milled in the ball mill and with the introduction of gases into the ball mill, has intensive contact, a particularly homogeneous, enrichment of powdery titanium aluminide is also achieved, as a result of which the halogens are distributed in the whole of the alloy produced or molded. The distribution of the halogens in the alloy is such that the (relative) content of halogens (per volume) is or will be kept almost constant or constant in any specified volume or partial volume or also in small partial volumes of the finished alloy.

[0020] Instead of pre-alloyed metal powder, that is, titanium aluminides in powder form, or in addition to the pre-alloyed metal powder, it is possible, according to the invention in this second method to use or provide also elementary powdery titanium and elementary powdery aluminum, so that a TiAl alloy in powder form arises from milling the titanium powder and the aluminum powder, the halogen content of which is or will be enriched in the ball mill as a result of the presence of the halogen-containing gas at a high pressure in the ball mill.

[0021] The implementation of the aforementioned steps of the method achieves the same, preferably uniform, distribution of the halogens at the surface as well as at a depth below the surface of an alloy as is achieved with the method described above for treating the metal melt with halogen gases. In this respect, the realizations of the first method apply in the same way as the steps of the method for producing the alloy described here.

[0022] Moreover, the atmosphere, enriched with halogens, is supplied as a gaseous and/or liquid atmosphere in a further step of the method, by means of which an intensive exchange or an intensive enrichment of the powder is carried out in the gaseous or in the liquid halogen-containing atmosphere, for example, in liquid carbon tetrachloride (CCl₄).

[0023] Preferably, the atmosphere, in particular the gaseous atmosphere, which is enriched with halogen, is supplied with at least one inert gas, such as argon or helium. Furthermore, a component is produced from the alloy having a constant (relative) proportion of halogens in each volume or partial volume or spatial volume of the alloy.

[0024] The present invention further resides in a method for producing an alloy based on titanium aluminides is provided, wherein powdery titanium aluminide, in particular titanium aluminide metal powder, will be or is heated for a predetermined time in a, preferably closed, container, wherein an atmosphere, enriched with halogens, is or will be provided in the container, so that halogen-enriched titanium aluminide metal powder is formed during the heating time and subsequently the titanium aluminide metal powder, enriched with halogens, is molded into an alloy by, preferably hot isostatic, pressing.

[0025] For this third method also, an alloy is provided, which in the same way has the advantages of the alloys produced by the method described above. In carrying out the

steps of the method, titanium aluminide alloys are also produced, for which halogens are alloyed with the whole of the material, the (relative) proportion of halogen (per volume) in the alloy remaining constant over the whole volume or in a (small) partial volume of the component or of the alloy, wherein it is entirely possible that the proportion of halogens may vary typically over a range of about $\pm 15\%$, preferably of about $\pm 10\%$, and particularly of about $\pm 5\%$, since the proportion of halogens in the alloy typically may fluctuate between about 0.005 atom percent and about 1.5 atom percent, preferably between about 0.005 atom percent or about 0.01 atom percent and about 0.9 atom percent. Aside from fluorine and/or chlorine, which are distributed in an alloy, further halogens, such as bromine and/or iodine may also be used.

[0026] In order to make the alloy, produced according to all three of the method introduced, resistant to oxidation at the surface, a desired surface of an object or component, which is produced from the alloy and for which oxidation resistance is desired, is oxidized.

[0027] Moreover, within the scope of the invention, it is conceivable that halogen-like compounds, such as silicon halogen-containing compounds or silicon halogen mixtures, which also have a positive effect on the oxidation resistance of the alloy, are used for the three methods named.

[0028] Furthermore, a halogen-containing gas is understood to be a gas which, aside from other gases, preferably inert gases, also contains a halogen element or also a mixture of several halogen elements.

[0029] In a further step of the method, the powdery titanium aluminide, in particular a titanium aluminide metal powder, is exposed to a vacuum in the container, before the container is heated. Moreover, a further step of the method is distinguished in that, for the gassing of the metal powder, the atmosphere, enriched with halogen, is supplied with at least one inert gas, in particular after an evacuation of the container.

[0030] In order to achieve a good and homogeneous enrichment of the titanium aluminide metal powder in the container, the container and/or the powdery titanium aluminide is heated for a period of 15 minutes to 25 hours, preferably of 30 minutes to 10 hours. By these means, a sufficiently high, uniform enrichment of titanium aluminides in accordance with the desired degree of halogen enrichment in the molded titanium alloy is attained.

[0031] Moreover, the container and/or the powdery titanium aluminide are/is heated to a temperature between 300° C. and 1300° C. and preferably between 500° C. and 1000° C. By these means, a good enrichment of the metal powder with halogens or halogen-like compounds is achieved.

[0032] The evacuating, gassing and heating steps of the method can also be carried out several times consecutively, in order to achieve higher halogen enrichment.

[0033] In addition, in a further step of the method after the container is heated, the powdery titanium aluminide, in particular titanium aluminide metal powder, is exposed to a reduced pressure or a vacuum.

[0034] Finally, a component is produced from the alloy molded by hot isostatic pressing.

[0035] Moreover, the object is solved by a component, which is or will be produced from an alloy, which is produced according to one of the aforementioned methods or method steps.

[0036] Titanium aluminide alloys are produced preferably using casting metallurgical or powder metallurgical techniques. For carrying out the methods, the titanium aluminide

alloys usually are present in the form of a powder, in order to enrich the metal powder according to the invention with halogens. Components of titanium aluminides usually are produced appropriately with known molding methods and atomization methods.

[0037] For example, for the mentioned methods, the TiAl-based intermetallic compounds may be alloys with a general composition of titanium and aluminum corresponding to the desired and specified requirements for the alloy.

[0038] Titanium aluminide alloys, which are produced according to the inventive method introduced, generally may have, for example, between about 30 atom percent and about 70 atom percent aluminum, wherein in addition further materials or elements, which are mentioned further below, may be taken up in accordance with the desired requirements, which are to be met by the alloy or the material.

[0039] In technically important areas of alloys, in which the TiAl alloys may be used, for example, as a light-weight construction material, the alloys may contain between about 44 atom percent and about 49 atom percent aluminum. In addition, further components, such as chromium (Cr), niobium (Nb), manganese (Mn), vanadium (V), tantalum (Ta), molybdenum (Mo), zirconium (Zr), tungsten (W), silicon (Si) and optionally additions of carbon (C) and/or boron (B) may be contained, these additional materials being present in an amount of about 0.1 atom percent to about 10 atom percent.

[0040] For industrial practice, in particular alloys, which are based on the intermetallic phase γ (TiAl) of a tetragonal structure, are also of interest. These γ titanium aluminide alloys are distinguished by such properties as a low density (about 3.85 to 4.3 g/cm³), a high modulus of elasticity and a high strength as well as creep resistance up to about 700° C.

[0041] In particular, a preferred alloy has a composition comprising Ti—(about 45 atom percent to about 49 atom percent) Al—(about 5 atom percent to about 10 atom percent) X, wherein X=Cr, Nb, Mn, V, Ta, Mo, Zr, W, Si and is formed optionally with additions of carbon and/or boron.

[0042] A titanium aluminide alloy of a particularly high strength has a composition comprising titanium, aluminide and niobium, to which optionally components of boron and/or carbon may still be added, the proportion of boron and/or carbon in the alloy being less than about 0.5 atom percent. Typically, the titanium aluminide alloy has a composition of Ti—45 atom percent Al—x Nb with 5 atom percent $\leq x \leq 10$ atom percent and optionally up to 0.5 atom percent B (boron) and/or up to 0.5 atom percent C (carbon).

[0043] Moreover, titanium aluminide alloys with a fine and homogeneous structure morphology may also be provided by the inventive methods, the titanium aluminides having an alloy composition of Ti—z Al—y Nb with 44.5 atom percent $\leq z \leq 47$ atom percent, in particular with 44.5 atom percent $\leq z \leq 45.5$ atom percent, and 5 atom percent $\leq y \leq 10$ atom percent, wherein this composition contains molybdenum (Mo) ranging in amounts from about 0.1 atom percent to about 3.0 atom percent. The remainder of the alloy consists of Ti (titanium).

[0044] Especially for Ti—(44.5 atom percent to 45.5 atom percent) Al—(5 atom percent to 10 atom percent) Nb, the addition of about 1.0 atom percent to about 3.0 atom percent of molybdenum has led to good microstructures with a high degree of structural homogeneity.

[0045] In accordance with a further advantageous development, the aforementioned alloy also contains boron, preferably in an amount in the alloy ranging from about 0.05 atom

percent to about 0.8 atom percent. The addition of boron advantageously leads to the formation of stable precipitates, which contribute to the mechanical hardening of the inventive alloy and to the stabilization of the structure of the alloy.

[0046] Moreover, it is advantageous if the alloy contains carbon, preferably in an amount of about 0.05 atom percent to about 0.8 atom percent. The addition of carbon, preferably in combination with the aforementioned additive, boron, leads to the formation of stable precipitates, which also contributes to the mechanical hardening of the alloy and to the stabilization of the structure.

[0047] A titanium aluminide alloy with a fine and homogeneous structure morphology with formation of a stable β phase at high temperatures above 700° C. is also provided by an alloy based on titanium aluminide, produced by using melt metallurgy and powder metallurgy techniques, with an alloy composition of Ti—z Al—y Nb—x B with 44.5 atom percent $\leq z \leq 47$ atom percent, in particular with 44.5 atom percent $\leq z \leq 45.5$ atom percent, 5 atom percent $\leq y \leq 10$ atom percent and 0.05 atom percent $\leq x \leq 0.8$ atom percent, this alloy containing 0.1 atom percent to 3 atom percent molybdenum (Mo).

[0048] Moreover, an alloy composition of Ti—z Al—y Nb—w C with 44.5 atom percent $\leq z \leq 47$ atom percent and in particular with 44.5 atom percent $\leq z \leq 45.5$ atom percent, 5 atom percent $\leq y \leq 10$ atom percent and 0.05 atom percent $\leq w \leq 0.8$ atom percent, containing about 0.5 atom percent to about 3 atom percent of molybdenum (Mo), has a fine and homogeneous structure morphology, the β phase formed being stable up to temperatures of 1320° C.

[0049] The β phase, which is stable up to temperatures of 1320° C., is also formed with an alloy composition of Ti—z Al—y Nb—x B—w C with 44.5 atom percent $\leq z \leq 47$ atom percent, in particular with 44.5 atom percent $\leq z \leq 45.5$ atom percent, 5 atom percent $\leq y \leq 10$ atom percent, 0.05 atom percent $\leq x \leq 0.8$ atom percent and 0.05 atom percent $\leq w \leq 0.8$ atom percent, containing between about 0.1 atom percent and 3 atom percent molybdenum (Mo).

[0050] An appropriate TiAl alloy, given above, is provided within the scope of the invention in accordance with the requirements desired, as a metal powder or in powder form for the implementation of one of the methods named, in order to obtain, as a result of the inventive halogenation or halogen enrichment of the TiAl metal powder, a TiAl alloy, which has an almost constant relative proportion of halogens in a small partial volume at the surface and at a depth away from the surface, as a result of which the oxidation resistance of the material or of the whole alloy is improved.

[0051] Preferably, in one embodiment, silicon-containing halogens or combinations of silicon and halogens furthermore are used for the implementation of the method, as a result of which the oxidation resistance of the titanium aluminide alloys produced is improved, owing to the fact that the elements or compounds, increasing the oxidation resistance, are contained distributed entirely homogeneously or randomly at the surface as well as in the material.

[0052] In this respect, it is furthermore possible within the scope of the invention to use, aside from halogens, also further materials or mixtures, which increase the oxidation resistance of titanium aluminide alloys.

What is claimed is:

1. A method for producing an alloy based on titanium aluminides, wherein metal droplets are obtained from a titanium aluminide metal melt using the gas atomization method,

the metal droplets being enriched with halogens by exposure to a halogen-containing gas, so that halogen-enriched titanium aluminide metal droplets are formed and subsequently the alloy is molded from the halogen-enriched titanium aluminide metal droplets by, preferably hot isostatic, pressing.

2. The method of claim 1, wherein at least one of the metal melt and the metal droplets is treated with a carrier gas, and wherein the carrier gas will be or is mixed with the halogen-containing gas.

3. The method of claim 1, wherein a titanium aluminide metal powder is formed from the halogen-enriched metal droplets and molded into the alloy.

4. The method of one of claim 1, wherein a component is produced from the alloy.

5. A method for producing an alloy on the basis of titanium aluminides, wherein titanium-containing powder and aluminum-containing powder or powdery titanium aluminide, is milled wherein a halogen enriched atmosphere is provided during the milling process in the mill, so that a halogen enriched titanium aluminide metal powder is formed during the milling process and subsequently the powdery titanium aluminide, enriched with halogens, is molded into an alloy by, hot isostatic, pressing.

6. The method of claim 5, wherein the atmosphere, enriched with halogens, is supplied as one of a gaseous and liquid atmosphere.

7. The method of claim 5, wherein the atmosphere, enriched with halogens, is supplied with at least one inert gas.

8. The method of claim 5, wherein a component is produced from the alloy.

9. A method for producing an alloy based on titanium aluminides, wherein titanium aluminide powder, is heated for a predetermined time in a container, wherein an atmosphere, enriched with halogens is provided in the container, so that halogen-enriched titanium aluminide metal powder is formed during the heating time and subsequently the titanium aluminide metal powder, enriched with halogens, is molded into an alloy by, hot isostatic, pressing.

10. The method of claim 9, wherein before the container is heated, the titanium aluminide powder is exposed to a vacuum in the container.

11. The method of claim 9, wherein an atmosphere, enriched with halogens, is supplied with at least one inert gas, after evacuation of the container.

12. The method of claim 9, wherein at least one of the container and the titanium aluminide powder is heated for a predetermined period of about 15 minutes to about 24 hours.

13. The method of claim 9, wherein at least one of the container and the titanium aluminide powder is heated to a predetermined temperature between about 300° C. and about 1300° C.

14. The method of claim 9, wherein after the container is heated, the titanium aluminide powder, is exposed to a vacuum.

15. The method of claim 9, wherein a component is produced from the alloy.

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