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(54) **Nickel-based superalloy**

(57) A nickel-based superalloy comprising in wt% Co=1-8%, W=7-15%, Mo=1-8%, Ta=7-15%, Al=4-9%, having a mechanical strength at very high temperature, up to 1300°C, higher than that of the known superalloys by raising the T_{solidus} of the alloy and developing an in-

termetallic γ phase in high percentages by volume, higher than 70%, which maintains its properties practically unchanged until the incipient melting of the alloy, having a T_{solvus} , i.e. a solvus temperature of the γ phase higher than the T_{solidus} of the alloy, i.e. the temperature at which the liquid phase starts being present.

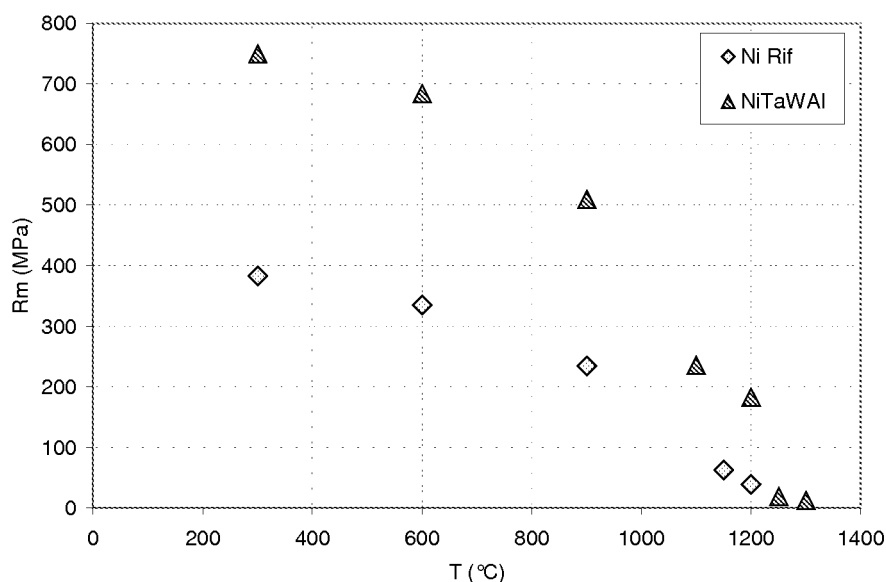


Fig. 5

DescriptionField of the invention

5 **[0001]** The present invention relates to a nickel-based superalloy which can be applied, for example, for making both tools for the iron and steel industry, used for the hot deformation of steels and alloys, and aerospace components, i.e. for applications in which high mechanical properties and/or resistance to wear/erosion at high temperature, up to 1300°C, are required.

10 State of the art

[0002] Nickel-based superalloys are today the most used for making components working at high temperature, up to 1000°C, and subjected to severe stresses. They are currently the best compromise in terms of high and low temperature mechanical properties, mechanical and thermal fatigue strength, creep resistance, and resistance to oxidation and to corrosion.

15 **[0003]** Various nickel-based superalloys are known, with the corresponding manufacturing and thermal treatment process.

[0004] The components with single crystal structure exhibit the best performance in terms of creep resistance, followed by the directional structures (formed by columnar grains) and equiaxial structures, in which the weakest part is represented by the grain boundaries. Indeed, elements such as B, Zr and Hf, strengthening the grain boundaries, are added to the equiaxial and directional components. The directional components are better than the equiaxial components because they exhibit columnar grains along the direction of application of stress and the transverse grain boundaries are virtually absent; single crystal structures, in which the grain boundaries do not exist, exhibit a strength which depends only on the composition of the matrix.

25 **[0005]** A typical nickel-based superalloy consists of a nickel alloy matrix (γ austenitic phase with face-centered cubic lattice, fcc), solid-solution strengthened by adding refractory elements and a series of precipitated phases of intermetallic compounds and carbides, which contribute to further strengthening and thermal stabilization of the metal.

[0006] The various chemical elements must be properly balanced to confer stability to the material, in addition to creep resistance and to hot oxidation/corrosion resistance. The superalloy composition may be described in general terms by splitting the various elements into groups:

- a first group of elements, such as Co, Fe, Cr, W, Mo (more recently also Re and Ru), which act as solid-solution strengtheners of the austenitic matrix;
- a second group of elements, such as Al, Ti, Ta and Nb, which form precipitates coherent with the matrix of the Ni_3X type (γ' phase), causing precipitation hardening of the matrix; the γ' phase is generally present in fractions from 15% to 65% by volume;
- a third group of elements, consisting of C, B, Zr and Hf; carbon forms carbides, such as MC, $M_{23}C_6$ and M_6C reacting with Cr, Mo, W, Ta, Ti and Nb, while B, Zr and Hf segregate at the grain boundaries, thus improving ductility and strength of the material (in the case of equiaxial and directional components);
- 40 - yttrium (Y) and other elements belonging to the rare earth metals (REM) group are often added to increase high-temperature oxidation resistance; also aluminium, when present in contents higher than 5%, contributes to considerably increasing the resistance to high-temperature oxidation by forming a protective $\alpha-Al_2O_3$ based film.

45 **[0007]** Today, the maximum working temperature of a superalloy is approximately 1100°C and related to the third-generation SX alloy CMSX-1 0 with a high content of Re (up to 6%). Second-generation alloys, such as, for example, the CMSX-4 alloy described in document US4643782, contain 3% of Re, while rhenium was absent from the first-generation alloys. Such alloys are used for the construction of gas turbine blades subject to high mechanical and thermal working stresses (typical application in the first stages of turbines).

[0008] The introduction of rhenium (Re), in addition to other refractory elements, allows a further strengthening of the matrix and contributes to maintaining high corrosion resistance, even though the content of Cr is lowered, with respect to first-generation alloys.

[0009] The CMSX-4 alloy was designed so as to have a high creep resistance and can work for a short time at up to 1093°C.

55 **[0010]** The CMSX-10 alloy exhibits excellent castability, high creep resistance, high fatigue strength for both Low Cycle Fatigue (LCF) and High Cycle Fatigue (HCF) and good resistance to corrosion and to oxidation of the component as such.

[0011] The thermal treatment of the as-cast alloy is a key step in improving the features of these materials and stability at high temperatures. Strength is optimized by means of microstructural homogenization, solution heat treatment, and

reprecipitation of the γ' phase into very fine particles. Therefore, the alloy composition is always designed to provide an adequate metallurgical window (i.e. a considerable difference between the solvus temperature of the γ' phase and the solidus temperature of the alloy, with $T_{\text{solidus}} > T_{\text{solvus}}$) so as to allow to obtain a complete dissolution and reprecipitation of the γ' phase by means of appropriate treatments, before working at high temperature.

[0012] The aforesaid considerable temperature difference varies from 40 to 150°C, being T_{solidus} of the alloy higher than T_{solvus} of the γ' phase.

[0013] The complex third-generation alloys usually contemplate a thermal ageing treatment, often in two steps, to induce the fine precipitation of the γ' phase after solution heat treatment and controlled cooling treatment.

[0014] Also in third-generation alloys, Cr, although in lower content, is always present in percentages by weight higher than 1 %, e.g. in ranges from 1-4% to 3-12%. Disadvantageously, nickel-based superalloys offering a higher strength at very high temperature, specifically up to 1300°C, are not currently available, which would allow, for example:

- in the iron and steel field, to avoid the limits presented by the currently used materials by increasing thermo-mechanical stress at high temperature;
- and in the aerospace field, to facilitate an increase of the system speeds (e.g. missiles), closely connected to the raising of temperatures to which some specific components, such as propulsion system parts and control surfaces directly concerned by the aero-thermodynamic stress, are subjected.

[0015] The need for a nickel-based superalloy which allows to fulfill the aforesaid needs is therefore felt.

Summary of the invention

[0016] It is the main object of the present invention to make a nickel-based superalloy which offers a strength at very high temperature, up to 1300°C, higher than that of the known superalloys by raising the T_{solidus} of the alloy and developing an intermetallic phase γ' (gamma prime) in high percentages by volume, higher than 70%, which maintains its features practically unchanged until the incipient melting of the alloy, having a T_{solvus} , i.e. a dissolution temperature of the γ' phase, higher than the T_{solidus} of the alloy, i.e. the temperature at which the liquid phase starts being present.

[0017] It is a further object of the present invention to provide a more cost-effective manufacturing process of the aforesaid nickel-based superalloy.

[0018] The present invention thus proposes to reach the aforesaid objects by making a nickel-based superalloy which, in accordance with claim 1, has a composition by weight percentage comprising cobalt from 1 to 8%; tungsten from 7 to 15%; molybdenum from 1 to 8%; tantalum from 7 to 15%; aluminium from 4 to 9%; chromium lower than 0.5%; carbon lower than or equal to 0.1%; the remaining being nickel and inevitable impurities; said superalloy comprising an intermetallic phase (γ') of the Ni_3X type where X is aluminium and/or tantalum, and having a solvus temperature (T_{solvus}) of the intermetallic phase (γ') higher than the solidus temperature (T_{solidus}) of the alloy.

[0019] A second aspect of the present invention relates to a manufacturing process of the aforesaid nickel-based superalloy in which, in accordance with claim 12, said superalloy is cast by means of either an equiaxial solidification method, or a directional solidification method, or a single crystal solidification method.

[0020] Further aspects of the invention relate to a component for iron and steel tooling according to claim 13, such as for example an industrial plug for piercing steel billets, and an aerospace component according to claim 15, such as the nozzle flap of an aeronautic engine.

[0021] The objective of obtaining a high-temperature strength, until 1300°C, higher than that of the known superalloys is reached by means of a chemical composition of the superalloy so to:

- have a high content of elements strengthening the matrix by solid-solution hardening;
- have an intermetallic γ' phase, as further matrix strengthening phase, stable to high temperatures.

[0022] The superalloy has a very low chromium content (< 0.5% by weight): such an element was not introduced in the composition, or however was introduced in a very low percentage with respect to the known superalloys, so as to increase the matrix solubility of other elements, such as W, Ta and Mo, which have a higher solid solution hardening effect on the matrix.

[0023] According to a preferred embodiment, the alloy is of the dual-phase type, formed by intermetallic γ' phase of the Ni_3X type, where X is aluminium and/or tantalum, i.e. of the $\text{Ni}_3(\text{Al}, \text{Ta})$ type, distributed in a nickel solid solution (matrix). The intermetallic phase is formed during solidification, thus its T_{solvus} is higher than the T_{solidus} of the alloy.

[0024] The high mechanical strength is thus promoted by the fact that the intermetallic γ' phase, which contributes to matrix hardening, having a T_{solvus} higher than the T_{solidus} of the matrix, is not dissolved during high-temperature operation, thus maintaining its properties until the incipient melting of the alloy.

[0025] The ($T_{\text{solvus}} - T_{\text{solidus}}$) difference is higher than 5°C. In an example below, it is equal to 9 °C, but may also reach

15-20 °C or more.

[0026] The superalloy according to the present invention, named NiTaWAl, has a nickel rich composition, with predetermined additions of tungsten and tantalum, refractory elements and aluminium.

[0027] The alloy also contains a predetermined amount of molybdenum, while it is essentially free from chromium.

[0028] The chemical composition was designed and optimized to improve strength at high temperatures, specifically up to 1300°C.

[0029] The alloy may be mainly used for the production by investment casting of components with equiaxial, directional or single crystal structure.

[0030] It may also be used as powder, after specific gas-atomization process, for making coatings, by using thermal spraying techniques, such as HVOF (High Velocity Oxy Fuel), APS (Air Plasma Spray), VPS (Vacuum Plasma Spray) and PTA (Plasma Transferred Arc).

[0031] The applications of the superalloy, object of the present invention, relate to various industries.

[0032] In the iron and steel field, the tooling for forming metallic semi-finished products at high-temperature are generally made of steels for hot applications and of Cobalt and Nickel based superalloys.

[0033] Such materials exhibit their limits as the high-temperature thermo-mechanical stresses increase, caused by the need to process high-alloy steel materials which present a high hot deformation strength and which cause problems of wear and degradation of the forming tools.

[0034] In the aerospace industry, the generalized increase of system speeds (e.g. missiles) is closely linked to the temperature increase to which some specific components are subjected.

[0035] We can mention some control surfaces directly concerned by the aerothermodynamics stress (which increases with speed and contributes to increasing surface temperatures) and parts of the propulsion systems, the development trend of which is generally based on the increase of combustion temperatures.

[0036] The main advantage of the invention with respect to the alloys currently in use can be identified in high strength, high wear resistance and high thermal fatigue strength up to 1300°C.

[0037] The high mechanical properties of the alloy are due to its chemical composition, to contents of Cr lower than 0.5% and thus to the presence of a higher content of solid-solution matrix strengthening elements and to the presence of the intermetallic phase up to the incipient melting temperature of the alloy. Furthermore, the as-cast alloy in virtue of its features can be used without thermal treatment after casting, contrary to the last-generation alloys which, instead, require complex, extremely expensive cycles of solution heat treatment and ageing in furnace.

[0038] The dependent claims describe preferred embodiments of the invention.

Brief description of the figures

[0039] Further features and advantages of the present invention will be more apparent in the light of the detailed description of preferred, but not exclusive, embodiments of a nickel-based superalloy and of a manufacturing process thereof, illustrated by way of non-limitative example, with the aid of the accompanying drawings, in which:

Figure 1 depicts the microstructure of the superalloy according to the invention, observed under an optical microscope at different magnifications;

Figure 2 depicts the microstructure of the superalloy according to the invention, observed under a SEM at different magnifications;

Figure 3 depicts the microstructure of the intermetallic γ' phase observed under a SEM;

Figure 4 depicts the yield strength pattern according to the test temperature of the superalloy of the invention (NiTaWAl) and of the nickel-based reference alloy (Ni-Ref);

Figure 5 depicts the ultimate tensile strength pattern according to the test temperature of the superalloy of the invention (NiTaWAl) and of the nickel-based reference alloy (Ni-Ref);

Figure 6 depicts the wear resistance of the superalloy according to the invention (NiTaWAl), compared with the Ni- and Co-based reference alloys shown in Table 9, following a hot sliding wear test;

Figure 7 depicts the thermal fatigue strength of the superalloy according to the invention, compared with the Ni- and Co-based reference alloys;

Figure 8 depicts, from left to right, a resin prototype of an industrial plug, ceramic shells for casting the molten bath and some pilot industrial bits made in said shells;

Figure 9 depicts the comparison between two industrial plugs, formed by NiTaWAl superalloy and nickel-based reference superalloy, respectively, after laboratory piercing tests;

Figure 10 depicts some steps of the plug manufacturing process, such as shell sintering and shell breakage, and some finished components;

Figure 11 depicts nozzle flaps of an aeronautic afterburner;

Figure 12 depicts a thermodynamic cycle with an afterburner turbojet in flight; the ideal cycle is shown by a dashed line;

Figure 13 depicts the thrust increase of a turbojet in step of afterburning;

Figure 14 depicts the temperature variation (single cycle) measured on the surface and at a depth of 1 mm of superalloy specimens subjected to thermal cycles;

Figure 15 depicts a superalloy specimen invested by a high-temperature, highspeed gas flow.

Detailed description of preferred embodiments of the invention

Chemical composition of the superalloy

[0040] Tables from 1 to 3 and Tables from 4 to 6 respectively show the composition of the nickel-based superalloy, according to the invention, named NiTaWAl, in Equiaxial (EQ) or Directionally Solidified version (DS) and Single Crystal version (SX).

[0041] The tables show the ranges of percentage by weight of the chemical composition; specifically, the broadest ranges (Tab. 1 and Tab. 4), the preferred ranges (Tab. 2 and Tab. 5) and the narrowest ranges (Tab. 3 and Tab. 6) of the superalloy chemical composition of the invention are shown for each version, EQ/DS and SX. The alloy was designed so as to obtain a material with high mechanical performance at high temperatures, up to 1300°C. Its composition was optimized on the basis of the following criteria:

- a high predetermined content of W, Ta and Mo, matrix strengthening elements by solid-solution and by means of the formation of carbides. Ta improves hot oxidation resistance, while W and Mo tend to reduce it. Ta increases the fraction by volume of the γ' phase, $\text{Ni}_3(\text{Al}, \text{Ta})$, and strengthens it; furthermore, it allows the formation of primary carbides which are very stable also at very high temperatures. High concentrations of Ta, however, contribute (strongly depending on the content of elements with a high atomic number) to formation of the γ' eutectic phase with a reduction of the high-temperature mechanical strength; excessively high Mo and W contents also lead to the formation of embrittling phases;
- a high predetermined content of aluminium which strengthens the matrix by forming the γ' phase, $\text{Ni}_3(\text{Al}, \text{Ta})$, persistent up to the alloy melting temperature. Indeed, the γ' phase exhibits a solvus temperature higher than the solidus temperature of the alloy; however, Al values higher than 10% promote the formation of the γ' eutectic phase, with the decrease of the high-temperature mechanical strength;
- presence of C, Zr, Hf and B in the case of equiaxial or directional castings, for improving grain boundary strength and thus material ductility.

Table 1 - Broadest nominal composition (% by weight) of the NiTaWAl alloy, EQ and DS versions

Ni (%)	Co (%)	W (%)	Mo (%)	Ta (%)	Al (%)	C (%)	Hf (%)	Zr (%)	B (%)	Cr (%)	Ti (%)	Si (%)	S (%)	P (%)
base	1-8	7-15	1-8	7-15	4-9	0.01-0.1	<0.5	<0.05	<0.05	<0.5	<0.1	<0.05	<0.002	<0.003

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Table 2 - Preferred nominal composition (% by weight) of the NiTaWAl alloy, EQ and DS versions

Ni (%)	Co (%)	W (%)	Mo (%)	Ta (%)	Al (%)	C (%)	Hf (%)	Zr (%)	B (%)	Cr (%)	Ti (%)	Si (%)	S (%)	P (%)
base	3-7	9-12	3-6	9-12	5-8	0.01-0.1	<0.5	<0.05	<0.05	<0.5	<0.1	<0.05	<0.002	<0.003

Table 3 - Narrowest nominal composition (% by weight) of the NiTaWAl alloy, EQ and DS versions

Ni (%)	Co (%)	W (%)	Mo (%)	Ta (%)	Al (%)	C (%)	Hf (%)	Zr (%)	B (%)	Cr (%)	Ti (%)	Si (%)	S (%)	P (%)
base	4-5.5	9.5-11	4.5-6	9.5-11	5.5-7	0.01-0.1	<0.5	<0.05	<0.05	<0.5	<0.1	<0.05	<0.002	<0.003

Table 4 - Broadest nominal composition (% by weight) of the NiTaWAl alloy, SX version

Ni (%)	Co (%)	W (%)	Mo (%)	Ta (%)	Al (%)	C (%)	Cr (%)	Ti (%)	Si (%)	S (%)	P (%)
base	1-8	7-15	1-8	7-15	4-9	<0.01	<0.5	<0.1	<0.05	<0.002	<0.003

Table 5 - Preferred nominal composition (% by weight) of the NiTaWAl alloy, SX version

Ni (%)	Co (%)	W (%)	Mo (%)	Ta (%)	Al (%)	C (%)	Cr (%)	Ti (%)	Si (%)	S (%)	P (%)
base	3-7	9-12	3-6	9-12	5-8	<0.01	<0.5	<0.1	<0.05	<0.002	<0.003

Table 6 - Narrowest nominal composition (% by weight) of the NiTaWAl alloy, SX version

Ni (%)	Co (%)	W (%)	Mo (%)	Ta (%)	Al (%)	C (%)	Cr (%)	Ti (%)	Si (%)	S (%)	P (%)
base	4-5.5	9.5-11	4.5-6	9.5-11	5.5-7	<0.01	<0.5	<0.1	<0.05	<0.002	<0.003

[0042] Minor elements, considered impurities, may be present, such as:

Nb < 500 ppm,
Y < 20 ppm,
Mn < 1000 ppm,
N < 50 ppm.

[0043] Rare earth metals (REM) and yttrium are not deliberately added, although they improve hot oxidation resistance, because they lower the solidus temperature of the alloy.

[0044] The chromium content is maintained very low, lower than 0.5% by weight, both to increase solubility in matrix of elements, such as W, Ta and Mo, which are much more effective in solid solution matrix hardening, and to prevent the formation of embrittling phases.

[0045] The amount of the individual elements to be introduced in the alloy, which may vary according to the previously indicated ranges (Tables from 1 to 6), is selected according to the fundamental requirements that embrittling phases are not formed and that the solvus temperature of the intermetallic phase γ' is higher than the solidus temperature of the alloy, so as to reach the required final properties, primarily high tensile/compression strength, resistance to erosion, high-temperature wear, and to thermal fatigue, as well as a good hot oxidation behaviour.

[0046] The as-cast alloy can be used without any thermal treatment, because as there is no metallurgical window ($T_{\text{solvus}} > T_{\text{solidus}}$) the intermetallic phase cannot be dissolved during high-temperature operation.

[0047] An example of the microstructure of the alloy, object of the invention, is shown in Figure 1, showing the micrographs acquired under the optical microscope at different magnifications. The white phase is the γ' intermetallic phase. Figure 2 shows the images taken by a Scanning Electronic Microscope (SEM) with different magnifications and the following Table 7 shows the SEM microanalysis with EDS system (Energy Dispersion Spectrometry) of the present phases: the matrix B, the intermetallic phase A and the carbides C rich in W, Ta and Mo.

Table 7- EDS analysis (ref. Figure 2 a-b)

Area	Al (%)	Co (%)	Ni (%)	Mo (%)	Ta (%)	W (%)
A (intermetallic phase)	6	6	65	1	12	10
B (matrix)	5	7	66	4	6	12
C (carbides)	1	4	18	18	21	38

[0048] The γ' fine phase has dimensions of about 1 μm . The coarse intermetallic phase presents dimensions of about

100 μm . The γ' fine phase is shown in Figure 3. The fraction by volume of the alloy γ' phase varies within the composition range mainly according to the contents of Ta and Al.

[0049] The percentage by volume of the γ' phase is advantageously comprised in the 70-90% range.

[0050] Table 8 shows the relation between Al and Ta content and the percentage by volume of γ' phase present in the alloy of the invention.

Table 8 - Percentage by volume of the γ' phase according to the Ta and Al contents (% by weight)

Ta (%)	Al (%)	Percentage of γ' phase (%)
11	5	74
12	5	76
9	6	83
9	7	91
9	8	90

Properties of the NiTaWAl superalloy

[0051] The mechanical properties, wear resistance, thermal shock resistance and oxidation resistance of the alloy, object of the present invention, are shown below. The features of the alloy are compared with the features of some Ni- and Co-based reference alloys, the composition of which is shown in Table 9, used at high-temperatures in the iron and steel field.

Tab. 9 - Composition (% by weight) of the comparison alloys

	Ni (%)	C (%)	Si (%)	Mn (%)	Co (%)	Cr (%)	Mo (%)	W (%)	Fe (%)	Al (%)
Ni-Ref	base	0.03	0.17	0.34	---	15.90	17.40	4.7	1.20	---
Co-Ref	---	0.32	0.30	1.4	base	29.90	3.40	---	---	---
NiMoWAl	base	0.04	---	---	---	---	9.90	10.10	---	6

■ Hot mechanical resistance

[0052] Table 10 shows the yield strength $R_{p0.2}$ and the ultimate tensile strength R_m of the NiTaWAl alloy measured at various temperatures, from 300°C to 1300°C. These values are compared with those of the Ni-based reference alloy, indicated by Ni-Ref, commonly used for iron and steel industry applications, the composition of which is shown in Table 9. The corresponding graphs are shown in Figures 4 and 5.

[0053] The NiTaWAl alloy up to 1200°C shows an increase of yield strength of over 80 MPa and an increase of the ultimate tensile strength of over 130 MPa with respect to the reference alloy Ni-Ref.

Table 10 - High-temperature traction test results

T (°C)	Rp _{0.2} (MPa)		Rm (MPa)	
	Ni-Ref	NiTaWAl	Ni-Ref	NiTaWAl
300	204	742	383	749
600	269	644	335	684
900	163	465	234	509
1100	---	213	---	236
1150	60	---	63	---
1200	36	126	39	183
1250	---	17	---	19

(continued)

T (°C)	Rp _{0.2%} (MPa)		Rm (MPa)	
	Ni-Ref	NiTaWAl	Ni-Ref	NiTaWAl
1300	---	10	---	13

[0054] Furthermore, the hardness at ambient temperature of the NiTaWAl alloy is equal to 445 HV; that of the Ni-Ref alloy is equal to 220 HV.

■ Wear resistance

[0055] Figure 6 shows the wear resistance of the NiTaWAl alloy compared with the Ni- and Co-based alloys shown in Table 9, determined by a hot sliding test.

[0056] The test conditions are:

- Test time: 8 hours
- Test temperature: 1200°C on the NiTaWAl alloy
- Load: 400N
- Relative speed between specimens in contact: 0.5 m/s.

[0057] The wear properties are shown in terms of weight variations of the specimen. It is worth noting that the alloy according to the present invention exhibits a wear resistance approximately double with respect to that of the nickel-based reference alloy.

■ Thermal fatigue strength

[0058] Figure 7 shows the thermal fatigue strength of the NiTaWAl alloy compared with the Ni-Ref and Co-Ref reference alloys. Such a property is shown in terms of crack density (number of cracks per surface unit found on specimen, on the sample section, at determined magnifications). The crack density of the NiTaWAl superalloy is approximately 1/4 with respect to the Ni-based reference alloy (Ni-Ref).

[0059] The tests were carried out on cylindrical specimens with a thermal cycle from 100°C to 1200°C for 500 cycles.

■ Oxidation resistance

[0060] The alloy of the invention (NiTaWAl) subjected to static oxidation tests is more resistant than the Ni-Ref and Co-Ref reference alloys (described in Table 9). Indeed, oxidation tests carried out on approximately 20 mm in diameter, 50 mm long cylindrical samples show that at the end of the test:

- the cylindrical sample formed by NiTaWAl appears shiny, metallic grey in color, with approximately 0,5 mm thick scale, compact and strongly adherent to the matrix;
- the cylindrical sample formed by Ni-Ref appears crumbly and consumed from the surface inwards;
- the cylindrical sample formed by Co-Ref tends to descale, exhibits the formation of a thin scale, extremely weak and poorly adhering to the matrix.

Melting process for manufacturing the superalloy of the invention

[0061] The melting process for manufacturing the nickel-based superalloy according to the present invention contemplates the following steps:

- heating the charge material comprising Ni, Co, W, Mo, Ta, C with the respective percentages by weight shown in Table 1 or Table 4;
- melting the charge elements Ni, Co, W, Mo, Ta, C to obtain a liquid bath;
- first degassing of the liquid bath by means of rotary vacuum pumps, with pressure lower than 0.2 mbar in the melting chamber;
- adding Al to reach the percentage by weight shown in Table 1 or 4;
- second degassing of the liquid bath by means of rotary vacuum pumps;
- possible addition of Zr and B, so as to reach the percentages by weight shown in Table 1, if an equiaxial or directional

structure is required.

[0062] The idea of the suggested solution is tested in the various examples which are related to the above-described embodiment.

EXAMPLE 1

Example of manufacturing of components for tooling of iron and steel industry by means of a casting process

[0063] The NiTaWAl alloy may be mainly used for the production by investment casting of equiaxial, directional or single crystal components.

[0064] Specifically, said alloy was cast for making industrial plugs used during the billet piercing stage for the production of seamless pipes made of medium-high alloy steels. A series of pilot scale plugs, tested by a pilot piercer, was carried out before making the industrial plugs.

[0065] The components are made by means of VIM (Vacuum Induction Melting) technology which is the most versatile melting technology for nearly all special Fe-, Ni- and Co-based alloys, for the production of both ingots and castings.

[0066] The composition used for the component above is such to advantageously confer the *solvus*, *solidus* and *liquidus* temperatures to the alloy shown in Table 11. Such temperatures were measured by means of DTA (Differential Thermal Analysis).

Table 11 - T_{solvus} , T_{solidus} and T_{liquidus} of the NiTaWAl alloy

T_{solidus} (°C) of the alloy	T_{liquidus} (°C) of the alloy	T_{solvus} (°C) of the γ' phase
1357	1379	1366

[0067] In this case, the difference between T_{solvus} and T_{solidus} is 9°C.

Description of the process

[0068] A water cooled copper coil is used in the melting process of the charge, said coil being crossed by an alternating current which encompasses the refractory crucible thus generating eddy currents in the charge material which is heated by joule effect.

[0069] The magnetic stirring that the process generates in the bath guarantees both homogenization and a more accurate control of the chemistry and temperature of the molten mass, and transportation of material needed for performing the required chemical-physical reactions, such as, for example, degassing. It also allows exact composition and reproducibility of the product.

[0070] The superalloy melting cycle in VIM furnace consists of various steps: charging, melting, refining, chemical analysis and composition correction, casting.

[0071] The charge material includes alloying elements, except for reactive constituents which are introduced later by means of a charging system arranged on the top of the furnace. Reactions, such as degassing and deoxidizing, occur during the steps of melting and refining.

[0072] At the end of the refining period, the reactive elements, such as, for example, Al, Ti, Si, Zr, Hf, are introduced.

[0073] After a time required for the optimal mixing of the bath, the chemical analysis is carried out with possible additions of alloying elements if lacking in the composition. At the end, the molten mass is cast into a ceramic shell or, in the case of semi-finished products which are later machined by means of a machine tool to make the final item, into an ingot mould.

[0074] Raw materials only with purity of at least 99.9% were used as charge materials in order to prepare the NiTaWAl alloy.

[0075] The following operative practice was used for making equiaxial ingots and castings:

- heating the charge material;
- melting the charge elements Ni, Co, W, Mo, Ta, C;
- first degassing of the liquid bath by means of rotary vacuum pumps, with pressure lower than 0.2 mbar in the casting chamber;
- adding Al;
- second degassing of the liquid bath by means of rotary vacuum pumps;

- adding Zr and B, the most reactive elements;
- casting into ceramic shell, preheated to 1130-1170°C, or into ingot mould.

[0076] Zr and B are added a few instants before the casting itself, respecting only the times needed for solubilisation and homogenization in the liquid bath due to their tendency to form oxides.

Making of prototype/industrial components

[0077] A series of prototype plugs, to be tested on a pilot system, was made before proceeding with the manufacturing of industrial plugs for piercing steel billets.

[0078] The various manufacturing steps of the components contemplate making a series of resin prototypes which are assembled for making appropriate ceramic shells within which the molten bath is cast, with consequent manufacturing of the plugs. Figure 8 shows, from left to right, a resin prototype of an industrial plug, ceramic shells for casting the molten bath and some pilot industrial plugs made in said shells.

[0079] The alloy according to the invention was compared to the Ni-based reference alloy (Ni-Ref). The standard plug formed by Ni-based reference alloy, mounted on the pilot piercer, could not pierce more than three billets: a considerable deformation of the plug nose and a considerable amount of material stuck thereto was observed after the first three piercings. The NiTaWAl alloy plugs pierced 14 billets (a factor approximately 5 times higher) without presenting any deformation and only a slight layer of material stuck thereto was observed. Figure 9 shows the comparison between the two plugs during piercing.

[0080] For the NiTaWAl alloy plugs various test parameters were used, among which extremely different thermal conditions, in order to verify the effect of thermal shock:

- a plug was preheated and its temperature was maintained over 800°C: after 14 perforations, the bit was as new;
- a plug was not preheated, the test was carried out starting from cold and cooling in still air to 500°C and then, for the last five parts, it was rapidly cooled from 1100°C to approximately 200°C by means of compressed air, for a total of 14 parts. The plug remained sound also in this case.

[0081] The industrial components were made after making the pilot scale plugs: they were cast according to the previously described melting process. Figure 10 shows some steps of the process, such as shell sintering and shell breakage, and some finished components.

EXAMPLE 2

Example of manufacturing of an aerospace component

[0082] A further application of the invention is in the aeronautic field for components subject to high-temperature erosive wear. In the specific case, it relates to aeronautic engine nozzle flaps, shown in Figure 11. Such components are subjected to high thermo-mechanical stress in particular steps of the aircraft motion, in which a considerable addition propulsion thrust is required. The need to correctly adapt the section of the exhaust pipe to jet speed variations, which may be very large, normally implies that turbojets with afterburner have variable geometry nozzles: the latter need is generally fulfilled by nozzle flaps in which a crown of hydraulic jacks acts on fans which can be either closed or opened according to the operating conditions of the turbo reactor. Furthermore, the adoption of an adjustable nozzle facilitates starting of the turbojet, while the possibility of varying the exhaust gas ejection conditions allows a certain reduction of specific consumptions. Thus, the above-described operating needs require the use of nozzle flaps also during standard operation and not only during the steps of afterburning. Such a condition induces a higher thermo-mechanical stress on such components and therefore the need to adopt better performing materials, both from the point of view of mechanical resistance and from the point of view of wear and erosion resistance, is stringent. The operating temperatures at which they work can be inferred from the graph shown in Figure 12, exemplifying the thermodynamic cycle of a turbojet with afterburner. The materials usually used, such as commercial Ni- and/or Co-based superalloys, disadvantageously limit the time of use of such propulsion systems. The graph in Figure 13 shows the increase of thrust, and therefore of load, to which the nozzle flaps are subjected in particular operating conditions.

[0083] Some NiTaWAl alloy specimens were subjected to a high-temperature erosion test designed and made for the purpose, and compared with the Ni-based alloy named Ni-Ref above. A thermal depositing apparatus, commonly known as HVOF (High Velocity Oxy Fuel), capable of generating high-temperature supersonic flows, was used. Generally, such systems are used for surface coating processes by means of wear and corrosion resistance materials; in such a case, the HVOF was instead used as liquid fuel rocket engine for producing a controlled gaseous flow, because this is more similar to that actually occurring during the steps of emission. The temperature profile on the surface of the specimens

was obtained by controlling the kinematics of the torch mounted on a 6-axis robot.

[0084] Figure 14 shows the temperature variation in a single cycle, measured at the surface (curve 1) and at 1 mm of depth (curve 2) in superalloy specimens subjected to thermal cycles repeated 100 times.

[0085] The flow speed at torch outlet (kerosene-oxygen combustion products) was equal to approximately mach 2,5. In order to make the test more severe, alumina powder with a grain size of 80-100 μm and a flow rate of 10 g/min was injected in the highspeed gaseous flow. Figure 15 shows an image of the HVOF system during the test.

[0086] The test results in Table 12, while indicating a progressive erosive wear damage for both alloys (NiTaWAl and Ni-Ref), have shown a better behaviour of the NiTaWAl alloy of the invention.

Table 12 - High-temperature erosion test results

Number of test cycles	Alloy	Percentage loss by weight with respect to the initial value (%)
20	Ni-Ref	2
	NiTaWAl	2
40	Ni-Ref	4
	NiTaWAl	3
60	Ni-Ref	8
	NiTaWAl	7
80	Ni-Ref	13
	NiTaWAl	10
100	Ni-Ref	16
	NiTaWAl	12

Claims

1. A nickel-based superalloy having a composition by weight percentage comprising cobalt from 1 to 8%; tungsten from 7 to 15%; molybdenum from 1 to 8%; tantalum from 7 to 15%; aluminium from 4 to 9%; chromium lower than 0.5%; carbon lower than or equal to 0.1%; the remaining being nickel and inevitable impurities; said superalloy comprising an intermetallic phase (γ') of the Ni_3X type, where X is aluminium and/or tantalum, and having a solvus temperature (T_{solvus}) of the intermetallic phase (γ') higher than the solidus temperature (T_{solidus}) of the alloy.
2. A superalloy according to claim 1, wherein the difference between said solvus temperature (T_{solvus}) and said solidus temperature (T_{solidus}) of the alloy is at least 5°C.
3. A superalloy according to claim 1 or 2, wherein the percentage by volume of the intermetallic phase (γ') is at least 70%.
4. A superalloy according to claim 3, wherein the percentage by volume of the intermetallic phase γ' is comprised in the 70-90% range.
5. A superalloy according to claim 1, wherein titanium lower than 0.1%; silicon lower than 0.05%; sulfur lower than 0.002% and phosphorus lower than 0.003% are present in percentage by weight.
6. A superalloy according to any of the preceding claims, wherein carbon is present in the range from 0.01 to 0.1 %, in case of an equiaxial (EQ) or directional (DS) structure.
7. A superalloy according to any claim from 1 to 5, wherein carbon is lower than 0.01 %, in case of a single crystal (SX) structure.
8. A superalloy according to claim 6, wherein hafnium lower than 0.5%; zirconium lower than 0.05% and boron lower than 0.05% are present in percentage by weight.
9. A superalloy according to any of the preceding claims, wherein there are present impurities, such as Nb < 500ppm,

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Y < 20ppm, Mn < 1000ppm and N < 50ppm.

5 **10.** A superalloy according to any of the preceding claims, wherein cobalt from 3 to 7%; tungsten from 9 to 12%; molybdenum from 3 to 6%; tantalum from 9 to 12%; aluminium from 5 to 8% are present in percentage by weight.

11. A superalloy according to claim 10, wherein cobalt from 4 to 5.5%; tungsten from 9.5 to 11%; molybdenum from 4.5 to 6%; tantalum from 9.5 to 11%; aluminium from 5.5 to 7% are present in percentage by weight.

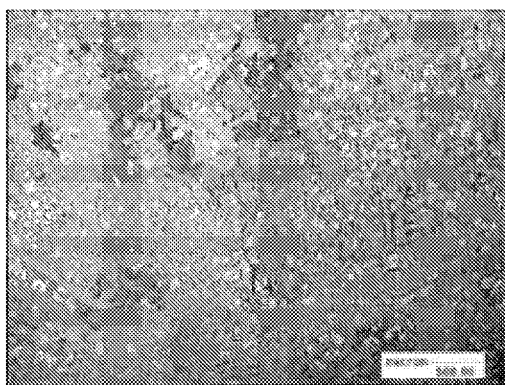
10 **12.** A manufacturing process of a nickel-based superalloy according to claim 1, wherein said superalloy is cast by means of an equiaxial solidification method, a directional solidification method or a single crystal solidification method.

13. A component for tooling of the iron and steel industry for making tubular elements, wherein a nickel-based superalloy according to claim 1 is at least part of its structure.

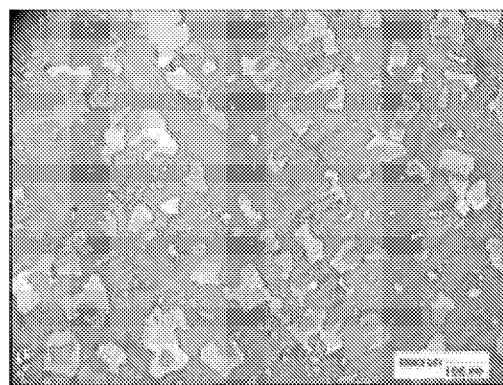
15 **14.** A component for tooling of the iron and steel industry according to claim 13, wherein said component is a plug for piercing steel billets.

15. An aerospace component, wherein a nickel-based superalloy according to claim 1 is at least part of its structure.

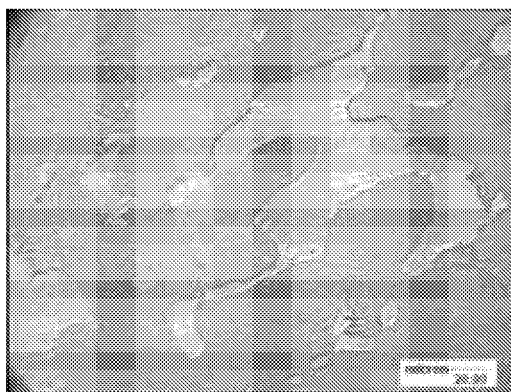
20 **16.** An aerospace component according to claim 15, wherein said component is an aeronautic engine nozzle flap.



a) 25X



b) 100X



c) 500X

Fig. 1

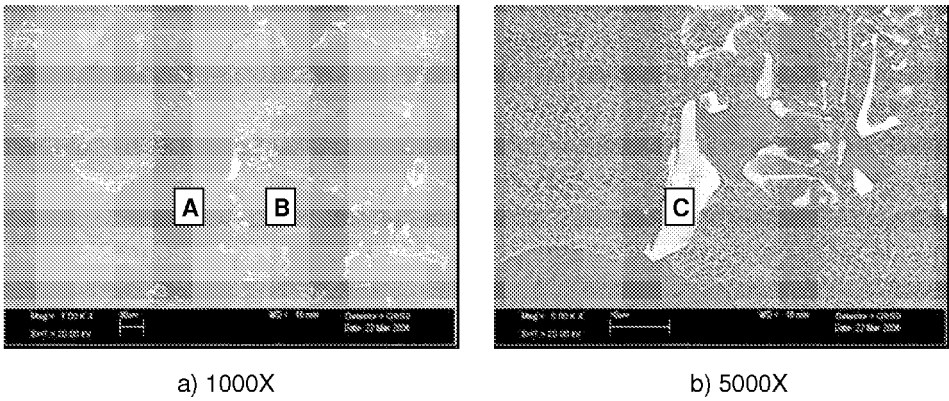


Fig. 2

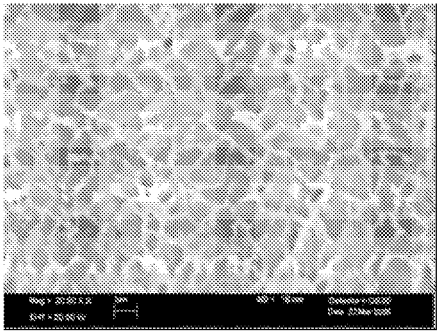


Fig. 3

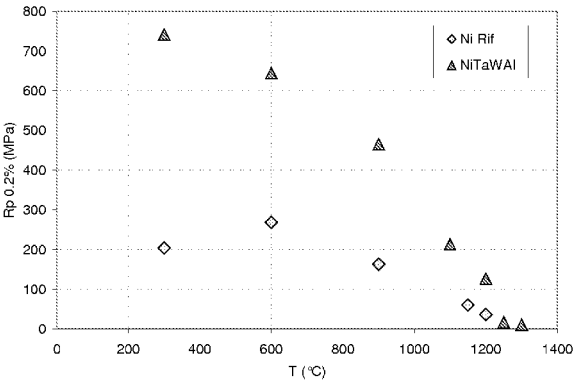


Fig. 4

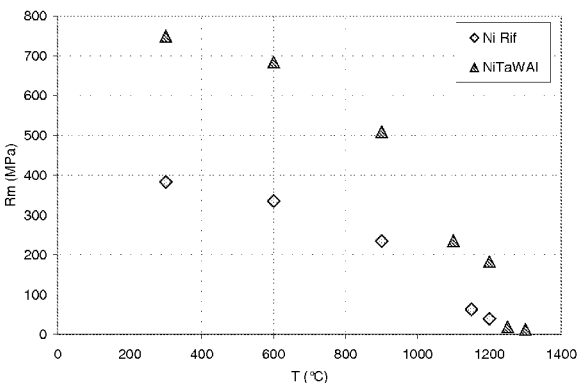


Fig. 5

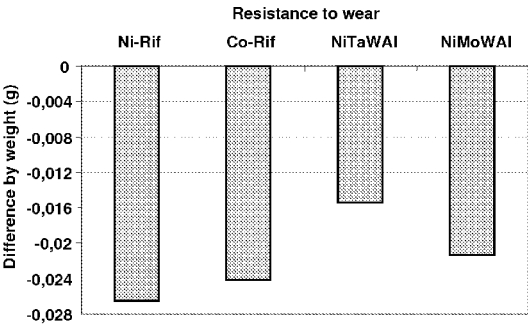


Fig. 6

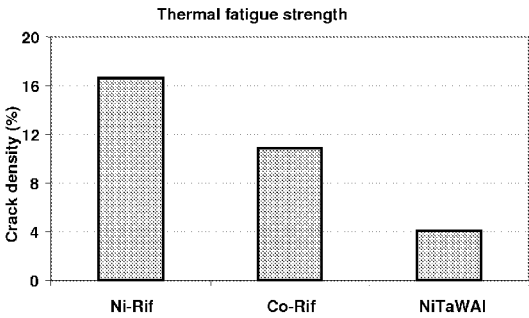
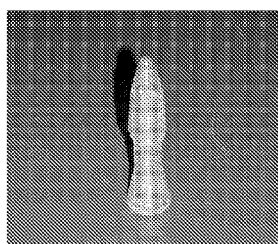
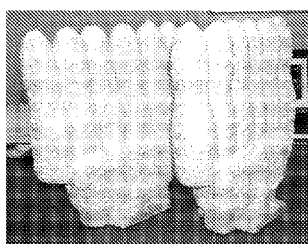


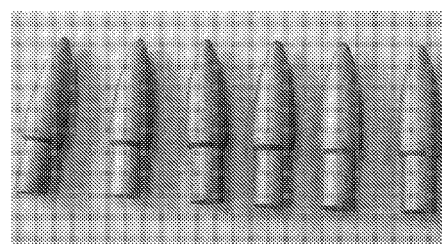
Fig. 7



Resin prototype



Ceramic shell

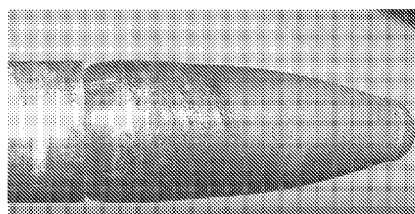


Pilot bits

Fig. 8

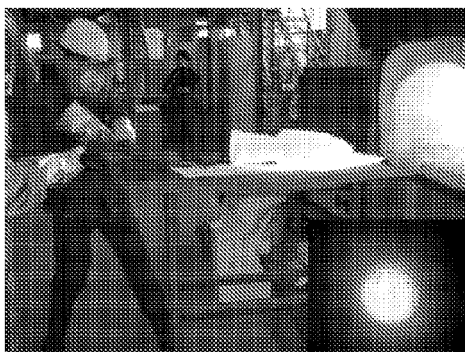


NiTaWAl alloy



Ni-rif alloy

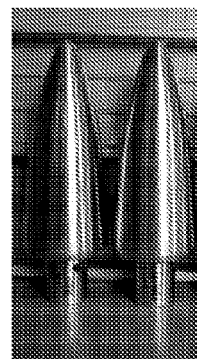
Fig. 9



Shell sintering



Shell breakage



Bits

Fig. 10

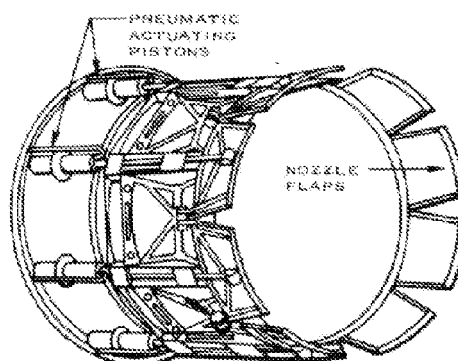


Fig. 11

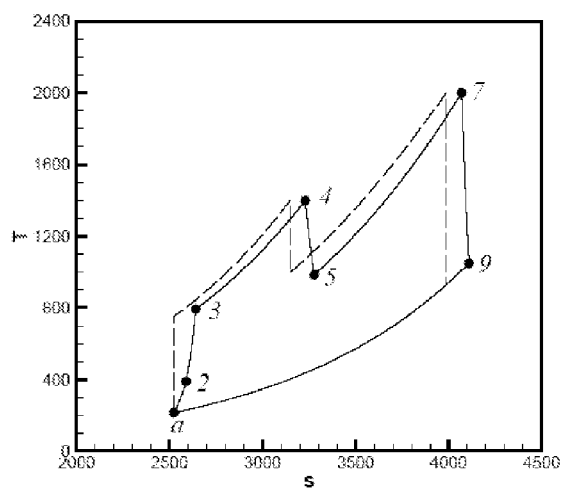


Fig. 12

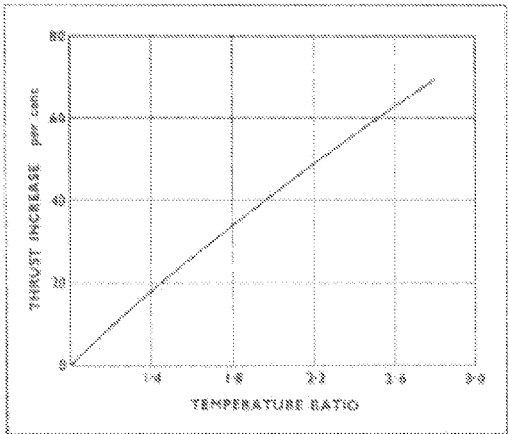


Fig. 13

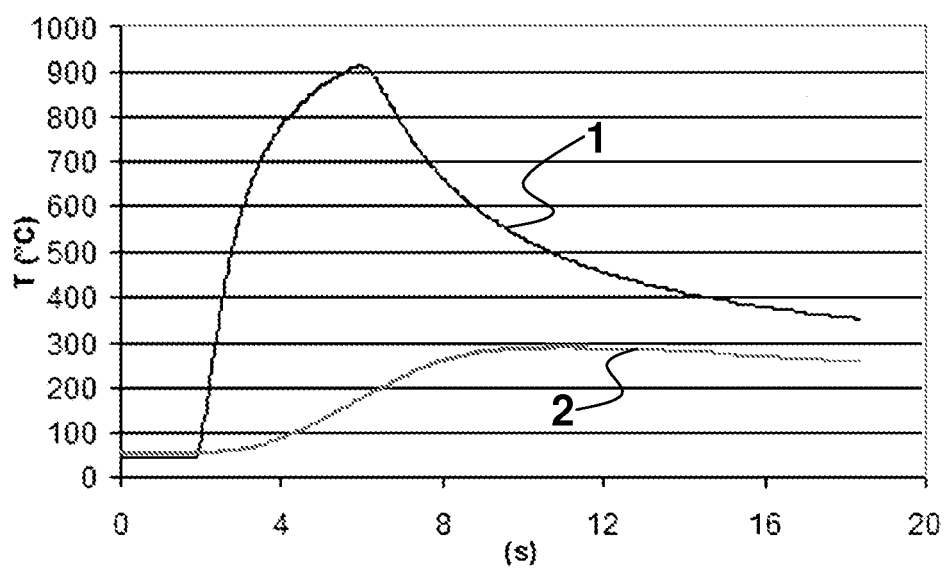


Fig. 14

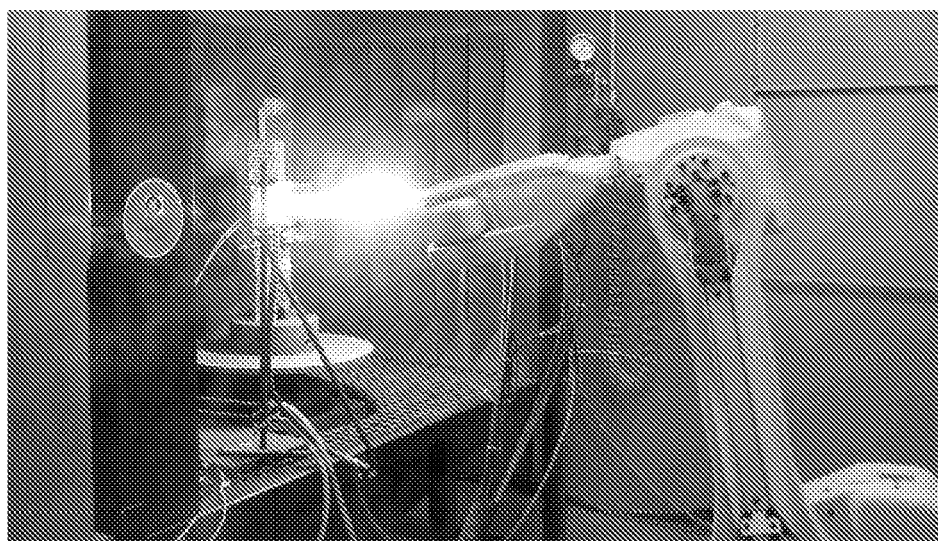


Fig. 15



EUROPEAN SEARCH REPORT

Application Number
EP 09 42 5052

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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 18 August 2009	Examiner González Junquera, J
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