



(11) **EP 1 818 121 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:  
**07.01.2009 Bulletin 2009/02**

(51) Int Cl.:  
**B22D 29/00 (2006.01)**

(21) Application number: **07101569.7**

(22) Date of filing: **01.02.2007**

(54) **Method for removal of cores from niobium-based part**

Verfahren zum Entfernen von Kernen aus Teilen auf der Basis von Niobium

Procédé de suppression de noyaux de la partie à base de niobium

(84) Designated Contracting States:  
**DE FR GB**

(30) Priority: **09.02.2006 US 276002**

(43) Date of publication of application:  
**15.08.2007 Bulletin 2007/33**

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**Description**

**[0001]** The present invention relates generally to turbine parts, and more particularly, to a cast part having passages cast therethrough.

**[0002]** Due to the harsh environment associated with operation of a turbine engine, the parts thereof must consist of materials which can withstand the fluid speeds, temperatures, and stresses created during operation of a turbine engine. The turbine parts, especially the blades, must be constructed to satisfy minimums associated with oxidation resistance, intermediate-temperature pulverization resistance, fracture toughness, fatigue resistance, and impact resistance. Understandably, these are but a few of many design considerations which are addressed to determine the operability of a part formed of a selected material. Additionally, due to the exacting nature associated with the assembly of the turbine engine, casting performance, manufacturability, and machinability are also important considerations to the selection of a part material.

**[0003]** It is well understood that the operating temperature of a turbine is one aspect of a turbine's operating efficiency. Advanced turbine engine designs require parts formed of materials which can withstand ever-increasing operating temperatures to attain improvements in engine performance. Refractory-metal intermetallic in-situ composite materials, such as Niobium and molybdenum based silicides, possess a useful range of mechanical properties, such as low-temperature toughness as well as high-temperature strength and creep resistance. Understandably, these alloys are but two examples of refractory-metals which have been found to satisfy the ever increasing material, mechanical, and thermal demands of turbine parts.

**[0004]** In addition to the high temperatures and pressures associated with turbine operation, a turbine generally includes a plurality of parts with relatively complex geometries. For example, a turbine often includes several cast blades, fins, and/or vanes which individually have a generally airfoil shaped cross-section. Due to the temperature associated with operation of the turbine, these parts often include cooling passages which are integrally formed in the part, usually through casting. Casting a part with integral cooling passages requires providing a mold and a core such that the passages are formed during casting of the part. Once the part is removed from the mold, the core material must be removed from the cooling passages. Several considerations must be addressed in removing the core material from the cast part.

**[0005]** The process of removing a core material from a cast part often includes subjecting the cast part to a caustic bath. That is, when the part is formed of a nickel-based, and/or other "super-alloy", materials, the cores used for casting such parts are often formed from ceramic-based materials which including alumina, zircon, and/or silica. The material of these cores is substantially non-reactive with the material of the part during the casting process and thereby, does not detrimentally affect the quality of the part being formed. After the material of the cast part solidifies and cools, to remove the core from the part, the cores are chemically dissolved and drained from the passages of the part.

**[0006]** The time required to chemically remove the cores significantly affects process efficiencies. The time required to remove these cores with an acidic solution is often too long to prove feasible in a dynamic processing environment. Furthermore, it has been shown the quality of the part can be adversely affected when the cores are removed with certain acidic solutions. Caustic solutions, particularly KOH and NaOH, have proven to be particularly efficient at dissolving the material of the ceramic-based cores without detrimentally affecting the quality of the nickel-based, and/or other super-alloy, parts.

**[0007]** Parts cast from refractory-metal intermetallic in-situ composite materials such as niobium-based and molybdenum-based silicides, have been shown to possess desirable characteristics of oxidation resistance, intermediate-temperature pulverization resistance, fracture toughness, fatigue resistance, and impact resistance. Accordingly, producing parts of such materials increases the operable range of a device so equipped. However, the ceramic-based cores of silica, alumina and/or zircon usable for casting the nickel-based or other super-alloy parts reacts with these niobium-based materials during the casting process and thereby detrimentally affect the quality of the cast part. Accordingly, a core material other than the ceramic-based core material of silica, alumina and/or silica must be utilized when casting a niobium-based part. Furthermore, removal of the core material must be expeditious to allow for economical production of parts and must be accomplished without detrimentally affecting the properties of the cast part.

**[0008]** Therefore, it would be desirable to design a system and method of producing a niobium-based material part having removable cores wherein removal of the cores is relatively rapid and does not adversely affect the quality of the part.

**[0009]** Various aspects of the present invention provide a system and method of producing a part from a niobium-based material that addresses the aforementioned problems. The system and method includes removing an yttria-based core material from the niobium-based part with any of acetic acid, hydrochloric acid, nitric acid, phosphoric acid, nitric/phosphoric acid, sulfuric acid, and/or any combination thereof. The yttria-based core material is rapidly removed from the niobium-based part and the process of removing the cores does not detrimentally affect the quality of the part.

**[0010]** According to one aspect of the present invention, a method of removing an yttria-based core from a niobium-based part is disclosed. The method includes the step of contacting the yttria-based core with an effective amount of a composition which comprises at least one acid selected from the group consisting of hydrochloric acid, nitric acid, phosphoric acid, nitric/phosphoric acid, sulfuric acid, and acetic acid.

**[0011]** Another aspect of the present invention includes a method of casting a part. The method of casting the part includes positioning an yttria-based core within a mold, introducing a molten niobium-based alloy into the mold to cast a part, and dissolving the yttria-based core with at least one acid selected from the group consisting of acetic acid, hydrochloric acid, nitric acid, phosphoric acid, nitric/phosphoric acid, and sulfuric acid.

**[0012]** A further aspect of the present invention includes a method of forming a turbine blade. The method of forming the turbine includes casting a blade having at least one passage defined by a core formed of an yttria-type material by pouring a niobium-type material into a mold and removing the core from the blade by contacting the core with an acid which comprises at least one acid selected from the group consisting of acetic acid, hydrochloric acid, a nitric acid, a phosphoric acid, a nitric/phosphoric acid, and a sulfuric acid.

**[0013]** Various other features, objects and advantages of the present invention will be made apparent from the following detailed description and the drawings, in which:

Fig. 1 is a perspective view of a turbine in partial cross-section having a plurality of cast parts according to an embodiment of the present invention.

Fig. 2 is a perspective view of a cast blade usable with a turbine such as that shown in Fig. 1.

Fig. 3 is an elevational view of a cross-section of a mold for forming a cast part such as that shown in Fig. 2.

Fig. 4 is a partial cross-sectional view of the cast part along line 4-4 shown in Fig. 2.

Fig. 5 is a graphical representation of the weight loss of an yttria-based core material when exposed to various acids and various acid concentrations in accordance with an embodiment of the present invention.

Fig. 6 is a graphical representation of the removal rate of a niobium-based material when exposed to various acids and various acid concentrations in accordance with an embodiment of the present invention.

**[0014]** Fig. 1 shows an exemplary turbine engine, or turbine 10 having a plurality of parts cast according to the present invention. Turbine 10 includes an intake end 14 and a discharge end 16. A housing or shroud 18 is positioned about an exterior 20 of turbine 10 and includes a shroud cooling passage 21 formed therethrough. An air flow, indicated by arrow 22, enters turbine 10 through intake end 14 and passes through a first compressor stage or a fan 24. Fan 24 includes a plurality of blades 26 radially positioned about a hub 28. After air flow 22 has passed through fan 24, a first portion 30 of air flow 22 is directed to a compressor 32 and a second portion, or a bypass flow 34, of air flow 22 is directed through a perforated panel 36 and into shroud passage 21 thereby bypassing the remaining operational components of turbine 10.

**[0015]** Compressor 32 includes a plurality of fins or blades 38 attached to alternating stator hubs 40 and rotor hubs 42. During operation of turbine 10, blades 38 attached to each of rotor hubs 42, rotate past the blades 38 of adjacent stator hubs 40. The orientation of blades 38, the rotational speed of a particular hub as compared to adjacent hubs, and the shape of the blades are selected to generate a desired increase in the pressure and velocity of air flow 30. This specific hub configuration/orientation is merely exemplary and other hub configurations are envisioned and within the scope of the invention.

**[0016]** The highly pressurized, increased velocity air flow 30 exiting compressor 32 is then directed to a combustor 44. Combustor 44 introduces a preferably highly atomized fuel to air flow 30. Combustion of the air/fuel mixture even further increases the pressure and velocity of air flow 30. Air flow 30 is then directed to a turbine stage 46 of turbine engine 10. Turbine stage 46 includes a plurality of hubs 48 wherein each hub 48 includes a plurality of vanes or blades 50. As air flow 30 passes between adjacent blades 50 of each hub 48, a portion of the pressure and velocity of air flow 30 is utilized to rotate the respective hub 48. For the aircraft engine shown, one or several of hubs 48 are connected through concentric shafts to drive fan 24 and rotor hubs 42 of compressor 32. Air flow 30 exiting turbine stage 46 of turbine 10 accentuates the thrust of air flow 34 generated by fan 24 and is discharged from turbine 10 through a nozzle 52 positioned about discharge end 16.

**[0017]** As one skilled in the art will appreciate, the components of turbines vary greatly depending on the intended application of the turbine. That is, an aircraft turbine engine may have a different configuration of components and parts than hydroelectric, geothermal, or other application specific turbine engines/generators. Specifically, the construction of the turbine is commonly tailored to the fluid passed therethrough, the operational environment of the turbine, and the intended use of the turbine. For example, a turbine intended to generate electrical power may include a turbine stage having a first set of hubs utilized to rotate the rotors of the compressor and another set of hubs utilized to drive a utility generator. Regardless of the intended application of the turbine, each of the blades of the turbine must be constructed to withstand the motion, pressure, and temperature associated with turbine operation. As used herein, turbine part or component includes any component of the turbine including but not limited to buckets, nozzles, blades, rotors, vanes,

stators, shrouds, combustors, and blisks.

**[0018]** Fig. 2 shows blade 50 removed from turbine 10. Blade 50 includes a body 52 that is cast from a niobium-based material. Preferably, blade 50 is cast from a niobium-silicide based composite. The niobium-based composites exhibit desirable qualities with respect to low temperature toughness, high-temperature strength, and creep resistance for turbine blade construction. Furthermore, the niobium-based material construction of blade 50 allows the blade to operate at higher temperatures than a blade constructed from an iron, nickel, titanium, or other material based "super alloy". Although the niobium-based construction of blade 50 allows the blade to operate at temperatures that are higher than blades constructed of other materials, even greater operating temperatures can be achieved with integral cooling of the blade.

**[0019]** Body 52 of blade 50 includes a passage 54 that is integrally cast therethrough. Passage 54 includes an inlet 56 and an outlet 58 such that a flow, indicated by arrows 59, can be passed through body 52 of blade 50. Understandably, the orientation of passage 54, as well as the relative positions of inlet 56 and outlet 58, are merely exemplary and in no way limit the scope of the invention. As discussed further with respect to Fig. 3, passage 54 is formed during the casting of blade 50 by traversing the cavity of a mold with a core and casting blade 50 within the mold and about the core.

**[0020]** Passage 54 allows flow 59 to pass into and through body 52 of blade 50 of turbine 10. Flow 59 removes heat associated with operation of turbine 10 from blade 50 and thereby allows blade 50 to withstand higher operating temperatures than a blade having a similar shape and formed of a similar material without passages therethrough. The increased turbine operating temperatures achievable with blade 50 increases the operating efficiency of an engine equipped with blades 50. That is, the efficiency of turbine 10 is directly related to the operating temperature thereof. Thereby, blade 50 provides for increased turbine operating temperatures thereby increasing the operating efficiency of turbine 10.

**[0021]** Blade 50 includes a shank 64 extending therefrom. Shank 64 is constructed to allow blade 50 to be quickly and securely attached to hub 48, as shown in Fig. 1. As shown in Fig. 2, shank 64 has a geometric cross-section 66 which allows shank 64 to slidably engage the hub of turbine 10 such that blade 50 is securely attached thereto to withstand the rotational forces associated with operation of turbine 10. Blade 50 is formed by pouring a molten material having properties of low temperature toughness, high-temperature strength, and creep resistance that are generally similar or the same as to the material properties of a niobium-based alloy into a mold.

**[0022]** As shown in Fig. 3, a mold 68 includes a body having a cavity 70 formed therein. Cavity 70 has a shape 72 which substantially matches, or is a near net equivalent of, the shape of blade 50. A core 78 extends into cavity 70 and is encased by the niobium-based material of the part during the casting process. Core 78 is formed of an yttria-based material. Additionally, it is further appreciated and within the scope of the invention that the yttria-based material be a pure yttria material or an yttria material that includes an oxide of any of magnesium, calcium, strontium, niobium, silicon, hafnium, titanium, zirconium, rare earth metal of the lanthanide series, and/or any combination thereof. Minimally, the composition of the yttria-based cores is selected such that the core is non-reactive with the niobium-based material of the part during the casting process.

**[0023]** Core material 78 is selected to withstand the temperatures associated with the casting process and be formable to a desired core shape. Core material 78 is further selected to be removable from the cast part with minimal or negligible interference with the cast part by the means applied to remove the cores. That is, the yttria-based material is removed from the part, as discussed further with respect to Figs. 5 and 6, by subjecting the cores to an effective amount of an acid. The yttria-based material has been determined to be readily dissolvable by any of acetic acid, hydrochloric acid, nitric acid, phosphoric acid, nitric/phosphoric acid, sulfuric acid, or combinations thereof without detrimentally affecting the quality of the niobium-based part. Understandably, several considerations must be addressed in removing the yttria-based core material from the niobium-based part including, the rate of reaction of the selected acid with the yttria-based core, the concentration of the acid selected, the temperature and pressure at which the process is carried out, as well as the reaction between the acid and the part. That is, an acid cannot be selected simply because it sufficiently dissolves an yttria-based core but must also non-detrimentally affect the part being produced. Preferably, the acid is selected for the acid's reactivity with the yttria-based material and the acids comparatively non-reactive nature with the material of the part.

**[0024]** It is further appreciated that some acids are more readily commercially available than other acids. Understandably, such considerations are relevant to the selection of an acid from a group of acids that are capable of providing desired results. For example, nitric acid is commonly commercially available at up to 91 % concentration and performs acceptably between about 5% and 91% concentration. As used hereinafter, reference to the concentration of an acid refers to the weight percent concentration of the acid.

**[0025]** Preferably, when nitric acid is utilized to remove the core material, it is maintained between about 20% and 70% concentration. Furthermore, nitric acid has an azeotropic attribute wherein the acid solution of nitric acid and water will gravitate to a concentration of 68% when maintained at about 120.5 degrees Celsius. The azeotropic nature of the nitric acid solution allows the concentration of the solution to remain relatively constant during boiling (and thereby evaporation) of the solution. Understandably, the acid selected will have a desired concentration that is not necessarily

the same as other applicable acids. Hydrochloric acid performs adequately between about 2% and 37% concentration and is preferably maintained between about 10% to about 20% concentration. Phosphoric acid performs adequately between about 50% to about 85% and is preferably maintained between about 65% to about 70% concentration. Sulfuric acid performs adequately between about 5% to about 30% and is maintained between preferably about 10% and about 20% concentration. Acetic acid performs adequately between about 30% and about 90%. Understandably, these ranges are merely exemplary and manipulating other variables of the system could result in beneficial results with acids having concentration beyond those expressly stated. Furthermore, it is appreciated that the concentration of the acid of acid mixtures, such as nitric/phosphoric be tailored to a range wherein the mixture adequately dissolves the core material without detrimentally affecting the material of the part. Understandably concentration, pressure, and temperature associated with the core removal process will need to be tailored to the acid used.

**[0026]** Referring to Fig. 3, during the casting process, as the molten niobium-based cast material is introduced into cavity 70, the cast material generally encompasses core 78. When mold body 69 is removed from the cast part, core 78 remains in the cast part due to the generally internal position of core 78 relative to an outer surface of the cast part indicated by an interface 76 of cavity 70 and mold 69. Such a casting process allows internal areas of the cast part to be a material that is different than a material of the cast part. When core 78 is removed from the cast part, passage 54, as shown in Fig. 2, is formed through the cast part. Although core 78 is configured to form a passage through the cast part, other core shapes and orientations are envisioned and within the scope of the invention such as providing a core member completely internal to the cast part or having a single opening thereto.

**[0027]** As shown in Fig. 4, cast blade 50 has been removed from a mold similar to mold 68 shown in Fig. 3. A shape 82 of blade 50, although shown in cross-section, substantially matches shape 72 of cavity 70 of mold 68. Core 78, as shown in Fig. 3, has been removed from blade 50 thereby clearing passage 54 formed through blade 50. Passage 54 provides a cooling path through body 52 of blade 50. Flow 59 is directed into inlet 56 and through passage 54 and passes through blade 50 in a generally serpentine manner thereby cooling blade 50 and removing operational heat therefrom. Understandably, surface passages could also be formed through the blade 50 and fluidly connected to passage 54 to allow surface cooling of blade 50 during operation thereof.

**[0028]** Core 78, regardless of its shape, is removed from blade 50 by exposing core 78 of blade 50 to an acid. The acid is selected such that there is minimal or negligible reaction between the acid and the niobium-based material of the part and the acids ability to readily dissolve, or react with, the yttria-based material of the cores. Understandably, several acids are envisioned and within the scope of the invention. Preferably, the core removal material/solution is substantially non-reactive with the niobium-silicide based materials of blade 50, while being very reactive with the yttria-based material of the cores. Such an association ensures that the removal of core 78 from blade 50 maintains a desired quality of the cast part and manufacturing efficiency.

**[0029]** It is further understood and within the scope of the claims that the conditions associated with the acid application process are tailored to produce a desired part. That is, the temperature of the acid is generally maintained at temperatures approximately between 50 degrees Celsius and about 120 degrees Celsius. Preferably, the upper temperature limit is generally defined by the boiling point of the acid selected. Those skilled in the art will appreciate that a boiling point is sometimes expressed as a constant boiling point and that some acids, such as nitric and HCl acids, have an azeotrope with water. An azeotrope will boil without changing composition. Since each acid and/or acid combination has a specific boiling point, the upper temperature limit can be selected for the specific acid and/or acid combination utilized. Understandably, manipulating the operating pressure of the process affects the boiling temperature of the acid such that higher operating temperatures can be achieved through the use of an autoclave or like equipment. With the use of an autoclave, temperatures higher than 120 degrees Celsius can be achieved and are not outside the scope of the invention. It is further understood but not required to manipulate the interaction of the acid with the core material through agitation of the interface therebetween. Such agitation could include physically manipulating the part and/or the acid to providing a stirring function, sonic stirring of the interface of the acid with the core, manipulating the temperature to provide intermittent boil stirring, or manipulating pressure, such as through the control of the pressure of an autoclave, to allow intermittent boil stirring of the process. Understandably, such agitation expedites the interaction between the core and the acid but is not necessary to ensure a desired reaction therebetween. Furthermore, it is appreciated that dissolved and/or loosened core material or residue be removed with techniques such as rinsing, blowing with gas, and the like.

**[0030]** It has been determined that after a period of approximately 24 hours, a nitric acid solution dissolves the yttria-based material of the cores without substantially affecting the niobium-based material of the blade. Understandably, the temperature, pressure, and concentration of the acid, as well as the duration of exposure of the core and/or cast part to the acid, affect both the rate of removal of the cores and the effect of the acid on the cast part. For parts cast of a material having material properties of low temperature toughness, high-temperature strength, and creep resistance that are generally similar to the properties of a niobium-based alloy, acids such as of acetic acid, hydrochloric acid, nitric acid, phosphoric acid, nitric/phosphoric acid, sulfuric acid, and/or combinations thereof, have been determined to adequately remove the yttria-based core material with minimal or negligible effect of the cast part.

**[0031]** Understandably, the selection of an acid to remove the yttria-based core requires consideration of several

parameters including the specific composition of niobium-based part material, the level of acceptable interaction between the niobium-based material and the acid, the temperature and duration of exposure of the part to the acid, the availability and cost of the acid and/or its constituents, the specific composition of the yttria-based core material, and the density of the core material. Understandably, these are but a few of the many considerations which must be addressed to realize a feasible core material process.

**[0032]** Figs. 5 and 6 show a graphic comparison of the dissolution of yttria-based core material and niobium-based part material for a plurality of acids, respectively. As shown in Fig. 5, 20% HCl acid nearly completely, if not completely, dissolves a 69% density yttria-based core after two hours at 95 degrees Celsius. When HCl acid is utilized to remove a 69% density yttria-based core material, preferably, the concentration is maintained below 20 wt% and preferably between 1 wt% and 10 wt% in an effort to minimize the effect of the acid on the material of the cast part. Comparatively, 20% and 70% phosphoric and 50% sulfuric acids displayed no appreciable yttria-based core removal when maintained at these same parameters. That is, Fig. 5 graphically shows the yttria-based core removal that can be achieved with a plurality of acids.

**[0033]** Comparatively, Fig. 6 shows the detrimental affect of the indicated acids on the niobium-based material of the part. For example, the nitric acids minimally attacked the niobium based material of the part whereas the 50% sulfuric acid showed a greatly increased removal rate of the niobium-based material. Preferably an acid is selected which aggressively dissolves the yttria-based core and correspondingly, minimally or negligibly affects the niobium-based material of the part. Selecting an acid which satisfies these criteria allows for efficient production of quality niobium-based parts. Several examples were conducted and, some of which are set forth below, further indicate the effectiveness of selected acids. The specific examples provided below are merely exemplary and in no way limit the scope of the invention.

**[0034]** As a first example, an yttria-based bar and a NbSi alloy of similar size and having compositions and densities, respectively, for use as materials in a turbine engine, were placed in an autoclave. The autoclave contained a 20 wt% NaOH solution. The autoclave was heated to 290 degrees Celsius and held at temperature for 2.5 hours. After exposure to these conditions, the yttria-based bar was still largely intact but swelled to a larger dimension. The NbSi alloy was mostly dissolved and the remaining reaction products from the alloy were present at the bottom of the container as multiple flakes. Such a process evidenced that the NbSi alloy dissolved faster than the yttria bar thereby showing that a caustic solution of NaOH would be unfeasible to remove an yttria-based core from a niobium-based part.

**[0035]** In another example, similarly sized yttria-based bars and pieces of NbSi alloy, both of composition and density desirable for use as materials in a turbine engine, were placed in nitric acid concentrations of 20 wt% and 69 wt% as shown in the following table. The yttria bar was substantially dissolved after 2 hours at 95 degrees Celsius while very limited attack of the NbSi alloy occurred after 24 hours at 95 degrees Celsius. The relative rate of dissolution was high for the yttria and low for the alloy. Nitric acid is useful for removing the yttria without significantly attacking the alloy. Understandably, other parameters of concentration, temperature, and pressure are envisioned and within the scope of the invention.

Acid/ Concentration	Weight Loss of 69% Density Yttria after 2 hrs at 95C (%)	Weight Loss of NbSi Alloy after 24 hrs at 95C (%)	relative dissolution rate of Yttria	Relative dissolution rate of NbSi containing Alloy
Nitric Acid 20%	73%	0.02%	High	Low
NitricAcid 69%	78%	0.01%	High	Low

**[0036]** In another example, similarly sized yttria-based bars and pieces of NbSi alloy, both of composition and density desirable for use as materials in a turbine engine, were placed in a nitric acid concentrations of 69 wt% as shown in the following table. The yttria bar was substantially dissolved after 1 hour at 115 degrees Celsius while very limited attack of the NbSi alloy occurred after 24 hours at 115 degrees Celsius. Compared to the previous example at 95 degrees Celsius, the dissolution rate of the yttria-based material substantially increased while the dissolution rate of the alloy was relatively unchanged. The relative rate of dissolution was high for the yttria-based material and low for the alloy thereby showing that nitric acid is useful for removing the yttria-based material without significantly attacking the alloy. Understandably, other parameters of concentration, temperature, and pressure are envisioned and within the scope of the invention.

<b>Acid/ Concentration</b>	<b>Weight Loss of 69% Density Yttria after 1 hr at 115C (%)</b>	<b>Weight Loss of NbSi Alloy after 24 hrs at 115C (%)</b>	<b>relative dissolution rate of Yttria</b>	<b>relative dissolution rate of NbSi containing Alloy</b>
Nitric Acid 69%	86%	0.02%	High	Low

**[0037]** In a further example, yttria-based bars and similarly sized pieces of NbSi, both of composition and density useful in turbine engines, were placed in hydrochloric acid concentrations of 10 wt% and 20 wt% as shown in the following table. The yttria-based bar was substantially dissolved after 2 hours at 95 degrees Celsius while very limited attack of the NbSi alloy occurred after 24 hours at 95 degrees Celsius. The relative rate of dissolution was high for the yttria-based core material and low for the alloy part material when the hydrochloric acid was at 10 wt%. At the higher acid concentration of 20 wt%, the dissolution rate of the alloy increased, but was still at a substantially lower rate of dissolution than the yttria-based core material. Hydrochloric acid at 10 wt% is particularly useful for removing the yttria-based core material without significantly affecting the niobium-based alloy material. The higher concentration of 20 wt% also effectively removed the yttria-based core material without significantly attacking the niobium-based material of the part when the part size is reduced thereby reducing the contact time therebetween. The acid concentrations of 10 wt% and 20 wt% are merely exemplary and do not limit the invention to these concentrations.

<b>Acid/ Concentration</b>	<b>Weight Loss of 69% Density Yttria after 2 hrs at 95C (%)</b>	<b>Weight Loss of NbSi Alloy after 24 hrs at 95C (%)</b>	<b>relative dissolution rate of Yttria</b>	<b>relative dissolution rate of NbSi containing Alloy</b>
HCl 10%	69%	0.03%	High	Low
HCl 20%	100%	0.56%	High	High

**[0038]** In yet another example, yttria-based core material bars and NbSi alloy part material pieces of similar size, both of composition and density generally used in forming turbine engines, were placed in a mixture of 1:1 phosphoric/nitric acid of concentrations of 20 wt% and 70 wt%, as shown in the following table. The yttria-based core material bar was substantially dissolved after 2 hours at 95 degrees Celsius while very limited attack of the NbSi part material occurred after 24 hours at 95 degrees Celsius. The relative rate of dissolution was higher for the yttria-based material and lower for the alloy when the 1:1 phosphoric/nitric acid content was 70 wt%. At the lower acid concentration of 20 wt% the dissolution rate of the yttria-based material decreased and even with the lower dissolution rate, the removal rate of the yttria-based material was still orders of magnitude greater than the dissolution rate of the alloy of the part material. The 1:1 phosphoric/nitric acid mixture at 70wt% proved particularly useful for removing the yttria-based core material without significantly attacking the alloy of the part material. The lower concentration of 20 wt% can also be effectively used to remove yttria-based material without significant attack of the part material when the time for removal of the core material from the part is of little or no concern. Understandably, the acid concentrations of 20 wt% and 70 wt% and the 1:1 ratio of the phosphoric to nitric acid of the mixture are for purposes of example and do not limit the invention.

<b>Acid/ Concentration</b>	<b>Weight Loss of 69% Density Yttria after 2 hrs at 95C (%)</b>	<b>Weight Loss of NbSi Alloy after 24 hrs at 95C (%)</b>	<b>relative dissolution rate of Yttria</b>	<b>relative dissolution rate of NbSi containing Alloy</b>
Nitric/Phosphoric 20%	19%	0.10%	Medium	Low
Nitric/Phosphoric 70%	45%	0.14%	High	Low

**[0039]** In a further example, similarly sized yttria-based bars of core material and pieces of NbSi alloy part material, both of composition and density useful for use as materials in turbine engines, were placed in phosphoric acid concentrations of 20 wt% and 70 wt% as shown in the following table. The 69% dense yttria-based bar was substantially intact after 2 hours at 95 Celsius, while the NbSi alloy was substantially attacked after 24 hours at 95 Celsius. The rate of

dissolution of the yttria-based material was low the rate of attack of the niobium-based material was high for both concentrations employed. The dissolution rate of the high density yttria was orders of magnitude lower than the dissolution rate of the alloy. Phosphoric acid at 70 wt% concentration was determined to be useful to remove low density (56% dense) yttria bars while less effective at dissolving higher density (69% density) yttria-based materials. The dissolution rate of the lower density yttria-based material was orders of magnitude higher than the dissolution rate of the alloy when the 70 wt% acid was used for 24 hours at 95 degrees Celsius. Accordingly, 70 wt% phosphoric acid can be effectively used to remove low density yttria without significant damage to the alloy when the part size is small enough such that the time of exposure of the part to the acid is short. Understandably, other concentrations of acid, density of yttria-based material, and process temperature and pressure are envisioned and within the scope of the claims.

Acid/ Concentration	Weight Loss of 69% Density Yttria after 2 hrs at 95C (%)	Weight Loss of NbSi Alloy after 24 hrs at 95C (%)	relative dissolution rate of Yttria	relative dissolution rate of NbSi containing Alloy
Phosphoric 20%	0%	0.61%	Low	High
Phosphoric 70%	0%	0.52%	Low	High

Acid/ Concentration	Weight Loss of 56% Density Yttria after 24 hrs at 95C (%)	Weight Loss of NbSi Alloy after 24 hrs at 95C (%)	relative dissolution rate of Yttria	relative dissolution rate of NbSi containing Alloy
Phosphoric 20%	0%	0.61%	Low	High
Phosphoric 70%	100%	0.52%	High	High

**[0040]** Another example exposed like size parts, having turbine related composition and density, yttria-based core material and NbSi alloy part material to sulfuric acid at concentrations of 20 wt% and 50 wt% as shown in the following table. The yttria-based core material was partially dissolved after 2 hours at 95 degrees Celsius while limited attack of the NbSi part material occurred when the 20 wt% sulfuric acid was employed at 24 hours at 95 degrees Celsius. The relative rate of dissolution for the yttria-based material and the part material was medium when the components were subjected to the 20 wt% sulfuric acid. At the acid concentration of 20 wt%, the dissolution rate of the yttria-based material was still orders of magnitude greater than the dissolution rate of the NbSi. The concentration of 20 wt% can be effectively used to remove yttria-based material without significant attack to the alloy part material when the exposure time of the part to the acid limited.

**[0041]** Sulfuric acid at 50 wt% significantly attacked the NbSi part material after 24 hours at 95 degrees Celsius, while the yttria-based material remained substantially undissolved after 2 hours at 95 degrees Celsius. The relative rate of dissolution was low for the yttria and high for the alloy for the 50 wt% sulfuric acid concentration. The dissolution rate of the yttria-based material was orders of magnitude lower than the dissolution rate of the alloy.

Acid/ Concentration	Weight Loss of 69% Density Yttria after 2 hrs at 95C (%)	Weight Loss of NbSi Alloy after 24 hrs at 95C (%)	relative dissolution rate of Yttria	relative dissolution rate of NbSi containing Alloy
Sulfuric 20%	10%	0.35%	Medium	Medium
Sulfuric 50%	0%	0.80%	Low	High

**[0042]** In yet another example, a nickel-based super-alloy useful in the manufacture of jet engine turbine blades was placed in 68 wt% nitric acid at 95 degrees Celsius for 99 hours. The sample was removed from the acid, a polished section was prepared and the surface roughness of the sample was examined in a scanning electron microscope and compared to an untreated sample of alloy. The acid treated surface was severely pitted and would be unacceptable for conventional jet engine construction.



**[0043]** As one of ordinary skill in the art will appreciate, the heretofore examples are merely exemplary and in no way limit the scope of the invention. Understandably, other acids and acids at concentrations other than those explicitly provided are envisioned. Furthermore, it is appreciated that the composition of the acid is determined/selected by the composition of the part material, the composition of the core material, the temperature and pressure associated with removing the core materials, the availability of the acid, and the cost associated therewith. Understandably, variable parts and processes will affect the relative importance of any one of these parameters. As an example, longer contact times may compensate for lower acid concentrations and/or lower treatment temperatures. Accordingly, the herein provided examples are in no way intended to limit the scope of the claimed invention. It is further understood and appreciated that combinations and compositions of the part material, the core material, and the acid other than those explicitly stated herein are envisioned and within the scope of the invention.

**[0044]** Therefore, in accordance with one embodiment of the present invention, a method of removing an yttria-based core from a niobium-based part includes the step of contacting the yttria-based core with an effective amount of a composition which comprises at least one acid selected from the group consisting of hydrochloric acid, nitric acid, phosphoric acid, nitric/phosphoric acid, sulfuric acid, and acetic acid.

**[0045]** Another embodiment of the present invention includes a method of casting a part which includes positioning an yttria-based core within a mold, introducing a molten niobium-based alloy into the mold to cast a part, and dissolving the yttria-based core with at least one acid selected from the group consisting of acetic acid, hydrochloric acid, nitric acid, phosphoric acid, nitric/phosphoric acid, and sulfuric acid.

**[0046]** A further embodiment of the present invention is a method of forming a turbine blade which includes casting a blade having at least one passage defined by a core formed of an yttria-type material by pouring a niobium-type material into a mold and removing the core from the blade by contacting the core with an acid which comprises at least one acid selected from the group consisting of acetic acid, hydrochloric acid, a nitric acid, a phosphoric acid, a nitric/phosphoric acid, and a sulfuric acid.

**[0047]** The present invention has been described in terms of the preferred embodiment, and it is recognized that equivalents, alternatives, and modifications, aside from those expressly stated, are possible and within the scope of the appending claims.

Parts List

10	exemplary turbine engine, or turbine
14	intake end
16	discharge end
18	housing or shroud
20	exterior
21	shroud cooling passage
22	air flow, indicated by arrow
24	fan
26	plurality of blades
28	hub
30	first portion
32	compressor
34	bypass flow
36	perforated panel
38	plurality of fins or blades
40	stator hubs
42	rotor hubs
44	combustor
46	turbine stage
48	plurality of hubs

(continued)

50	plurality of vanes or blades
52	nozzle
54	passage
56	inlet
58	outlet
59	flow, indicated by arrows
64	shank
66	geometric cross-section
68	mold
70	cavity
72	shape
78	core
69	mold body
76	interface
82	shape

## Claims

1. A method of removing an yttria-based core (78) from a niobium-based part (50), comprising the step of:  
 contacting the yttria-based core (78) with an effective amount of a composition which comprises at least one acid selected from the group consisting of hydrochloric acid, nitric acid, phosphoric acid, nitric/phosphoric acid, sulfuric acid, and acetic acid.
2. The method of claim 1 further comprising the step of heating the composition to a temperature effective to dissolve the yttria-based core (78).
3. The method of claim 2 wherein the temperature is the boiling temperature of the acid composition at a selected pressure.
4. The method of any preceding claim further comprising the step of agitating an interface of the acid composition with the yttria-based core (78).
5. The method of any preceding claim wherein the niobium-based part (50) comprises a niobium silicide material.
6. The method of any preceding claim wherein the yttria-based core (78) comprises a material selected from the group consisting of yttria, and oxides of at least one of magnesium, calcium, strontium, niobium, silicon, hafnium, zirconium, titanium, a rare earth metal of the lanthanide series, and combinations thereof.
7. The method of any preceding claim further comprising maintaining a temperature of the composition between about 50 degrees Celsius and about a boiling temperature of the composition.
8. The method of any preceding claim comprising dissolving the yttria-based core (78) with at least one of about 5% to about 91% concentration nitric acid, about 2% to about 37% concentration HCl acid, about 50% to about 85% concentration phosphoric acid, about 5% to about 30% concentration sulfuric acid, and about 30% to about 90% concentration acetic acid.
9. The method of any preceding claim wherein the niobium-based part (50) is a turbine component.

10. The method of any preceding claim further comprising forming the yttria-based core (78) to have a density between about 50% and about 100%.

## 5 Patentansprüche

1. Verfahren zum Entfernen eines Kerns auf Yttriumoxidbasis (78) aus einem Bauteil auf Niobbasis (50), aufweisend die Schritte:  
 10 In Kontakt bringen des Kerns auf Yttriumoxidbasis (78) mit einer wirksamen Menge einer Zusammensetzung, die zumindest eine Säure aufweist, ausgewählt aus der Gruppe bestehend aus Salzsäure, Salpetersäure, Phosphorsäure, Salpeter-/Phosphorsäure, Schwefelsäure und Essigsäure.
2. Verfahren nach Anspruch 1, weiterhin aufweisend den Schritt des Erwärmens der Zusammensetzung auf eine  
 15 Temperatur, die dabei wirksam ist, den Kern auf Yttriumoxidbasis (78) aufzulösen.
3. Verfahren nach Anspruch 2, wobei die Temperatur die Siedetemperatur der Säurezusammensetzung bei einem gewählten Druck ist.
- 20 4. Verfahren gemäß irgendeinem vorhergehenden Anspruch, weiterhin aufweisend den Schritt des Rührens einer Grenzfläche der Säurezusammensetzung mit dem Kern auf Yttriumoxidbasis (78).
5. Verfahren nach irgendeinem vorhergehenden Anspruch, wobei das Bauteil auf Niobbasis (50) ein Niobsilizidmaterial aufweist.
- 25 6. Verfahren nach irgendeinem vorhergehenden Anspruch, wobei der Kern auf Yttriumoxidbasis (78) ein Material aufweist, ausgewählt aus der Gruppe bestehend aus Yttrium und Oxiden von zumindest einem aus Magnesium, Kalzium, Strontium, Niob, Silizium, Hafnium, Zirkon, Titan, einem Seltenerdmetall der Lanthanid-Reihe, sowie Kombinationen davon.
- 30 7. Verfahren nach irgendeinem vorhergehenden Anspruch, weiterhin aufweisend das Halten einer Temperatur der Zusammensetzung zwischen etwa 50°C und etwa einer Siedetemperatur der Zusammensetzung.
8. Verfahren nach irgendeinem vorhergehenden Anspruch, aufweisend das Auflösen des Kerns auf Yttriumoxidbasis  
 35 (78) mit zumindest einem aus etwa 5 % bis etwa 91 % Konzentration Salpetersäure, etwa 2 % bis etwa 37 % Konzentration HCl-Säure, etwa 50 % bis etwa 85 % Konzentration Phosphorsäure, etwa 5 % bis etwa 30 % Konzentration Schwefelsäure und etwa 30 % bis etwa 90 % Konzentration Essigsäure.
9. Verfahren nach irgendeinem vorhergehenden Anspruch, wobei das Bauteil auf Niobbasis (50) eine Turbinenkomponente ist.
- 40 10. Verfahren nach irgendeinem vorhergehenden Anspruch, weiterhin aufweisend das Bilden des Kerns auf Yttriumoxidbasis (78), so dass er eine Dichte zwischen etwa 50 % und etwa 100 % hat.

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## Revendications

1. Procédé d'élimination d'un noyau à base d'oxyde d'yttrium (78) d'un composant à base de niobium (50), comprenant l'étape de :  
 50 mise en contact du noyau à base d'oxyde d'yttrium (78) avec une quantité efficace d'une composition qui comprend au moins un acide sélectionné à partir du groupe constitué par l'acide chlorhydrique, l'acide nitrique, l'acide phosphorique, l'acide nitrique/phosphorique, l'acide sulfurique, et l'acide acétique.
- 55 2. Procédé selon la revendication 1, comprenant, en outre, l'étape de chauffage de la composition à une température efficace afin de dissoudre le noyau à base d'oxyde d'yttrium (78).
3. Procédé selon la revendication 2, dans lequel la température est la température d'ébullition de la composition acide

à une pression sélectionnée.

4. Procédé selon l'une quelconque des revendications précédentes, comprenant, en outre, l'étape d'agitation d'une interface de la composition acide avec le noyau à base d'oxyde d'yttrium (78).

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel la partie à base de niobium (50) comprend un matériau à base de siliciure de niobium.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel le noyau à base d'oxyde d'yttrium (78) comprend un matériau sélectionné à partir du groupe constitué par l'oxyde d'yttrium, et des oxydes d'au moins l'un du magnésium, du calcium, du strontium, du niobium, du silicium, de l'hafnium, du zirconium, du titane, d'un métal de terre rare de la série des lanthanides, et de mélanges de ceux-ci.

7. Procédé selon l'une quelconque des revendications précédentes, comprenant, en outre, le maintien d'une température de la composition entre 50 degrés Celsius environ et sensiblement la température d'ébullition de la composition.

8. Procédé selon l'une quelconque des revendications précédentes, comprenant la dissolution du noyau à base d'oxyde d'yttrium (78) avec au moins l'un de l'acide nitrique à une concentration de 5 % environ à 91 % environ, l'acide chlorhydrique (HCl) à une concentration de 2 % environ à 37 % environ, l'acide phosphorique à une concentration de 50 % environ à 85 % environ, l'acide sulfurique à une concentration de 5 % environ à 30 % environ, et l'acide acétique à une concentration de 30 % environ à 90 % environ.

9. Procédé selon l'une quelconque des revendications précédentes, dans lequel le composant à base de niobium (50) est un composant de turbine.

10. Procédé selon l'une quelconque des revendications précédentes, comprenant, en outre, la formation du noyau à base d'oxyde d'yttrium (78) de manière à présenter une densité de 50 % environ à 100 % environ.

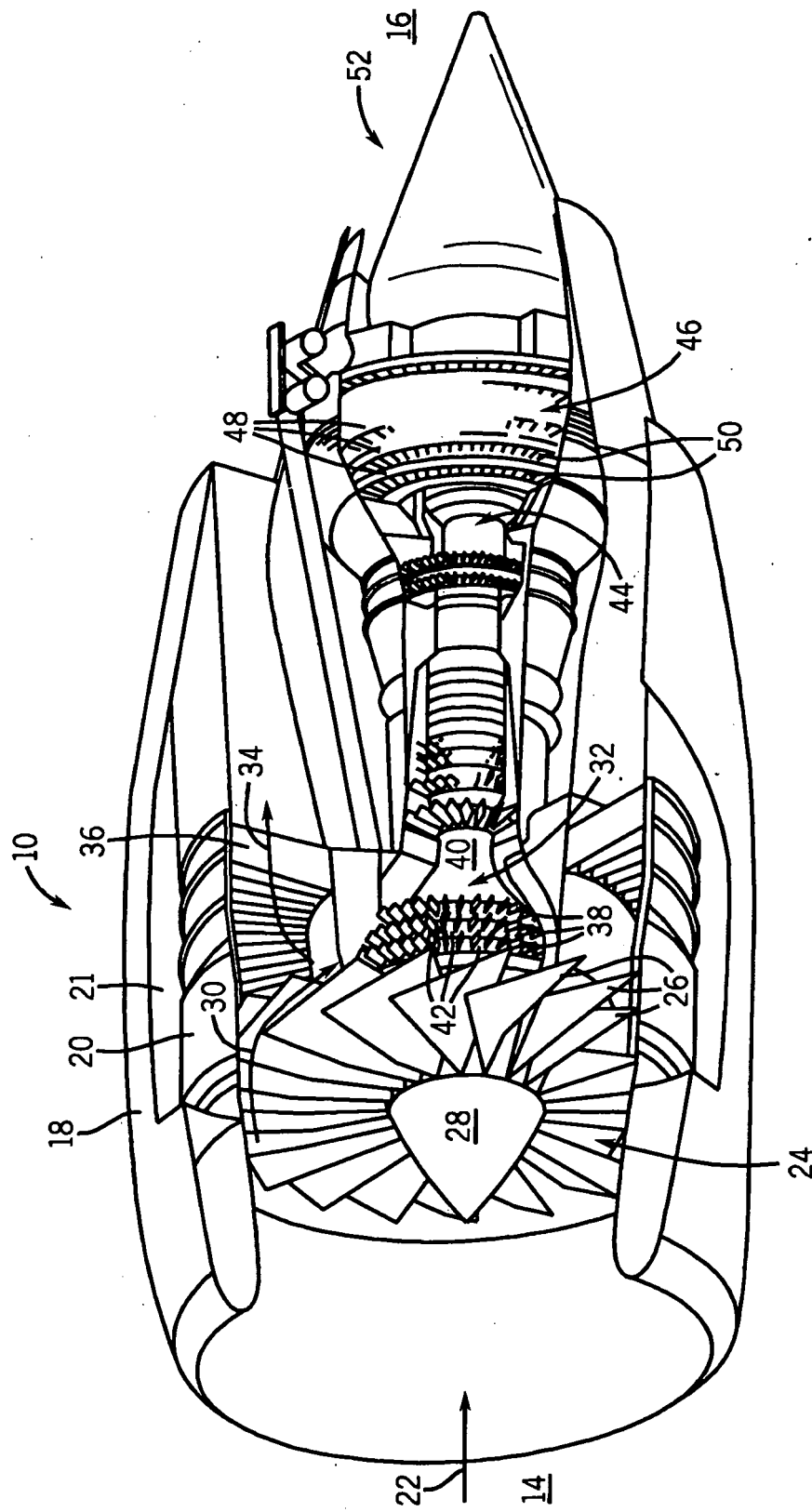
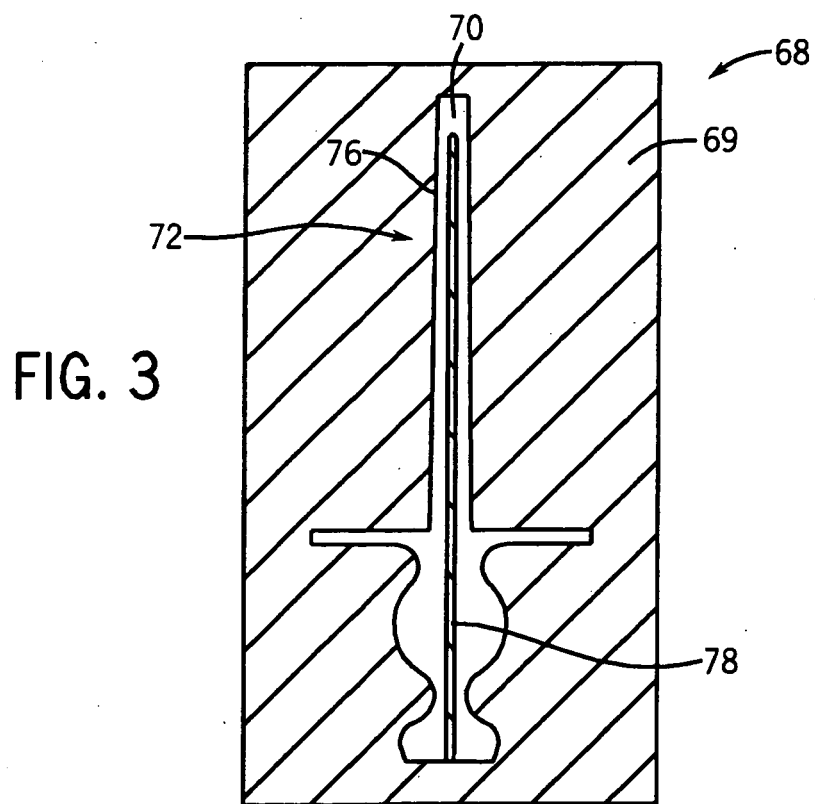
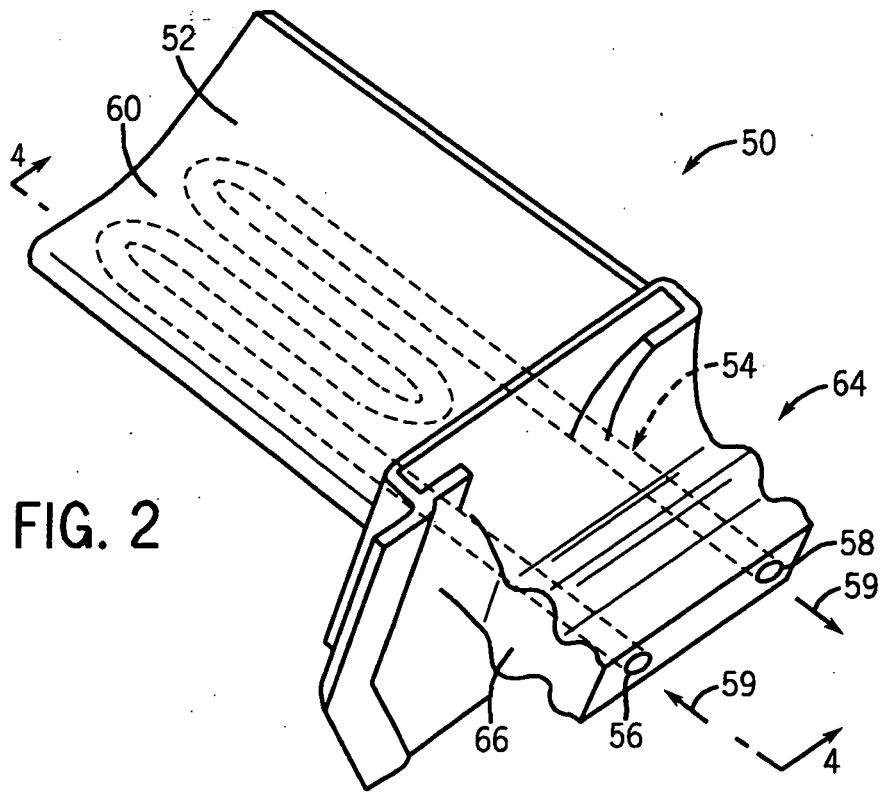


FIG. 1



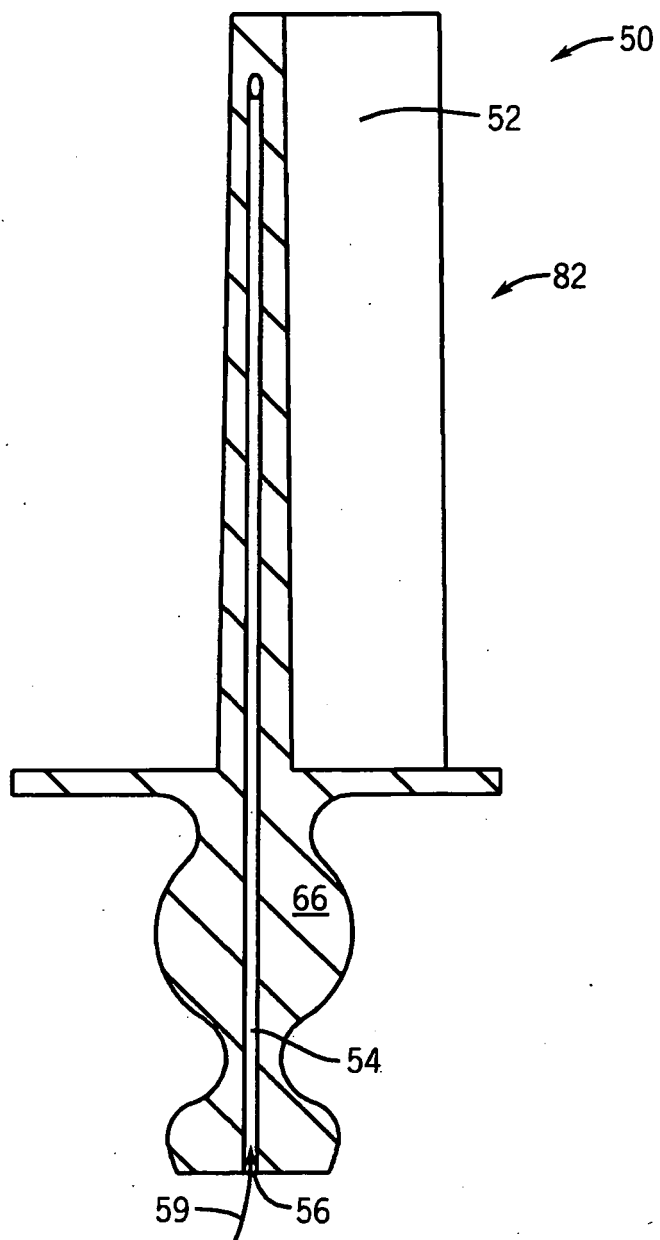


FIG. 4

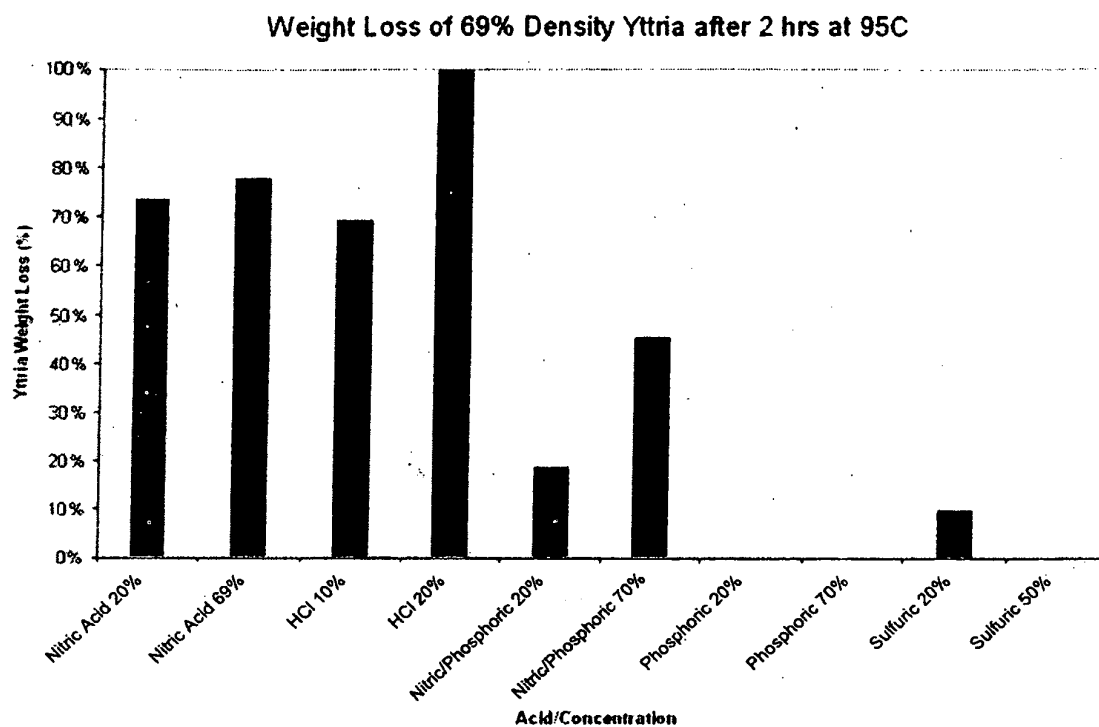


FIG. 5

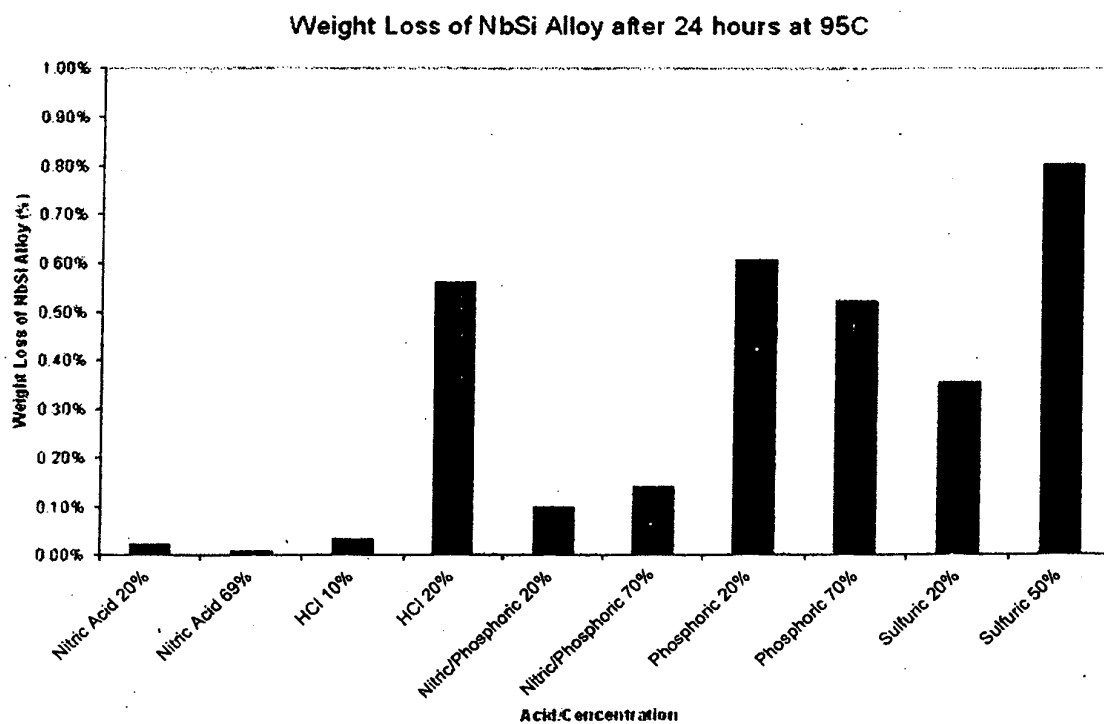


FIG. 6