

Coating process for manufacture or reprocessing of sputter targets and X-ray anodes

The present invention relates to a process for application
5 of layers to sputter targets or X-ray anodes, which layers contain only small amounts of gaseous impurities, such as oxygen.

The application of refractory metal layers to surfaces
10 displays numerous problems.

In the familiar processes, the metal is usually melted completely or partly, as a result of which the metals readily oxidize or take up other gaseous impurities.
15 Conventional processes, such as deposit welding and plasma spraying, must therefore be carried out under an inert gas or in vacuo.

In this case, a high outlay on apparatus is necessary, the
20 size of the structural components is limited and the content of gaseous impurities here is still not satisfactory.

The introduction of large amounts of heat transmitted into
25 the object to be coated leads to a very high potential for distortion and ensures that these processes cannot be employed in the case of complex structural components, which often also comprise components which melt at low temperatures. Such structural components are, in
30 particular, so-called sputtering targets, that is to say sources of metal which are employed in cathode sputtering of metal. Complex structural components must therefore be dismantled before processing, which as a rule means that

processing is uneconomical in practice, and merely recycling of materials (scrapping) of the structural components is carried out.

- 5 In vacuum plasma spraying, impurities of tungsten and copper which originate from the electrodes used are moreover introduced into the layer, which as a rule is undesirable. For example, if layers of tantalum or niobium are used for corrosion protection, these impurities reduce
10 the protective action of the coating by the formation of so-called micro-galvanic cells. In the case of sputter targets, this contamination can lead to components becoming unusable.
- 15 These processes moreover are melt metallurgy processes, which always involve their inherent disadvantages, such as, for example, unidirectional particle growth. This occurs in particular in laser processes, wherein a suitable powder is applied to the surface and is melted by a laser beam. A
20 further problem lies in the porosity, which can be observed in particular if a metal powder is first applied and this is then melted with a heat source. It has indeed been attempted in WO 02/064287 to solve these problems by merely superficially melting and sintering the powder particles by
25 a beam of energy, such as e.g. laser beams. However, the results are not always satisfactory, a high outlay on apparatus is necessary and the problems associated with an indeed reduced but nevertheless high introduction of heat into a complex structural component remain.

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WO-A-03/106,051 discloses a method and an apparatus for low pressure cold spraying. In this process a coating of powder

particles is sprayed in a gas substantially at ambient temperatures onto a workpiece. The process is conducted in a low ambient pressure environment which is less than atmospheric pressure to accelerate the sprayed powder particles. With this process a coating of a powder is formed on a workpiece.

EP-A-1,382,720 discloses another method and apparatus for low pressure cold spraying. In this process the target to be coated and the cold spray gun are located within a vacuum chamber at pressures below 80 kPa. With this process a workpiece is coated with a powder.

In view of this prior art it was the object of providing a novel process for recycling of sputtering targets or X-ray anodes in which no recycling of materials or dismantling of the target is necessary and which is distinguished by a low introduction of heat and outlay on apparatus and a broad applicability for various carrier materials and sputter materials or X-ray anode materials, and wherein the metal to be applied is not melted or superficially melted during processing.

The object of the present invention is achieved in that a desired refractory metal is applied to the desired surface by a process according to claim 1.

Processes in which, in contrast to the conventional processes of thermal spraying (flame, plasma, high-velocity flame, arc, vacuum plasma, low pressure plasma spraying) and deposit welding, no superficial melting or melting of the coating material, caused by thermal energy generated in

the coating apparatus, occurs are in general suitable for this. In this context, contact with a flame or hot combustion gases is to be avoided, since these can have the effect of oxidation of the powder particles and the oxygen content in the layers obtained therefore increases.

These processes are known to the person skilled in the art, for example, as cold gas spraying, cold spray processes, cold gas dynamic spraying, kinetic spraying and are described, for example, in EP-A-484533. The process described in the patent DE-A-10253794 is likewise also suitable according to the invention. The so-called cold spray process or the kinetic spray process are particularly suitable for the process according to the invention; the cold spray process which is described in EP-A-484533, to which reference is expressly made, is suitable in particular.

A process for application of coatings to surfaces of sputter targets or of X-ray anodes which is thus advantageously employed is a process wherein a gas flow forms a gas/powder mixture with a powder of a material chosen from the group consisting of niobium, tantalum, tungsten, molybdenum, titanium, zirconium, mixtures of at least two thereof or alloys thereof with one another or other metals, the powder has a particle size of 0.5 to 150 μm , wherein a supersonic speed is imparted to the gas flow and a jet of supersonic speed which ensures a speed of the powder in the gas/powder mixture of 300 to 2,000 m/s, preferably 300 to 1,200 m/s, is formed and the jet is directed on to the surface of an object.

On the surface of the object, the impinging metal powder particles form a layer, the particles becoming severely deformed. The powder particles are advantageously present in the jet in an amount which ensures a flow rate density of the particles of from 0.01 to 200 g/s cm², preferably 0.01 to 100 g/s cm², very preferably 0.01 g/s cm² to 20 g/s cm², or most preferred from 0.05 g/s cm² to 17 g/s cm².

The flow rate density is calculated from the formula $F = m / (\pi/4 \cdot D^2)$, where F = flow rate density, D = nozzle cross-section, m = powder delivery rate. A powder delivery rate of e.g. 70 g/min = 1.1667 g/s is a typical example of a powder delivery rate.

At low D values of below 2 mm values of markedly greater than 20 g/s cm² can be achieved. In this case F can easily assume values 50 g/s cm² or even higher at higher powder delivery rates.

An inert gas, such as argon, neon, helium or nitrogen or mixtures of two or more thereof, is in general used as the gas with which the metal powder forms a gas/powder mixture.

In particular cases, air can also be used. If safety regulations are met also use of hydrogen or mixtures of hydrogen with other gases can be used.

In a preferred version of the process the spraying comprises the steps of:

- providing a spraying orifice adjacent a surface to be coated by spraying;

- providing to the spraying orifice a powder of a particulate material chosen from the group consisting of niobium, tantalum, tungsten, molybdenum, titanium, zirconium, mixtures of at least two thereof or alloys thereof with one another or other metals, the powder having a particle size of 0.5 to 150 μm , said powder being under pressure;
- providing an inert gas under pressure to the spraying orifice to establish a static pressure at the spraying orifice and providing a spray of said particulate material and gas onto the surface to be coated; and
- locating the spraying orifice in a region of low ambient pressure which is less than 1 atmosphere and which is substantially less than the static pressure at the spraying orifice to provide substantial acceleration of the spray of said particulate material and gas onto said surface to be coated.

In another preferred version of the process the spraying is performed with a cold spray gun and the target to be coated and the cold spray gun are located within a vacuum chamber at pressures below 80 kPa, preferably between 0.1 and 50 kPa, and most preferred between 2 and 10 kPa.

Further advantageous embodiments can be seen from the claims.

The refractory metal, which is employed in powder form as the powder according to the invention, in general has a purity of 99 % or more, such as 99.5 % or 99.7 % or 99.9 %.

According to the invention, the refractory metal advantageously has a purity of at least 99.95 %, based on metallic impurities, in particular at least 99.995 % or at least 99.999 %, in particular at least 99.9995 %.

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If an alloy is employed instead of an individual refractory metal, at least the refractory metal has this purity, but preferably the entire alloy has this purity, so that a corresponding highly pure layer can be produced.

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The metal powder moreover has an oxygen content of less than 1,000 ppm oxygen, or less than 500, or less than 300, in particular an oxygen content of less than 100 ppm.

Refractory metal powders having a purity of at least

15 99.7 %, advantageously of at least 99.9 %, in particular 99.95 %, and a content of less than 1,000 ppm oxygen, or less than 500 ppm oxygen, or less than 300 ppm oxygen, in particular an oxygen content of less than 100 ppm, are suitable in particular.

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Refractory metal powders having a purity of at least 99.95 %, in particular of at least 99.995 %, and a content of less than 1,000 ppm oxygen, or less than 500 ppm oxygen, or less than 300 ppm oxygen, in particular an

25 oxygen content of less than 100 ppm, are suitable in particular.

Refractory metal powders having a purity of at least 99.999 %, in particular of at least 99.9995 %, and a

30 content of less than 1,000 ppm oxygen, or less than 500 ppm oxygen, or less than 300 ppm oxygen, in particular

an oxygen content of less than 100 ppm, are suitable in particular.

In all the abovementioned powders, the total content of
5 other non-metallic impurities, such as carbon, nitrogen or hydrogen, should advantageously be less than 500 ppm, preferably less than 150 ppm.

In particular, the oxygen content is advantageously 50 ppm
10 or less, the nitrogen content is 25 ppm or less and the carbon content is 25 ppm or less.

The content of metallic impurities is advantageously 500 ppm or less, preferably 100 ppm or less and most preferably
15 50 ppm or less, in particular 10 ppm or less.

Suitable metal powders are, for example, many of the refractory metal powders which are also suitable for the production of capacitors.

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Such metal powders can be prepared by reduction of a refractory metal compound with a reducing agent, and preferably subsequent deoxidation. In this procedure, for example, tungsten oxide or molybdenum oxide is reduced in a
25 stream of hydrogen at elevated temperature. The preparation is described, for example, in Schubert, Lassner, "Tungsten", Kluwer Academic/Plenum Publishers, New York, 1999 or Brauer, "Handbuch der Präparativen Anorganischen Chemie", Ferdinand Enke Verlag Stuttgart,
30 1981, p. 1530.

In the case of tantalum and niobium, the preparation is usually carried out by reduction of alkali metal heptafluorotantalates and earth alkaline metal heptafluorotantalates or the oxides, such as, for example, sodium heptafluorotantalate, potassium heptafluorotantalate, sodium heptafluoroniobate or potassium heptafluoroniobate, with an alkali metal or alkaline earth metal. In this procedure, the reduction can be carried out in a salt melt with the addition of, for example, sodium, or in the gas phase, calcium vapour or magnesium vapour advantageously being used. The refractory metal compound can also be mixed and heated with the alkali metal or alkaline earth metal. A hydrogen atmosphere may be advantageous. Numerous suitable processes are known to the person skilled in the art, and process parameters from which he can choose the suitable reaction conditions are known. Suitable processes are described, for example, in US 4483819 and WO 98/37249.

After the reduction, a deoxidation advantageously takes place. This can be effected, for example, by mixing the refractory metal powder with Mg, Ca, Ba, La, Y or Ce and subsequent heating, or heating the refractory metal in the presence of a getter substance in an atmosphere which renders possible transfer of oxygen from the metal powder to the getter substance. The refractory metal powder is then usually freed from the salts of the deoxidizing agent with an acid and water and dried. It is advantageous here if, when metals are used for decreasing the oxygen content, the metallic impurities can be kept low.

A further process for the preparation of pure powders having a low oxygen content comprises reduction of a refractory metal hydride with an alkaline earth metal as the reducing agent, thus such as disclosed, for example, in
5 WO 01/12364 and EP-A-1200218.

The invention moreover relates to a process for reprocessing or production of a sputter target (source of metal in cathode sputtering of metal), wherein a gas flow
10 forms a gas/powder mixture with a powder of a material chosen from the group consisting of niobium, tantalum, tungsten, molybdenum, titanium, zirconium or mixtures of two or more thereof or alloys thereof with at least two thereof or with other metals, the powder has a particle
15 size of 0.5 to 150 μm , wherein a supersonic speed is imparted to the gas flow and the jet of supersonic speed is directed on to the surface of the object to be reprocessed or produced.

20 A sputter target is a source of metal in the cathode sputtering of metal. These are employed in the production of integrated circuits, semiconductors and other electrical, magnetic and optical products. During the sputtering process, in general the metal surface of the
25 sputter target is worn away non-uniformly, which leads to a furrow on the surface. To avoid contamination with the material of the backing plate or even a catastrophic breakthrough of cooling liquid, the sputter targets are not used until the refractory metal layer is used up, but are
30 taken out of service promptly beforehand, so that only a relatively small amount of the refractory metal is used up when a new sputter target is employed. However, the

majority can merely be sold as scrap, or their materials recycled, since removal of the backing plate is required and connection to a new refractory metal plate is necessary. The backing plate here, however, is the part of
5 the sputter target which is of lower value.

There is therefore a need for a technique which either renders possible reprocessing of a sputter target without having to detach the backing plate for this or which
10 renders possible to deposit the sputter material direct to the backing.

For this purpose, the furrow in a used sputter target is topped up again with the particular refractory metal by the
15 cold spray process, as described above. For this, the jet of supersonic speed of the gas/powder mixture is directed on to the furrow and moved over the complete length and shape of the furrow. This is repeated as often as is necessary to top up the furrow again, so that the surface
20 of the sputter target forms a substantially flat area again and/or the topped-up material is raised slightly above the surface of the sputter target. Preferably, the jet of supersonic speed of the gas/powder mixture is then directed on to the remaining surface of the sputter target and
25 guided over the complete length, breadth and shape of the sputter target surface until a uniformly thick and flat layer which completely covers the surface of the sputter target has been obtained. The rough surface obtained can then be ground and polished by the conventional processes,
30 so that the desired smooth surface is obtained.

During production of a new sputter target, the layer is applied to a backing plate. Depending upon the construction of the target the jet of supersonic speed of the gas/powder mixture is therefore either directed on to the complete
5 surface of the backing plate of the sputter target and guided over the complete length, breadth and shape of the sputter target surface, until a uniformly and sufficiently thick and flat layer which completely covers the surface of the sputter target has been obtained or only the contact
10 area of the plasma is coated which results in a considerable saving of material.

The layer thickness is usually more than 0.01 mm. Preferred are layers with a thickness between 0.1 and 100 mm, more
15 preferred between 0.5 and 50 mm, still more preferred between 5 and 45 mm, still more preferred between 8 and 40 mm, still more preferred between 10 and 30 mm, still more preferred between 10 and 20 mm and most preferred between 10 and 15 mm.

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The purities and oxygen contents of the layers obtained should deviate not more than 50 % and preferably not more than 20 % from those of the powder.

25 This can advantageously be achieved if the sputter target to be reprocessed is coated under an inert gas. Argon is advantageously used as the inert gas, since because of a higher density than air, it tends to cover the object to be coated and to remain present, especially if the sputter
30 target is in a vessel which prevents the argon from escaping or flowing out and argon is topped up continuously.

- The process according to the present invention is particularly suitable for the processing or production of sputtering targets, because on the one hand during
- 5 production by thermomechanical processes crystallographic preferred orientations which can change at different intervals often occur, so that no uniform texture is obtained and instead so-called bands, that is to say regions of different preferred orientations. In thermo-
- 10 mechanical processes, this can be prevented only with a high outlay. In contrast, a uniform texture in which the preferred orientations vary, for example, less than 30 % with respect to any desired plane on the surface, these planes running perpendicular, parallel or diagonally to the
- 15 normal to the surface, and the preferred orientations varying by less than 30 % over the thickness of the refractory metal layer, may be obtained by the process according to the invention.
- 20 A uniform particle size distribution (grain size) is likewise obtained in the layers, so that also no bands of different particle size are obtained if this is not desired.
- 25 In processes in which powder is applied to the sputter target and melted, experience shows that bubbling and particle growth occurs. This also cannot be observed in the process according to the invention.
- 30 After application of the layer, the surface of the sputter target must be ground and polished in order to obtain a

suitable smooth surface. This can be carried out by the conventional processes according to the prior art.

In the production of a new sputter target, the layer is
5 applied to a backing means, e.g. to a backing plate. This plate is in general a plate of copper or aluminium or an alloy of at least one of these metals with beryllium. This backing plate can contain channels in which there is a cooling medium.

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The backing plate and therefore also the sputter target can be in the form of a plate having a circular or angular cross-section, as a rod, cylinder, block or any other desired shape. Additional structural components liquid
15 cooling coils and/or a larger coolant reservoir and/or complex flanges or other mechanical or electrical structures can also be attached.

The layers which are applied according to the invention, or
20 layers which are produced during production or reprocessing of a sputter target, have a high purity and a low oxygen content.

These layers advantageously have an oxygen content of less
25 than 1,000 ppm oxygen, or less than 500, or less than 300, in particular an oxygen content of less than 100 ppm.

In particular, these layers have a purity of at least 99.7 %, advantageously of at least 99.9 %, in particular of at least 99.95 %, and a content of less than 1,000 ppm
30 oxygen, or less than 500 ppm oxygen, or less than 300 ppm oxygen, in particular an oxygen content of less than 100 ppm.

In particular, these layers have a purity of at least 99.95 %, in particular of at least 99.995 %, and a content of less than 1,000 ppm oxygen, or less than 500 ppm oxygen, or less than 300 ppm oxygen, in particular an oxygen content of less than 100 ppm.

In particular, these layers have a purity of 99.999 %, in particular of at least 99.9995 %, and a content of less than 1,000 ppm oxygen, or less than 500 ppm oxygen, or less than 300 ppm oxygen, in particular an oxygen content of less than 100 ppm.

The layers according to the invention preferably have a total content of other non-metallic impurities, such as carbon, nitrogen or hydrogen, which is advantageously less than 500 ppm and most preferably less than 150 ppm. With the process of this invention layers with higher impurity contents can also be produced.

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The layer applied has a content of gaseous impurities which deviates not more than 50 %, or not more than 20 %, or not more than 10 %, or not more than 5 %, or not more than 1 % from the content of the starting powder with which this layer has been produced. In this context, the term deviation is to be understood as meaning, in particular, an increase; the layers obtained should thus advantageously have a content of gaseous impurities which is not more than 50 % above the content of the starting powder.

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The layer applied preferably has an oxygen content which deviates not more than 5 %, in particular not more than 1 % from the oxygen content of the starting powder.

- 5 In all the abovementioned layers, the total content of other non-metallic impurities, such as carbon, nitrogen or hydrogen, should advantageously be less than 500 ppm and most preferably less than 150 ppm.
- 10 In particular, the oxygen content is advantageously 50 ppm or less, the nitrogen content is 25 ppm or less and the carbon content is 25 ppm or less.

The content of metallic impurities is advantageously 50 ppm
15 or less, in particular 10 ppm or less.

In an advantageous embodiment, the layers moreover have a density of at least 97 %, preferably greater than 98 %, in particular greater than 99 % or 99.5 %. The density of the
20 layer here is a measure of the closed nature and porosity of the layer. 97 % density of a layer means that the layer has a density of 97 % of the bulk material. A closed, substantially pore-free layer always has a density of more than 99.5 %. The density can be determined either by image
25 analysis of a cross-section image (cross-section) of such a layer, or by helium pycnometry. The latter method is preferred less, since in the case of very dense layers, pores present in layers further-removed from the surface are not detected and a lower porosity than is actually
30 present is therefore measured. The density can be determined by image analysis by first determining the total area of the layer to be investigated in the image section

of the microscope, and then relating this area to the areas of the pores. Pores which are far-removed from the surface and close to the interface to the substrate are also recorded by this means. A high density of at least 97 %, preferably greater than 98 %, in particular greater than 99 % or 99.5 %, is important in particular in the production or reprocessing of sputter targets.

The layers show high mechanical strength which is caused by their high density and by the high deformation of the particles. In the case of tantalum, the strengths are therefore at least 80 MPa, more preferably at least 100 MPa, most preferably at least 140 MPa if nitrogen is the gas with which the metal powder forms a gas/powder mixture.

If helium is used, the strength usually is at least 150 MPa, preferably at least 170 MPa, most preferably at least 200 MPa and very most preferred greater than 250 MPa.

The present invention therefore also relates to sputter targets comprising at least one layer of the refractory metals niobium, tantalum, tungsten, molybdenum, titanium, zirconium, mixtures of two or more thereof or alloys of two or more thereof or alloys with other metals which have the abovementioned properties.

In particular, the layers are layers of tantalum or niobium.

Preferably layers of tungsten, molybdenum, titanium zirconium or mixtures of two or more thereof or alloys of two or more thereof or alloys with other metals, very

preferably layers of tantalum or niobium, are applied by cold spraying to the surface of a substrate to be coated. Surprisingly it has been found that with said powders or powder mixtures, preferably with tantalum and niobium

5 powders, possessing a reduced oxygen content, for example an oxygen content below 1000 ppm there can be produced cold sprayed layers with very high deposition rates of more than 90 %. In said cold sprayed layers the oxygen content of the metal is nearly unchanged compared to the oxygen content of

10 the powders. These cold sprayed layers show considerably higher densities than layers produced by plasma spraying or by vacuum spraying. Furthermore, these cold sprayed layers can be produced without any or with small texture, depending on powder properties and coating parameters.

15 Sputter targets comprising cold sprayed layers produce in the sputting process thin layers showing an uniformity and an electric resistivity comparable with thin layers prepared with conventional sputter targets.

20 Surprisingly it has been found that with decreasing oxygen content of the cold sprayed target layers density and other properties of the sputtered layers are improved (??OK??).

25 Metal powders which comprise alloys, pseudo-alloys and powder mixtures of refractory metals with suitable non-refractory metals are also suitable for use in the processes according to the invention. Sputtering targets which the same alloy or pseudo-alloy can be reprocessed or

30 also produced therewith. These include, in particular, alloys, pseudo-alloys or powder mixtures of a refractory metal chosen from the group consisting of niobium,

tantalum, tungsten, molybdenum, zirconium and titanium with a metal chosen from the group consisting of cobalt, nickel, rhodium, palladium, platinum, copper, silver and gold. Such powders belong to the prior art, are known in principle to the person skilled in the art and are described, for example, in EP-A-774315 and EP-A-1138420. These can be prepared by conventional processes; thus, powder mixtures are obtainable by homogeneous mixing of ready-made metal powders, it being possible for the mixing to take place on the one hand before the use in the process according to the invention, or also to be carried out during production of the gas/powder mixture.

Alloy powders are usually obtainable by melting and mixing of the alloying partners together. According to the invention, so-called pre-alloyed powders can also be used as alloy powders. These are powders which are produced by a process in which compounds, such as e.g. salts, oxides and/or hydrides, of the alloying partners are mixed and then reduced, so that intimate mixtures of the particular metals are obtained.

Pseudo-alloys can moreover also be used according to the invention. Pseudo-alloys are understood as meaning materials which are obtained not by conventional melt metallurgy, but e.g. by grinding, sintering, infiltration or by spray drying / agglomerating with and without subsequent sintering of the materials together.

Known materials are, for example, tungsten/copper alloys or tungsten/copper mixtures, the properties of which are known and are listed here by way of example:

Type	Density (g/cm ³)	HB (MPa)	Electrical conductivity (% IACS)	Thermal expansion coefficient (ppm/K)	Thermal conductivity (W/m.K)
WCu10	16.8-17.2	≥2,550	> 27	6.5	170-180
WCu15	16.3			7.0	190-200
WCu20	15.2-15.6	≥2,160	> 34	8.3	200-220
WCu25	14.5-15.0	≥1,940	> 38	9.0	220-250
WCu30	13.8-14.4	≥1,720	> 42		

Molybdenum/copper alloys or molybdenum/copper mixtures in the same ratios as stated above are also known.

Molybdenum/silver alloys or molybdenum/silver mixtures
5 which comprise e.g. 10, 40 or also 65 wt.% molybdenum are also known.

Tungsten/silver alloys or tungsten/silver mixtures which comprise e.g. 10, 40 or also 65 wt.% tungsten are also known.

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These can be employed e.g. in heatpipes, heat sinks or, generally, temperature management systems.

Tungsten/rhenium alloys can also be employed, but the metal
15 powder is an alloy of the following composition: molybdenum 94 to 99 wt.%, preferably 95 to 97 wt.%, niobium 1 to 6 wt.%, preferably 2 to 4 wt.%, zirconium 0.05 to 1 wt.%, preferably 0.05 to 0.02 wt.%. Like pure refractory metal
20 powders, these alloys can be used in a purity of at least 99.95 % for reprocessing or production of sputter targets with cold gas spraying.

Materials which are suitable for the processes according to the invention are listed in Tables 1 to 15. Individual
25 materials are designated by the number of the table

followed by the number of the combination of the components and the amount of the non-refractory metal as in Table 1. For example, material 22.0005 is a material described in Table 22, wherein the precise composition is defined with the non-refractory metal and the amount thereof as listed in Table 1, position no. 5.

Suitable niobium alloys are listed in Table 1.

10 Table 1

No.	Refractory metal	Non-refractory metal	Amount of non-refractory metal (wt.%)
1.001	niobium	cobalt	2-5
1.002	niobium	nickel	2-5
1.003	niobium	rhodium	2-5
1.004	niobium	palladium	2-5
1.005	niobium	platinum	2-5
1.006	niobium	copper	2-5
1.007	niobium	silver	2-5
1.008	niobium	gold	2-5
1.009	niobium	cobalt	5-10
1.010	niobium	nickel	5-10
1.011	niobium	rhodium	5-10
1.012	niobium	palladium	5-10
1.013	niobium	platinum	5-10
1.014	niobium	copper	5-10
1.015	niobium	silver	5-10
1.016	niobium	gold	5-10
1.017	niobium	cobalt	10-15

1.018	niobium	nickel	10-15
1.019	niobium	rhodium	10-15
1.020	niobium	palladium	10-15
1.021	niobium	platinum	10-15
1.022	niobium	copper	10-15
1.023	niobium	silver	10-15
1.024	niobium	gold	10-15
1.025	niobium	cobalt	15-20
1.026	niobium	nickel	15-20
1.027	niobium	rhodium	15-20
1.028	niobium	palladium	15-20
1.029	niobium	platinum	15-20
1.030	niobium	copper	15-20
1.031	niobium	silver	15-20
1.032	niobium	gold	15-20
1.033	niobium	cobalt	20-25
1.034	niobium	nickel	20-25
1.035	niobium	rhodium	20-25
1.036	niobium	palladium	20-25
1.037	niobium	platinum	20-25
1.038	niobium	copper	20-25
1.039	niobium	silver	20-25
1.040	niobium	gold	20-25
1.041	niobium	cobalt	25-30
1.042	niobium	nickel	25-30
1.043	niobium	rhodium	25-30
1.044	niobium	palladium	25-30
1.045	niobium	platinum	25-30
1.046	niobium	copper	25-30
1.047	niobium	silver	25-30
1.048	niobium	gold	25-30

Table 2: Table 2 consists of 48 alloys, tantalum instead of niobium being the refractory metal and the non-refractory metal and its content in per cent by weight being as listed
5 in Table 1.

Table 3: Table 3 consists of 48 alloys, tungsten instead of niobium being the refractory metal and the non-refractory metal and its content in per cent by weight being as listed
10 in Table 1.

Table 4: Table 4 consists of 48 alloys, molybdenum instead of niobium being the refractory metal and the non-refractory metal and its content in per cent by weight
15 being as listed in Table 1.

Table 5: Table 5 consists of 48 alloys, titanium instead of niobium being the refractory metal and the non-refractory metal and its content in per cent by weight being as listed
20 in Table 1.

Table 6: Table 6 consists of 48 pseudo-alloys, tantalum instead of niobium being the refractory metal and the non-refractory metal and its content in per cent by weight
25 being as listed in Table 1.

Table 7: Table 7 consists of 48 pseudo-alloys, tungsten instead of niobium being the refractory metal and the non-refractory metal and its content in per cent by weight
30 being as listed in Table 1.

Table 8: Table 8 consists of 48 pseudo-alloys, molybdenum instead of niobium being the refractory metal and the non-refractory metal and its content in per cent by weight being as listed in Table 1.

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Table 9: Table 9 consists of 48 pseudo-alloys, titanium instead of niobium being the refractory metal and the non-refractory metal and its content in per cent by weight being as listed in Table 1.

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Table 10: Table 10 consists of 48 powder mixtures, tantalum instead of niobium being the refractory metal and the non-refractory metal and its content in per cent by weight being as listed in Table 1.

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Table 11: Table 11 consists of 48 powder mixtures, tungsten instead of niobium being the refractory metal and the non-refractory metal and its content in per cent by weight being as listed in Table 1.

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Table 12: Table 12 consists of 48 powder mixtures, molybdenum instead of niobium being the refractory metal and the non-refractory metal and its content in per cent by weight being as listed in Table 1.

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Table 13: Table 13 consists of 48 powder mixtures, titanium instead of niobium being the refractory metal and the non-refractory metal and its content in per cent by weight being as listed in Table 1.

30

Table 14: Table 14 consists of 48 pseudo-alloys, niobium being the refractory metal and the non-refractory metal and

its content in per cent by weight being as listed in Table 1.

Table 15: Table 15 consists of 48 powder mixtures, niobium
5 being the refractory metal and the non-refractory metal and its content in per cent by weight being as listed in Table 1.

Metal powders which comprise alloys, pseudo-alloys and
10 powder mixtures of different refractory metals with one another are also suitable for use in the processes according to the invention.

Thus, for example, alloys of molybdenum and titanium in the
15 ratio of 50:50 atom-per cent or also alloys of tungsten and titanium in an amount of about 90:10 per cent by weight are known and are suitable for use in the processes according to the invention.

20 In principle, however, all alloys of the refractory metals with one another are suitable for use in the processes according to the invention.

Binary alloys, pseudo-alloys and powder mixtures of
25 refractory metals which are suitable for the processes according to the invention are listed in Tables 16 to 36. Individual materials are designated by the number of the table, followed by the number of the combination of the components as in Table 16. For example, material 22.005 is
30 a material described in Table 22, wherein the precise composition is defined by the refractory metals listed in

Table 16, position no. 5 and the amount as listed in Table 22.

Table 16: Suitable binary refractory metal alloys

	Component 1	Component 2
16.001	Nb	Ta
16.002	Nb	W
16.003	Nb	Mo
16.004	Nb	Ti
16.005	Ta	Nb
16.006	Ta	W
16.007	Ta	Mo
16.008	Ta	Ti
16.009	W	Ta
16.010	W	Nb
16.011	W	Mo
16.012	W	Ti
16.013	Mo	Ta
16.014	Mo	Nb
16.015	Mo	W
16.016	Mo	Ti
16.017	Ti	Ta
16.018	Ti	Nb
16.019	Ti	W
16.020	Ti	Mo

5

Table 17: Table 17 consists of 20 alloys, pseudo-alloys and powder mixtures according to Table 16, wherein component 1 is present in an amount of 2-5 per cent by weight, component 2 is present in an amount to 100 per cent by weight and the individual mixture partners is as listed in Table 16.

10

Table 18: Table 18 consists of 20 alloys, pseudo-alloys and powder mixtures according to Table 16, wherein component 1 is present in an amount of 5-10 per cent by weight,
5 component 2 is present in an amount to 100 per cent by weight and the individual components are as listed in Table 16.

Table 19: Table 19 consists of 20 alloys, pseudo-alloys and
10 powder mixtures according to Table 16, wherein component 1 is present in an amount of 10-15 per cent by weight, component 2 is present in an amount to 100 per cent by weight and the individual mixture partners are as listed in Table 16.

15 Table 20: Table 20 consists of 20 alloys, pseudo-alloys and powder mixtures according to Table 16, wherein component 1 is present in an amount of 15-20 per cent by weight, component 2 is present in an amount to 100 per cent by
20 weight and the individual mixture partners are as listed in Table 16.

Table 21: Table 21 consists of 20 alloys, pseudo-alloys and powder mixtures according to Table 16, wherein component 1
25 is present in an amount of 20-25 per cent by weight, component 2 is present in an amount to 100 per cent by weight and the individual mixture partners are as listed in Table 16.

30 Table 22: Table 22 consists of 20 alloys, pseudo-alloys and powder mixtures according to Table 16, wherein component 1 is present in an amount of 25-30 per cent by weight,

component 2 is present in an amount to 100 per cent by weight and the individual mixture partners are as listed in Table 16.

5 Table 23: Table 23 consists of 20 alloys, pseudo-alloys and powder mixtures according to Table 16, wherein component 1 is present in an amount of 30-35 per cent by weight, component 2 is present in an amount to 100 per cent by weight and the individual mixture partners are as listed in
10 Table 16.

Table 24: Table 24 consists of 20 alloys, pseudo-alloys and powder mixtures according to Table 16, wherein component 1 is present in an amount of 35-40 per cent by weight,
15 component 2 is present in an amount to 100 per cent by weight and the individual mixture partners are as listed in Table 16.

Table 25: Table 25 consists of 20 alloys, pseudo-alloys and
20 powder mixtures according to Table 16, wherein component 1 is present in an amount of 40-45 per cent by weight, component 2 is present in an amount to 100 per cent by weight and the individual mixture partners are as listed in Table 16.

25

Table 26: Table 26 consists of 20 alloys, pseudo-alloys and powder mixtures according to Table 16, wherein component 1 is present in an amount of 45-50 per cent by weight, component 2 is present in an amount to 100 per cent by
30 weight and the individual mixture partners are as listed in Table 16.

Table 27: Table 27 consists of 20 alloys, pseudo-alloys and powder mixtures according to Table 16, wherein component 1 is present in an amount of 50-55 per cent by weight, component 2 is present in an amount to 100 per cent by weight and the individual mixture partners are as listed in Table 16.

Table 28: Table 28 consists of 20 alloys, pseudo-alloys and powder mixtures according to Table 16, wherein component 1 is present in an amount of 55-60 per cent by weight, component 2 is present in an amount to 100 per cent by weight and the individual mixture partners are as listed in Table 16.

Table 29: Table 29 consists of 20 alloys, pseudo-alloys and powder mixtures according to Table 16, wherein component 1 is present in an amount of 60-65 per cent by weight, component 2 is present in an amount to 100 per cent by weight and the individual mixture partners are as listed in Table 16.

Table 30: Table 30 consists of 20 alloys, pseudo-alloys and powder mixtures according to Table 16, wherein component 1 is present in an amount of 65-70 per cent by weight, component 2 is present in an amount to 100 per cent by weight and the individual mixture partners are as listed in Table 16.

Table 31: Table 31 consists of 20 alloys, pseudo-alloys and powder mixtures according to Table 16, wherein component 1 is present in an amount of 70-75 per cent by weight, component 2 is present in an amount to 100 per cent by

weight and the individual mixture partners are as listed in Table 16.

Table 32: Table 32 consists of 20 alloys, pseudo-alloys and powder mixtures according to Table 16, wherein component 1 is present in an amount of 75-80 per cent by weight, component 2 is present in an amount to 100 per cent by weight and the individual mixture partners are as listed in Table 16.

10

Table 33: Table 33 consists of 20 alloys, pseudo-alloys and powder mixtures according to Table 16, wherein component 1 is present in an amount of 80-85 per cent by weight, component 2 is present in an amount to 100 per cent by weight and the individual mixture partners are as listed in Table 16.

Table 34: Table 34 consists of 20 alloys, pseudo-alloys and powder mixtures according to Table 16, wherein component 1 is present in an amount of 85-90 per cent by weight, component 2 is present in an amount to 100 per cent by weight and the individual mixture partners are as listed in Table 16.

Table 35: Table 35 consists of 20 alloys, pseudo-alloys and powder mixtures according to Table 16, wherein component 1 is present in an amount of 90-95 per cent by weight, component 2 is present in an amount to 100 per cent by weight and the individual mixture partners are as listed in Table 16.

Table 36: Table 36 consists of 20 alloys, pseudo-alloys and powder mixtures according to Table 16, wherein component 1 is present in an amount of 95-99 per cent by weight, component 2 is present in an amount to 100 per cent by weight and the individual mixture partners are as listed in Table 16.

In principle, X-ray anodes, preferably X-ray rotating anodes can also be reprocessed or produced in the same manner as sputter targets. In particular, tungsten/rhenium alloys or the metal powder an alloy of the following composition are suitable: molybdenum 94 to 99 wt.%, preferably 95 to 97 wt.%, niobium 1 to 6 wt.%, preferably 2 to 4 wt.%, zirconium 0.05 to 1 wt.%, preferably 0.05 to 0.02 wt.%.

X-ray anodes, preferably X-ray rotating anodes often carry on their reverse a usually soldered-on graphite layer for dissipation of heat. This layer for dissipation of heat can also be applied by the process of the invention, for example by applying a suitable alloy or a metal powder which comprises graphite particles or particles of another substance having a high thermal capacity with cold gas spraying.

Examples

Process for the preparation of suitable powders

5 Preparation of a tantalum powder

A tantalum hydride powder was mixed with 0.3 wt.% magnesium and the mixture was placed in a vacuum oven. The oven was evacuated and filled with argon. The pressure was 860 mmHg
10 and a stream of argon was maintained. The oven temperature was increased up to 650 °C in steps of 50 °C and, after a constant temperature had been established, maintained for four hours. The oven temperature was then increased up to 1,000 °C in steps of 50 °C and, after a constant
15 temperature had been established, maintained for six hours. After this time had elapsed, the oven was switched off and cooled to room temperature under argon. Magnesium and the compounds formed were removed in the conventional manner by washing with acid. The resulting tantalum powder had a
20 particle size of -100 mesh (< 150 µm), an oxygen content of 77 ppm and a BET specific surface area of 255 cm²/g.

Preparation of a titanium powder

The procedure was as for the preparation of the tantalum
25 powder. A titanium powder having an oxygen content of 93 ppm was obtained.

Preparation of a pre-alloyed titanium/tantalum powder

A mixture of tantalum hydride powder and titanium hydride
30 powder in the molar ratio of 1:1 was prepared and mixed with 0.3 wt.% magnesium, and the procedure was as for the

preparation of the tantalum powder. A titanium/tantalum powder having an oxygen content of 89 ppm was obtained.

Production of layers

5

Layers of tantalum and niobium were produced. AMPERIT® 150.090 was used as the tantalum powder and AMPERIT® 160.090 as the niobium powder, both being commercially obtainable materials from H.C. Starck GmbH in Goslar. The commercially obtainable nozzle of the type MOC 29 from CGT GmbH in Ampfing was used.

Material	Tantalum	Tantalum	Niobium	Niobium
Nozzle	MOC 29	MOC 29	MOC 29	MOC 29
Determination of the delivery rate at 0.52 Nm³/h:				
3.0 rpm (g/30s / g/min)	35.5 / 71.0	35.5 / 71.0	14.7 / 29.4	14.7 / 29.4
4.0 rpm (g/30s / g/min)			19.8 / 39.6	19.8 / 39.6
Movement data:				
Spray speed/speed of the nozzle over the substrate (m/min)	20 / 333	20 / 333	20 / 333	20 / 333
(mm/s)				
Line feed (mm)	1.5	1.5	1.5	1.5
Spray distance (mm)	30	30	30	30
Process gas:	nitrogen	helium	nitrogen	helium
Pressure (bar)	30	28	30	28
Flow rate (Nm ³ /h)	65	190 / He 181	60	190 / He 181
Content of conveying gas (%)	8	3 (N ₂)	8	3 (N ₂)
Powder delivery				
Powder delivery rate (g/min)	71	71	39.6	39.6
Number of passes	3	3	3	3
Substrates	1FTa 1FS 1FV 1FS 1RV 1RS	1FTa 1FV 2FS 1RV 1RS	2FS 2FV 1RS 1RV	2FS 2FV 1RV 1RS
Sheet thickness before (mm)	2.86	2.92	2.91	2.84
Sheet thickness after (mm)	3.38	3.44	3.35	3.36
Layer thickness, (µm)	520.00	520.00	436.00	524.00
Porosity/density	0.9% / 99.1%	2.2% / 97.8%		

Substrates: The substrates were placed side by side on the sample carrier and coated under the stated test conditions. The substrate designation is composed here as follows: The first number indicates the number of identical substrates lying side by side. The following letter

indicates whether a flat specimen (F) or round specimen (R, tube) has been initially introduced. The subsequent letters indicate the material, where Ta denotes tantalum, S a structural steel and V a rustproof steel (chromium/nickel steel).

Very firm and dense layers which have a low porosity and an excellent adhesion to the particular substrates were obtained.

10

Figures 1 to 10 show light microscopy photographs of cross-sections of the tantalum coatings obtained. No inclusions of copper or tungsten such as occur in corresponding layers produced with vacuum plasma spraying are detectable. The porosity was determined automatically by the Imageaccess image analysis program.

Figures 11 to 13 show tantalum disks as sputter targets prior to and after coating and ready for assembling after grinding and polishing.

20

Figure 1: Non-etched cross-section of a tantalum layer, process gas helium

Figure 2: Non-etched cross-section of a tantalum layer, process gas helium, general view of relatively low magnification.

25

Figure 3: Cross-section, etched with hydrofluoric acid, of a tantalum layer, process gas helium, general view of relatively low magnification.

Figure 4: Cross-section, etched with hydrofluoric acid, of a tantalum layer, process gas helium.

30

Figure 5: Image section used for determination of the porosity, cross-section of a tantalum layer, process gas helium

Figure 6: Cross-section, etched with hydrofluoric acid, of
5 a tantalum layer, interface to the substrate, process gas helium

Figure 7: Non-etched cross-section of a tantalum layer, process gas nitrogen, general view of relatively low magnification.

10 Figure 8: Non-etched cross-section of a tantalum layer, process gas nitrogen

Figure 9: Image section used for determination of the porosity, cross-section of a tantalum layer, process gas nitrogen

15 Figure 10: Non-etched cross-section of a tantalum layer, process gas nitrogen, high magnification

Figure 11: tantalum disk as sputter target prior to coating

Figure 12: tantalum disk as sputter target after coating
(12a: top view; 12b: side view)

20 Figure 13: tantalum disk as sputter target after coating and ready for assembling after grinding and polishing (one disk coated using nitrogen as process gas, one disk coated using helium as process gas).

Patent claims

1. A process for the reprocessing or production of a sputter target or of an X-ray anode, wherein a gas
5 flow forms a gas/powder mixture with a powder of a material chosen from the group consisting of niobium, tantalum, tungsten, molybdenum, titanium, zirconium, mixtures of two or more thereof and alloys thereof with at least two thereof or with other metals, the
10 powder has a particle size of 0.5 to 150 μm , wherein a supersonic speed is imparted to the gas flow and the jet of supersonic speed is directed on to the surface of the object to be reprocessed or produced.
- 15 2. A process as claimed in claim 1, wherein the powder is added to the gas in an amount such that a flow rate density of the particles of from 0.01 to 200 g/s cm^2 , preferably 0.01 to 100 g/s cm^2 , very preferably 0.01 g/s cm^2 to 20 g/s cm^2 , or most preferred from 0.05
20 g/s cm^2 to 17 g/s cm^2 . is ensured.
3. A process as claimed in claim 1, wherein the spraying comprises the steps of:
 - providing a spraying orifice adjacent a surface to
25 be coated by spraying;
 - providing to the spraying orifice a powder of a particulate material chosen from the group consisting of niobium, tantalum, tungsten, molybdenum, titanium, zirconium, mixtures of at
30 least two thereof or alloys thereof with one another or other metals, the powder having a

- particle size of 0.5 to 150 μm , said powder being under pressure;
- providing an inert gas under pressure to the spraying orifice to establish a static pressure at the spraying orifice and providing a spray of said particulate material and gas onto the surface to be coated; and
 - locating the spraying orifice in a region of low ambient pressure which is less than 1 atmosphere and which is substantially less than the static pressure at the spraying orifice to provide substantial acceleration of the spray of said particulate material and gas onto said surface to be coated.
4. A process as claimed in claim 1, wherein the spraying is performed with a cold spray gun and the target to be coated and the cold spray gun are located within a vacuum chamber at pressures below 80 kPa, preferably between 0.1 and 50 kPa, and most preferred between 2 and 10 kPa.
5. A process as claimed in one or more of the preceding claims, wherein the powder particles impinging on the surface of the object form a layer.
6. A process as claimed in claim 1, wherein the backing plate or other structural components present have not been removed before the reprocessing.
7. A process as claimed in one or more of the preceding claims, wherein the speed of the powder in the

gas/powder mixture is 300 to 2,000 m/s, preferably from 300 to 1,200 m/s.

8. A process as claimed in one or more of claims 1 to 3,
5 wherein the layer applied has a particle size of 5 to 150 μm , preferably 10 to 50 or 10 to 32 μm or 10 to 38 μm or 10 to 25 μm or 5 to 15 μm .
9. A process as claimed in one or more of the preceding
10 claims, wherein the metal powder has gaseous impurities of 200 to 2,500 ppm, based on the weight.
10. A process as claimed in one or more of the preceding
15 claims, wherein the metal powder has an oxygen content of less than 1,000 ppm oxygen, or less than 500, or less than 300, in particular less than 100 ppm.
11. A process as claimed in one or more of the preceding
20 claims, wherein the layer applied has an oxygen content of less than 1,000 ppm oxygen, or less than 500, or less than 300, in particular less than 100 ppm.
12. A process as claimed in one or more of the preceding
25 claims, wherein the layer applied has a content of gaseous impurities which deviates not more than 50 % from the content of the starting powder.
13. A process as claimed in one or more of the preceding
30 claims, wherein the layer applied has a content of gaseous impurities which deviates not more than 20 %,

or not more than 10 %, or not more than 5 %, or not more than 1 % from the content of the starting powder.

14. A process as claimed in one or more of the preceding
5 claims, wherein the layer applied has an oxygen content which deviates not more than 5 %, in particular not more than 1 % from the oxygen content of the starting powder.
- 10 15. A process as claimed in one or more of the preceding claims, wherein the oxygen content of the layer applied is not more than 100 ppm.
16. A process as claimed in claim 1, wherein the metal
15 layer applied comprises tantalum or niobium.
17. A process as claimed in one or more of the preceding claims, wherein the layer thickness is 10 μm to 10 mm or 50 μm to 5 mm.
- 20 18. A process as claimed in one or more of the preceding claims, wherein layers are applied by cold spraying to the surface of a object to be coated, preferably layers of tantalum or niobium.
- 25 19. A process as claimed in claim 18, wherein the layers produced possess an oxygen content below 1000 ppm.
- 30 20. The use of a powder of a material chosen from the group consisting of niobium, tantalum, tungsten, molybdenum, zirconium, titanium or alloys thereof with one another or other metals, which has a particle size

of 150 μm or less, in a process as claimed in one or more of the preceding claims.

21. The use of a powder of a material chosen from the group consisting of niobium, tantalum, tungsten, molybdenum, zirconium, titanium or alloys thereof with one another or other metals, which has a particle size of 150 μm or less, for the production or reprocessing of sputter targets or X-ray anode plates preferably X-ray rotating anode plates.
22. The use as claimed in claim 20 or 21, wherein the metal powder used has an oxygen content of 300 ppm or less and a particle size of 150 μm or less.
23. The use as claimed in claim 20 or 21, wherein a niobium or tantalum powder having a particle size of 150 μm or less and an oxygen content of less than 300 ppm is used.
24. The use as claimed in claim 20 or 21, wherein a tungsten or molybdenum powder having a particle size of 0.5 to 150 μm , preferably 3 to 75 μm , in particular 5 to 50 μm or 10 to 32 μm or 10 to 38 μm or 10 to 25 μm or 5 to 15 μm and an oxygen content of 500 ppm or less is used.
25. The use as claimed in one or more of the preceding claims 20 to 24, wherein the metal powder is an alloy of the following composition: molybdenum 94 to 99 wt.%, preferably 95 to 97 wt.%, niobium 1 to 6 wt.%,

preferably 2 to 4 wt.%, zirconium 0.05 to 1 wt.%,
preferably 0.05 to 0.02 wt.%.

26. The use as claimed in one or more of the preceding
5 claims 20 to 25, wherein the metal powder is an alloy,
pseudo-alloy or powder mixture of a refractory metal
chosen from the group consisting of niobium, tantalum,
tungsten, molybdenum, zirconium and titanium with a
metal chosen from the group consisting of cobalt,
10 nickel, rhodium, palladium, platinum, copper, silver
and gold.
27. The use as claimed in one or more of the preceding
claims 20 to 26, wherein the metal powder comprises a
15 tungsten/rhenium alloy.
28. The use as claimed in one or more of the preceding
claims 20 to 27, wherein the metal powder comprises a
mixture of a titanium powder with a tungsten powder or
20 a molybdenum powder.
29. A refractory metal layer on a sputter target or on an
X-ray anode, obtainable by a process as claimed in one
or more of the preceding claims 1 to 19.
25
30. A sputter target or a X-ray anode comprising at least
one layer of the refractory metals niobium, tantalum,
tungsten, molybdenum, titanium, zirconium, mixtures of
two or more thereof or alloys of two or more thereof
30 or alloys with other metals which is processed or
reprocessed using a process of one or more of the
preceding claims 1 to 19.