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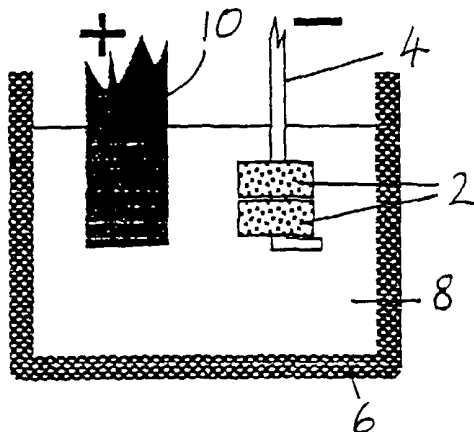
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(54) Title: METAL AND ALLOY POWDERS AND POWDER FABRICATION



(57) Abstract: A precursor powder comprising a metal compound is formed into a sample for electro-deoxidation, for example by slip-casting. The sample is then immersed in a melt comprising a molten salt and a cathodic potential applied to remove non-metal species from the precursor powder by electro-deoxidation and dissolution in the melt. This typically forms a metallic sample which can be fragmented to form a metallic powder. In a second aspect of the invention a powdered feed material is formed into a shaped precursor and more extensive electro-deoxidation carried out so as to form a near-net shaped product.

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METAL AND ALLOY POWDERS AND POWDER FABRICATION

Field of the Invention

This invention relates to a method and an apparatus for preparing metallic powders of well-defined particle sizes and composition, and to metallic powders so produced. In a further aspect the invention relates to powder fabrication and the production of near net-shaped products.

Background to the Invention

10 Metallic powders have many applications and these include:

(a) As feed materials for powder metallurgical techniques, which offer the possibility of making near net-shaped products rather than having to machine a component from a large billet. In some cases 90% of the material is removed during the machining process, and has to be recycled. A method for making near-net shaped products may advantageously reduce this wastage.

15 (b) Alloys; the use of metal powders in alloy preparation results in rapid dissolution and minimal segregation within an alloy.

20 (c) For their aesthetic properties; metal powders are used often in metallic paints.

(d) As fuels in rockets.

25 (e) As fine powders for mixing as alloy constituents, for example in making many high intensity magnetic phases.

There are a variety of conventional ways of making metallic particles. These include crushing and grinding, which are particularly energy-intensive processes as metals inherently resist deformation, and for reactive metals the grinding process needs to take place under inert conditions to avoid oxidation. Metal powders can also be obtained by the reduction of metal compounds such as oxides by hydrogen but this is generally restricted to oxides that are less stable than water vapour. To reduce the oxides of very reactive metals would require reactants such as calcium and the powders are then likely to be contaminated with calcium

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oxide. The injection of molten metal onto a spinning disc results in fine particles of liquid being centrifugally expelled from the disc as droplets that subsequently solidify. Liquid metals can be atomised by impinging a high velocity gas into a stream of molten metal. Metal powders can be produced by shock-cooling metallic vapours. For some metals with substantial solubility of hydrogen, it is possible to form brittle hydride phases which can subsequently be crushed or decrepitated into fine particles. By heating at elevated temperatures, the hydrides simply decompose to form metallic particles. Lastly, electrochemical deposition of metal from a compound of the metal dissolved in an aqueous or fused salt electrolyte can result in a dendritic deposit that can easily be crushed to a fine powder. Overall, these methods can give fine powders but frequently the powders are highly oxidised and contaminated with oxide products, and there is generally a substantial range of particle sizes. This is a particular problem when a metallic powder of a given particle size is required, which typically necessitates sieving of the product and rejection of a sizeable fraction. These problems are exacerbated when alloy powders are required, especially for those of the most reactive metals.

Metal oxide powders are much easier to obtain by grinding, as oxides are typically highly brittle and crush readily. Being oxides, they do not suffer from oxidation during this process. Very fine oxide powders can also be produced by precipitation from an aqueous or fused salt solution. Alternatively, by reacting a volatile compound with oxygen, it can be possible to form a fine oxide powder. For example the reaction of titanium tetrachloride with oxygen results in a very fine oxide powder. Frequently, these particles are of a uniform size, but the problem remains of producing fine metal powders.

Summary of the Invention

In a first aspect, the invention provides a method and an apparatus for producing a metallic powder, and a metallic powder, as defined in the appended independent claims. Preferred or advantageous features of the invention are set out in dependent subclaims.

This aspect of the invention is based on the surprising finding that powdered metal compounds such as metal oxide powders may be treated electrochemically to yield metal powders with a uniform structure and size. Thus, a method for producing a metallic powder may advantageously be provided, in which a precursor powder comprising a compound (M^1X) between a metal (M^1) and a non-metal species (X) is treated by electro-deoxidation. In this process, the precursor powder forms a cathode contacting a melt comprising a fused salt (M^2Y), under conditions such that the non-metal species dissolves in the melt. This may advantageously form a porous metallic sample which may be processed as required to form the metallic powder.

Surprisingly, the metal powders produced according to embodiments of the invention have been found to have a uniform microscopic structure, both in terms of the particle size of the metal powder and the microstructure of individual particles. In addition, it has been found that particles of similar shapes may be produced. For example, the powders may form a cube structure. The small, consistent particle sizes, and the metal purity, produced by this method may be particularly advantageous as the production of metal powders by prior art methods has failed to produce high yields of such materials; in prior art methods, sieving is generally required to produce consistent particle sizes and entails very significant wastage.

The term electro-deoxidation is used herein to describe the process of removing the non-metal species (X) from a compound in the solid state by contacting the compound with the melt and applying a cathodic voltage to it such that the

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non-metal species, or anionic species, dissolves. In electrochemistry, the term oxidation implies a change in oxidation state and not necessarily a reaction with oxygen. It should not, however, be inferred that electro-deoxidation always involves a change in the oxidation states of both (or all) of the components of the compound; this is believed to depend on the nature of the compound, such as whether it is primarily ionic or covalent. In addition, it should not be inferred that electro-deoxidation can only be applied to an oxide; any compound may be processed in this way. Other terms to describe the electro-deoxidation process in particular instances may be electro-decomposition, electro-reduction or solid-state electrolysis.

In a preferred embodiment, the cathodic voltage applied to the metal compound is less than the voltage for deposition of cations from the fused salt at the cathode surface. This may advantageously reduce contamination of the intermetallic compound involving the cations. It is believed that this may be achieved under the conditions of an embodiment in which the decomposition potential of the salt, or electrolyte, is not exceeded during electro-deoxidation, or electro-reduction, or under the conditions of an embodiment providing a method for producing a metallic powder by treating a powder of a metal compound (M^1X) by electrolysis in a fused salt M^2Y or a mixture of salts, under conditions whereby reaction, or ionisation, of X rather than M^2 deposition occurs at an electrode surface, and X dissolves in the electrolyte M^2Y .

Further details of the electro-deoxidation process are set out in International patent application number PCT/GB99/01781, which is incorporated herein by reference in its entirety.

In the method of invention, it is preferable that the metal produced has a higher melting point than that of the melt, or salt.

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Further, other metal compounds, such as metal oxides, may be present and the electrolysis product may be an alloy powder.

5 The method of the invention may advantageously give a product which is of very uniform particle size and free of oxygen or other contaminants.

10 In accordance with a preferred embodiment of the present invention, it has been found that electrochemical reduction of metal oxide powders, by cathodically ionising the oxygen away from the oxide, results in agglomerates of pure metal powder, the particle size of which depends upon the conditions of pre-forming and sintering of the metal oxide powders and the time and temperature of electro-deoxidation, or electrolysis. Other electrolysis parameters such as voltage, 15 current and salt composition may also be varied to control the metal powder morphology. Control of these parameters may advantageously be applicable to precursor powders other than oxides.

20 The metal compound or oxide should show at least some electronic conductivity or be used in contact with a conductor.

25 Metal alloy powders may advantageously be formed by electro-deoxidation of precursor powders comprising a mixture or solid solution of two or more metal compounds or one or more metals or alloys with one or more metal compounds.

30 In a second aspect, the invention may advantageously provide a method for forming a near net-shaped product. In this method, a shaped precursor is formed from a powdered feed material comprising a compound (M^1X) between a metal (M^1) and a non-metal species (X). The precursor is then treated by electro-deoxidation, the precursor forming a cathode contacting a melt comprising a fused salt (M^2Y) under conditions such that the non-metal species dissolves in the melt. The electro-deoxidation is carried out for a 35 sufficiently long time and/or at a sufficiently high temperature to form interconnections between the metallic

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powder particles produced by the electro-deoxidation, in order to produce the near net-shaped product strong enough for further processing.

5 The advantages of the powder production aspect of the invention described above may also be applicable to this aspect of the invention. For example, carrying out electro-deoxidation at a cathodic potential less than the potential for cation deposition from the melt may advantageously reduce contamination of the near net-shaped product, and using a feed
10 material comprising a mixture or solid solution of two or more metals may advantageously produce a near net-shaped product of a desired alloy. The skilled person would readily appreciate that other advantages described above may also be applicable to near net-shaped product formation.

15 Specific Embodiments and Best Mode of the Invention

Embodiments of the invention will now be described by way of example, with reference to the drawings, in which;

Figure 1 illustrates an apparatus for the electro-deoxidation of a metal oxide powder according to a first
20 embodiment of the invention;

Figure 2 illustrates an apparatus according to a second embodiment of the invention;

Figure 3 is a photomicrograph of a titanium oxide powder, as used as the starting material in Examples 1 and 2;

25 Figure 4 is a photomicrograph of a titanium powder produced from the oxide of Figure 3 in Example 1;

Figure 5 is a photomicrograph of a titanium powder produced from the oxide of Figure 3 in Example 2;

30 Figure 6 is a photomicrograph of a chromium powder as produced in Example 3;

Figure 7 is a photomicrograph of an AlNi₃ powder as produced in Example 5;

35 Figure 8 is an XRD (X-ray diffraction) spectrum for the powder of Figure 7, overlaid on a spectrum for a reference sample of AlNi₃;

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Figure 9 is a photomicrograph of a niobium oxide powder, as used as the starting material in Example 6;

Figure 10 is a photomicrograph of a niobium powder as produced in Example 6 from the oxide powder of Figure 9;

5 Figure 11 is a schematic diagram of an apparatus for electro-deoxidation as used in Example 6; and

Figure 12 is a plot of an XRD analysis of a niobium powder produced as in Example 6.

10 Figures 1 and 2 show pellets 2 of metal oxide in contact with a cathode conductor. Each pellet is prepared by powder processing techniques, such as pressing or slip-casting a submicron or micron-sized powder (Figure 3) such as titanium dioxide. The pellet may then be fired to give it structural strength before being made the cathode in a cell in which a
15 crucible 6 contains a fused salt 8. In the embodiment, the cell contains chloride salts, being either CaCl_2 or BaCl_2 or their eutectic mixture with each other or with another chloride salt such as NaCl .

20 In the embodiment of Figure 1, the pellets are annular and are threaded onto a cathodic conductor in the form of a Kanthal wire 4. The crucible is an inert crucible of graphite or alumina. In the embodiment of Figure 2 the crucible 12 is made of a conducting material such as titanium or graphite. The pellets sink in the melt and contact the crucible, to
25 which the cathodic voltage is applied. The crucible itself thus acts as a current collector.

30 In both embodiments the electrochemical process is the same, as follows. On the application of current, the oxygen ionises, dissolves in the salt and diffuses to a graphite anode 10 where it is discharged. The oxygen is thereby removed from the oxide, leaving the metal behind. The metal product is a very fine powder of very uniform size, as shown in Figure 4. It should be noted that the metal powder produced has a much larger grain size than the initial grain
35 size of the oxide powder. By varying the temperature, the time of electro-deoxidation (reduction), the voltage, the

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current and/or the salt, it is possible to change and control the size and morphology of the metallic powder.

5 The embodiment described above produces titanium metal powder but it is possible to make alloy powders by the same route simply by mixing the oxide powders together, and preferably firing or sintering them to strengthen the pellet. The pellet may also be fired so as to form a solid solution of the oxides. It is preferable that the oxide powders are not greater than microns in particle size and are finer than
10 the metal powder to be produced.

The electrolyte should consist of salts which are more stable than the equivalent salts of the metal which is being produced and, preferably, the salt should be as stable as possible to remove the oxygen to as low a concentration as possible. The choice of salt includes the chloride or other
15 halide salts of alkali and/or alkaline earth metals, particularly barium, calcium, cesium, lithium, strontium and yttrium.

To obtain a salt with a lower melting point than that given by a pure salt and/or to modify the interactions between the cathode and the electrolyte, a mixture of salts can be used, preferably the eutectic composition.
20

At the end of reduction, the reduced compact is withdrawn from the molten salt. Some of the salt is contained within the withdrawn pellet, however, and stops the powder oxidising. The salt can simply be removed by washing in water or an organic solvent such as ethanol. Generally, the pellets are very brittle and can easily be crushed to reveal the metal powder.
25

30 The following Examples illustrate the invention.

Example 1

Three pellets, 5 mm in diameter and 1 mm in thickness, prepared by pressing moisturised 0.25 μm titanium dioxide powder (Figure 3) followed by drying and sintering at 950°C in air for 2 hours, were placed in a titanium crucible filled with molten calcium chloride at 950°C. The cell arrangement
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is as shown in Figure 2. A potential of 3 V was applied between a graphite anode and the titanium crucible. After 10 hours, the electro-deoxidation was terminated, the salt allowed to solidify and then dissolved in water to reveal a black/metallic pellet which was then removed from the crucible and dried. Examination under the scanning electron microscope showed that the particulate structure of the pellet had been transformed from 0.25 μm particles of titanium dioxide to 12 μm particles of titanium (Figure 4). The titanium particle size was advantageously very uniform, being about $12\mu\text{m} \pm 3\mu\text{m}$. Within experimental errors, no oxygen was detected by energy dispersive X-ray analysis.

It should be mentioned that in other experiments it was observed that increasing the time of electrolysis would increase the size of the particles and, at the same time, interconnections between individual particles became significantly stronger. This could eventually lead to the production of strong metallic pellets which could not be crushed to powders and which are therefore a form of near net-shaped product. In addition, such strong pellets may be used directly as a feed-stock for various fabrication techniques, such as sintering. The microstructure in these strong pellets is believed to be similar to that in the conventional Kroll titanium sponge. The formation of the titanium pellets depended also on the nature of the molten salts and other experimental conditions such as the pre-forming conditions and sintering of the pellet.

Example 2

The TiO_2 powder as in Example 1 was mixed with water to form a slurry which was then slip cast into small pellets, dried and sintered at 950°C in air for 2 hours. The sintered pellets were about 8 mm in diameter and 2 mm in thickness. A hole, 1.5 mm in diameter, was drilled in each of the sintered TiO_2 pellets. Two of them were threaded onto a Kanthal wire, 1.5 mm in diameter, and then inserted into a molten eutectic mixture of calcium chloride and barium

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chloride at 950°C. An alumina crucible was used to accommodate the salts and the cell arrangement is as shown in Figure 1. A potential of 3.1 V was applied between a graphite anode and the Kanthal wire. After about 20 hours, the temperature was lowered to 700°C, the pellets on the Kanthal wire were removed from the crucible, cooled in air and then washed in water to reveal grey/metallic pellets. Examination under the scanning electron microscope showed that the particulate structure of each pellet had been transformed from 0.25 μm particles of titanium dioxide to two types of titanium particles, about 3 μm and about 20 μm respectively (see Figure 5).

As shown in Example 1 above, it is possible to produce titanium powder of a more consistent particle size than this by appropriate control of process parameters but it should be noted that the particle size range produced in Example 2 may advantageously be substantially more uniform than that produced by prior art methods.

Example 3

A 1 μm powder of chromic oxide was mixed with water to form a slurry which was slip cast into small samples, or pellets, about 8-10 mm in diameter and 3-5 mm in thickness, followed by drying and sintering at 950°C in air for 2 hours. After sintering, no significant change was observed on the colour (green) and size of the samples, but the mechanical strength was enhanced significantly. Three of the sintered samples were placed in a graphite crucible filled with molten calcium chloride at 990°C as shown in Figure 1. Better results have been obtained by adding NaCl to the melt to reduce dissolution of chromic oxide in the melt. A potential of 2.7 V was applied between a graphite anode and the graphite crucible. After 15 hours, the electrolysis was terminated, the salt allowed to solidify and then dissolved in water to reveal the grey/metallic pellets. Examination under a scanning electron microscope (Figure 6) revealed aggregates of crystallites in two sizes in the reduced samples: the

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larger crystallites were 20-50 μm in size while the smaller ones were 5-8 μm . Energy dispersive X-ray analysis confirmed both types of crystallites were pure chromium metal.

5 The particle size range produced in this Example may be reduced through process parameter control but is significantly narrower than the chromium particle size range produced by prior art methods, typically by mechanical grinding.

Example 4

10 Powders of titanium dioxide (0.25 μm particle size), alumina (0.25 μm) and vanadium oxide (1 - 2 μm) were mixed in a ratio such that the ratio of the metal elements was the same as a desired alloy, being in this example the Ti-6Al-4V alloy. The mixture was then made into a slurry with water and slip cast into pellets, followed by drying and sintering at 950°C
15 for 2 hours in air. After sintering, the colour of the pellets changed from light green to dark brown. The size of the sintered pellets was about 8 mm in diameter and 6 mm in thickness. After drilling a hole of 1.5 mm in diameter, one of the sintered pellets was threaded onto a Kanthal wire, and
20 then inserted into a molten eutectic mixture of barium chloride and calcium chloride at 950°C. An alumina crucible was used to accommodate the molten salts and the cell arrangement is shown in Figure 1. A potential of 3.1 V was applied between a graphite anode and the Kanthal wire. After
25 20 hours, the temperature of the salt was allowed to cool to 700°C and then the electro-deoxidation terminated. The pellets on the Kanthal wire were removed from the crucible, cooled in air and then washed/leached in water to reveal the grey/metallic pellets. Examination under the scanning
30 electron microscope showed that the particulate structure of the pellet was similar to that shown in Figure 3 for titanium. EDX analysis revealed no oxygen in the pellets and confirmed the presence of titanium, aluminium and vanadium in individual particles in the desired ratio, within experimental error.

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Example 5

Powders of Al_2O_3 and NiO were mixed in a molar ratio of 1:6, pressed into small cylindrical pellets (10 mm diameter, 5~10 mm height), and sintered in air at 980-1000°C for about 2 hours. After sintering, the grey-green colour of the pellets became only slightly paler. Holes of 1.7 mm diameter were drilled into the sintered pellets. Four of the sintered pellets, weighing about 4 grams, were threaded onto a Kanthal wire (1.0 mm diameter) to form an assembled cathode. Electrodeoxidation was carried out between the assembled cathode and a graphite anode in argon-protected molten CaCl_2 at 950°C and 3.1 V for about 18 hours, as shown in Figure 1. The pellets were removed from the molten salt upon reduction, cooled first in argon and then in air to room temperature. Water was used to wash the reduced pellets which were then dried in air, showing a grey metallic colour. The surfaces and cross sections of the reduced pellets consisted of nodular particles of 2~20 microns in size (see Figure 7) and which contained Al and Ni in the atomic ratio of 1:3. No oxygen was detected. The pellets were then manually ground into powder in an agate mortar. XRD (X-ray diffraction) was applied to the powder and the spectrum showed an almost identical pattern to a standard AlNi_3 sample (see Figure 8).

Example 6

Nb_2O_5 powders used in experiments were 99.97 wt % and 99.99 wt % pure, with mean particle sizes of 4.03 μm and 12.71 μm , respectively. The powders were pressed into porous compacts that were then strengthened by sintering. The sintered pellets were attached onto a cathodic current collector to form an assembled oxide cathode. The $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaCl employed for the melt were analytical reagents. All the chemicals were supplied by Aldrich Chemical. The $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was dehydrated in air at 373 K for 1 hour, heated up slowly to 573 K and then was held at 573 K for 12 hours. The dehydrated CaCl_2 and dried NaCl were mixed thoroughly and the mixture was then dried at 473 K before use. High-density

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graphite rods of 10 mm in diameter and 100 mm long were purchased from Graphite Technologies and were used as the anodes. A Kanthal[®] wire, 1.5 mm in diameter, was employed as the cathodic current collector.

5 The electrolytic cell for electrolysis is schematically shown in Figure 11. Two Farnell LS30-10 Autoranging Power Supplies were used for conducting the electrolysis under constant voltages. A first wire 50 for connecting the pellets of Nb₂O₅ 60 was led to the negative end of one power supply. 10 The stainless steel crucible 56 for holding the molten electrolyte 58 was connected by a second wire 62 to the negative end of the other power supply. Two positive ends of the two power supplies were both connected to the graphite rod anode 52. All electrical connections from the individual 15 electrodes to the power supplies were made by Kanthal[®] wires 50, 62. The electrolyte temperature was measured using a type K thermocouple in an alumina sheath 54. The cell was placed in a vertical Inconel[®] reactor tube closed at one end.

20 The electrolytic cell was flushed with high purity argon while it was heated to the required temperatures. When the cell reached its electrolysis temperature, the graphite rod anode was dipped into the molten electrolyte and the pre-electrolysis was performed at $U_2 = 2.8-3.0$ V and 1173 K until no anode bubbles could be visually observed, usually for 25 a period of 12 hours. After completing the pre-electrolysis, the oxide cathode was immersed in the melt. The electrolysis was carried out under constant voltages (U_1 and U_2) applied respectively to the cell as shown in Figure 11. The applied voltage (U_1), along with the resulting currents, were 30 displayed and logged by a PC with Serial RS232 plus ADAMS 4017-8 Channel Analogue-to-Digital Convertor during the course of electrolysis.

35 The samples as-reduced were removed quickly from the melt under a flow of the argon at 873 K and quenched and washed in cold water, followed by acid leaching, water rinse, and acetone wash. The resulting porous pellets were made into

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powders by grinding manually. The obtained niobium metal powders were then cleaned with acetone again and dried under vacuum at room temperature.

5 Morphology of the sintered or reduced pellets was observed using a Jeol JSM-5800LV scanning electron microscope (SEM) with an energy dispersive X-ray analysis (EDXA) attachment. Concentrations of impurities were determined by EDXA. Various phases present in the prepared powders were examined by powder X-ray diffractometry (XRD) using a Philips
10 diffractometer PW1710 with Cu $K\alpha_1$ radiation. Contents of oxygen were also determined by weighing the prepared niobium metal powders before and after re-oxidation in air, where a complete re-oxidation of the metal powders to the Nb_2O_5 was confirmed by XRD analysis. A level of chlorine in the
15 off-gasses was monitored using a Drager QuadGard Chlorine Detector.

The final product remaining at the cathode after electrolysis was found to be metallic niobium, in the form of porous pellets. Figures 9 and 10 show the typical
20 microstructures of cross sections of Nb_2O_5 pellets before (for 4.03 μm particle size Nb_2O_5) and after electro-deoxidation at $U_1 = 3.1$ V and 1123 K for 24 hours. It was interesting to observe that after the reduction the form of the as-reduced product was essentially a powder compact which had loosely
25 sintered together and also the particle sizes were enlarged to some extent. The prepared niobium metal powder contained 2311 mass ppm oxygen.

A typical measured XRD (X-ray diffraction) pattern is shown in Figure 12 for the niobium metal powders reduced at
30 1173 K for 48 hours, from which one can see that the powder is pure niobium, free of any oxide phases.

Overall, the present experimental results provide evidence that porous pellets of Nb_2O_5 can be easily deoxidised to the metallic niobium. The niobium metal powders prepared
35 are obviously acceptable for subsequent purification treatments, such as high vacuum sintering at high

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temperatures. Our experiments indicated that various ranges of particle sizes of the niobium metal powders could be readily prepared by a proper control of experimental conditions and by changing the particle sizes of Nb₂O₅ powders.

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CLAIMS

1. A method for producing a metallic powder, comprising the steps of:

5 treating by electro-deoxidation a precursor powder comprising a compound (M^1X) between a metal (M^1) and an non-metal species (X), the precursor powder forming a cathode contacting a melt comprising a fused salt (M^2Y), under conditions such that the non-metal species dissolves in the melt; and

10 processing a product of the electro-deoxidation as required to form the metallic powder.

2. A method according to claim 1, in which the electro-deoxidation is carried out under conditions whereby a cathodic potential less than a potential for the deposition of a cation (M^2) from the melt is applied to the cathode.

3. A method according to claim 1, in which the melt comprises a mixture of salts, including two or more cations (M^2), and the electro-deoxidation is carried out under conditions whereby a cathodic potential less than a potential for the deposition of any cation (M^2) from the melt is applied to the cathode.

25 4. A method according to claim 1, 2 or 3, in which the precursor powder is a conductor and is used as the cathode.

5. A method according to claim 1, 2 or 3, in which the precursor powder is an insulator and is used in contact with a conductor to form the cathode.

30 6. A method according to any preceding claim, in which electro-deoxidation is carried out at a temperature of 700 - 1000°C.

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7. A method according to any preceding claim, in which the precursor powder comprises particles between 0.05 and 20 μm in size.
- 5 8. A method according to any of claims 1 to 6, in which the precursor powder comprises particles between 0.25 and 2 μm in size.
- 10 9. A method according to any preceding claim, in which the metallic powder comprises particles between 1 and 30 μm in size.
- 15 10. A method according to any preceding claim, in which the fused salt comprises as a cation species (M^2) Ca, Ba, Li, Cs and/or Sr.
- 20 11. A method according to any preceding claim, in which the fused salt comprises as an anion (Y) Cl or F.
- 25 12. A method according to any preceding claim, in which the non-metal species comprises O, S, C or N.
- 30 13. A method according to any preceding claim, in which the metal (M^1) comprises Ti, Si, Ge, Zr, Hf, Sm, U, Al, Mg, Nd, Mo, Cr or Nb, V, Ta, Mb, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Be, Sr, Ga, In, Tl, lanthanides or actinides, or an alloy thereof.
- 35 14. A method according to any preceding claim, in which the precursor powder is formed into a sample for electro-deoxidation by powder processing techniques, for example slip-casting or compaction, and the product of the electro-deoxidation is ground or fragmented to form the metallic powder.

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15. A method according to claim 14, in which the formation of the precursor powder comprises sintering.
- 5 16. A method according to any preceding claim, in which the precursor powder comprises a mixture or solid solution of one or more metal compounds, and optionally one or more metals or alloys.
- 10 17. A metallic powder produced according to a method as defined in any preceding claim.
18. An apparatus for carrying out the method defined in any preceding claim.
- 15 19. A method for forming a near net-shaped product, comprising the steps of:
forming a shaped precursor from a powdered feed material comprising a compound (M^1X) between a metal (M^1) and a non-metal species (X);
20 treating the precursor by electro-deoxidation, the precursor forming a cathode contacting a melt comprising a fused salt (M^2Y) under conditions such that the non-metal species dissolves in the melt, the electro-deoxidation being carried out for a sufficiently long time and/or at a
25 sufficiently high temperature to form interconnections between metallic powder particles produced by the electro-deoxidation and to produce the near net-shaped product strong enough for further processing.
- 30 20. A method according to claim 19, in which the electro-deoxidation is carried out under conditions whereby a cathodic potential less than a potential for the deposition of a cation (M^2) from the melt is applied to the cathode.
- 35 21. A method according to claim 19, in which the melt comprises a mixture of salts, including two or more cations

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(M²), and the electro-deoxidation is carried out under conditions whereby a cathodic potential less than a potential for the deposition of any cation (M²) from the melt is applied to the cathode.

5

22. A method according to claim 19, 20 or 21, in which the precursor is a conductor and is used as the cathode.

10

23. A method according to claim 19, 20 or 21, in which the precursor powder is an insulator and is used in contact with a conductor to form the cathode.

15

24. A method according to any of claims 19 to 23, in which electro-deoxidation is carried out at a temperature of 700 - 1000°C.

20

25. A method according to any of claims 19 to 24, in which the powdered feed material comprises particles between 0.05 and 20 µm in size.

26. A method according to any of claims 19 to 24, in which the powdered feed material comprises particles between 0.25 and 2 µm in size.

25

27. A method according to any of claims 19 to 26, in which the fused salt comprises as a cation species (M²) Ca, Ba, Li, Cs and/or Sr.

30

28. A method according to any of claims 19 to 27, in which the fused salt comprises as an anion (Y) Cl or F.

29. A method according to any of claims 19 to 28, in which the non-metal species comprises O, S, C or N.

35

30. A method according to any of claims 19 to 29, in which the metal (M¹) comprises Ti, Si, Ge, Zr, Hf, Sm, U, Al, Mg,

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Nd, Mo, Cr, Nb, V, Ta, Mb, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Be, Sr, Ga, In, Tl, lanthanides or actinides, or an alloy thereof.

- 5 31. A method according to any of claims 19 to 30, in which the powdered feed material is formed into a sample for electro-deoxidation by slip-casting or compaction.
- 10 32. A method according to any of claims 19 to 31, in which the formation of the precursor comprises sintering.
- 15 33. A method according to any of claims 19 to 32, in which the powdered feed material comprises a mixture or solid solution of one or more metal compounds, and optionally one or more metals or alloys.
- 20 34. A method according to any of claims 19 to 33, in which the near net-shaped product is subsequently treated by sintering and/or machining.
35. A near net-shaped product formed by a method as defined in any of claims 19 to 34.
- 25 36. An apparatus for producing a near net-shaped product as defined in claim 35.

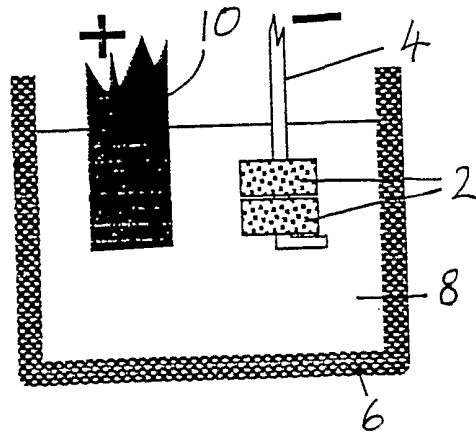


FIGURE 1

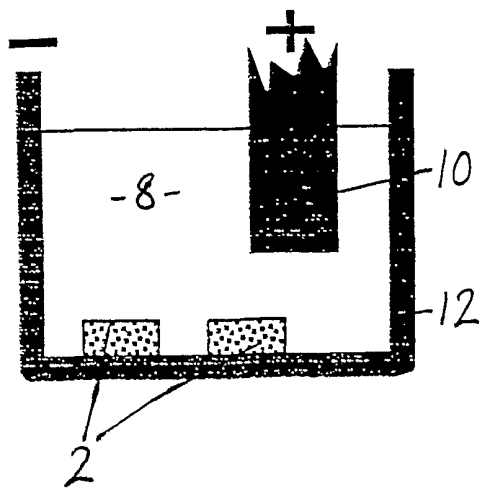


FIGURE 2

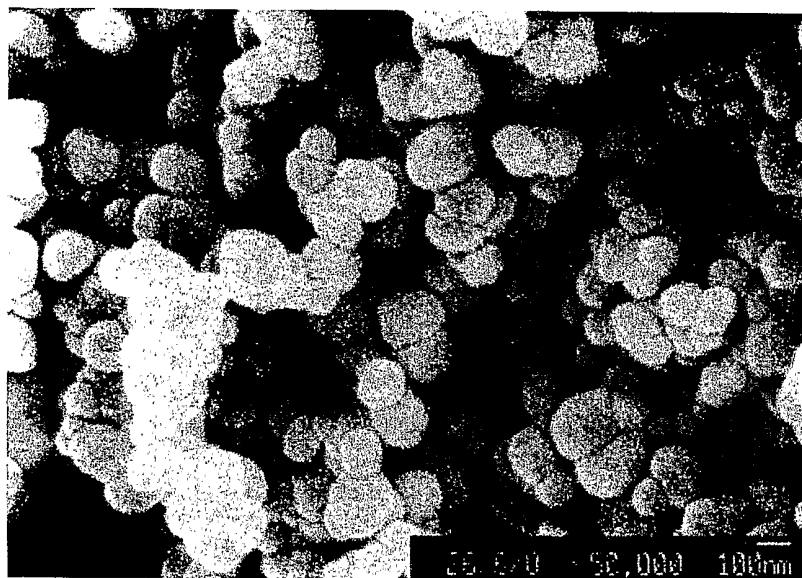


FIGURE 3

100nm

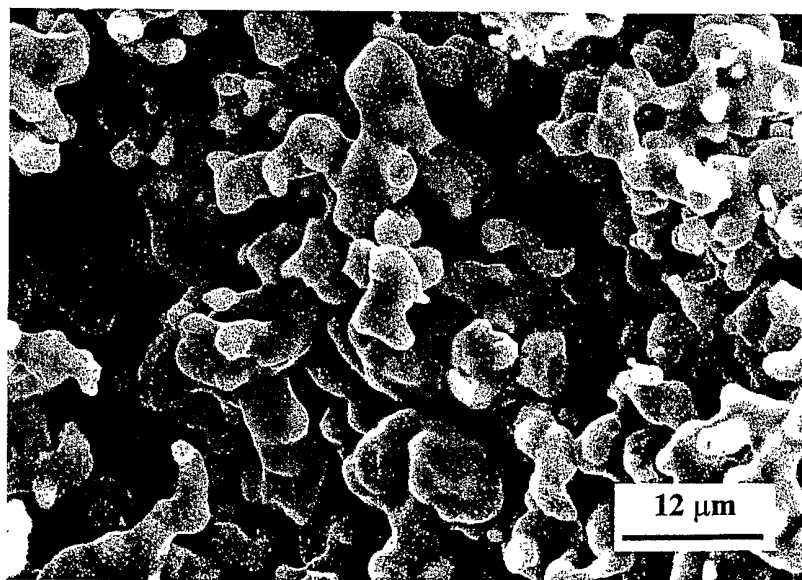


FIGURE 4

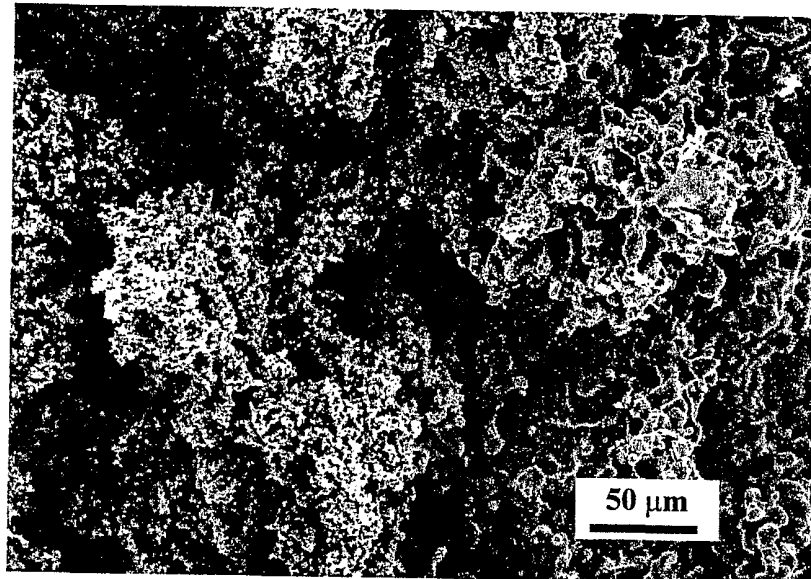


FIGURE 5

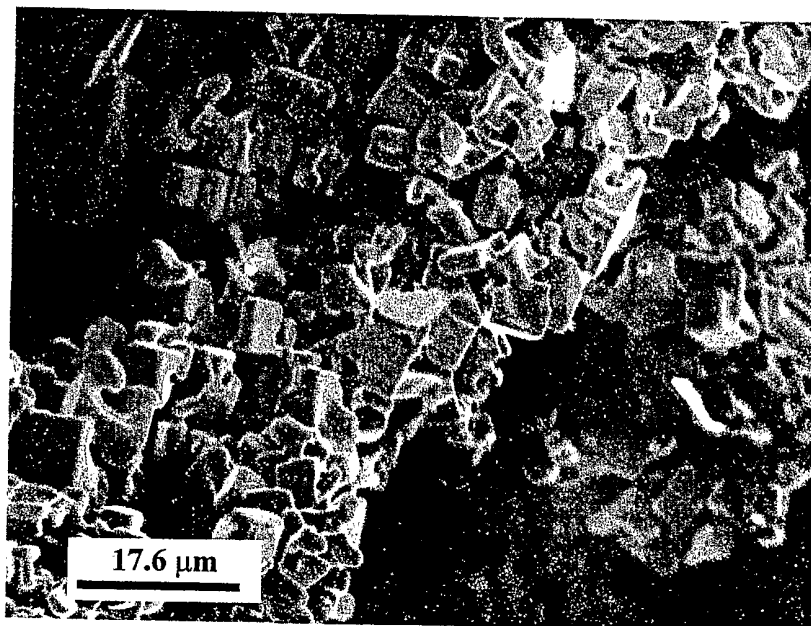


FIGURE 6

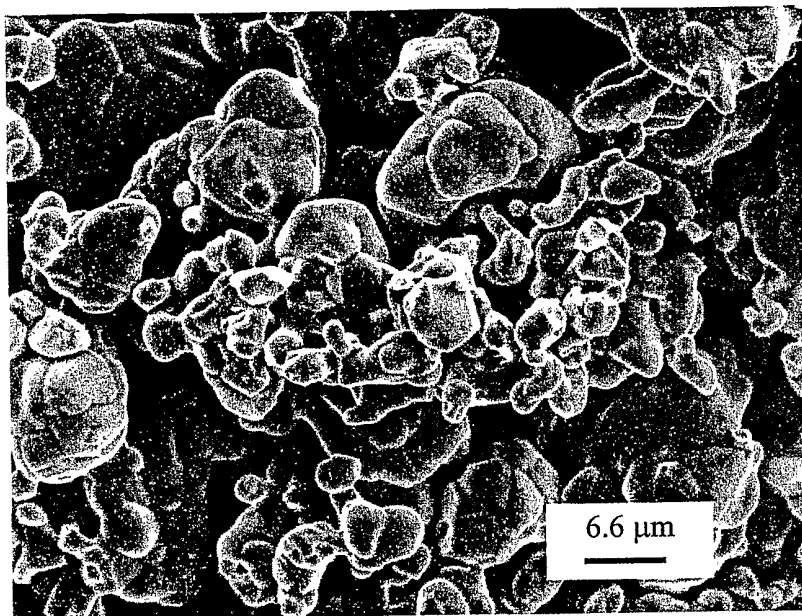


FIGURE 7

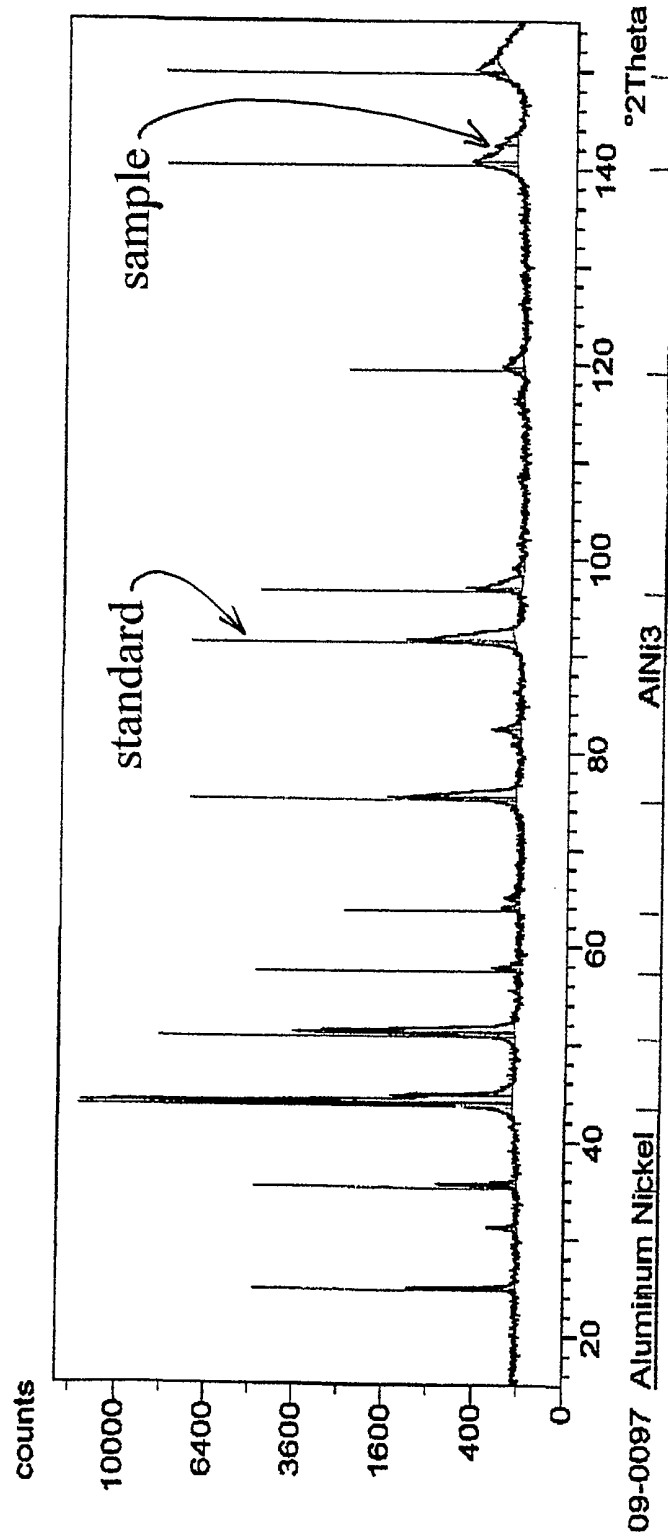


FIGURE 8

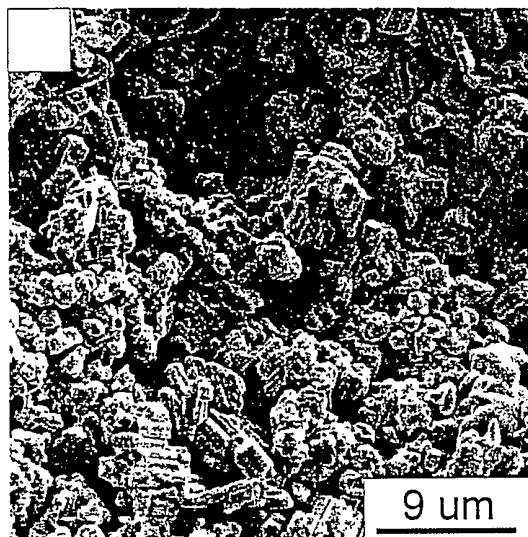


FIGURE 9

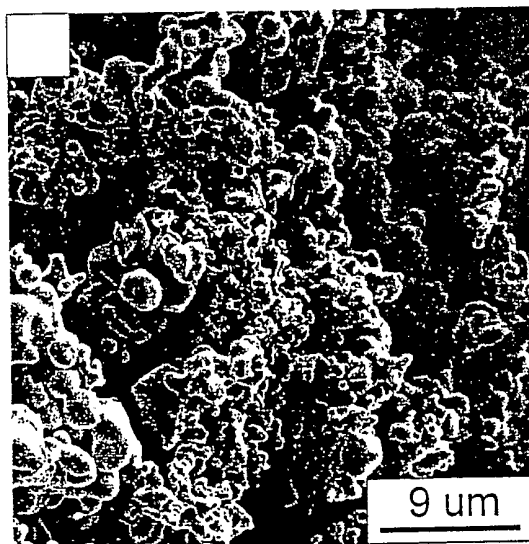


FIGURE 10

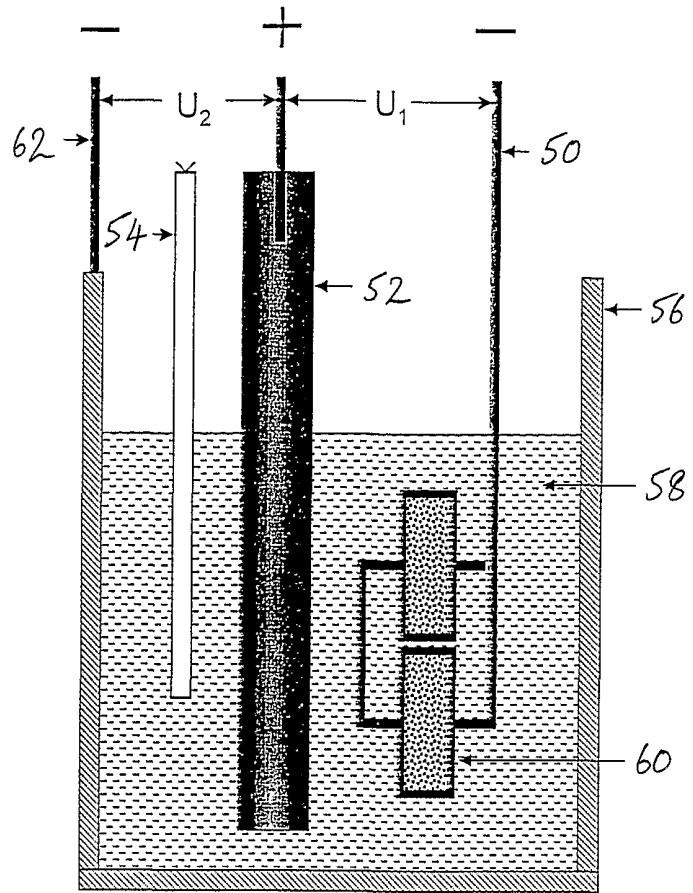


FIGURE 11

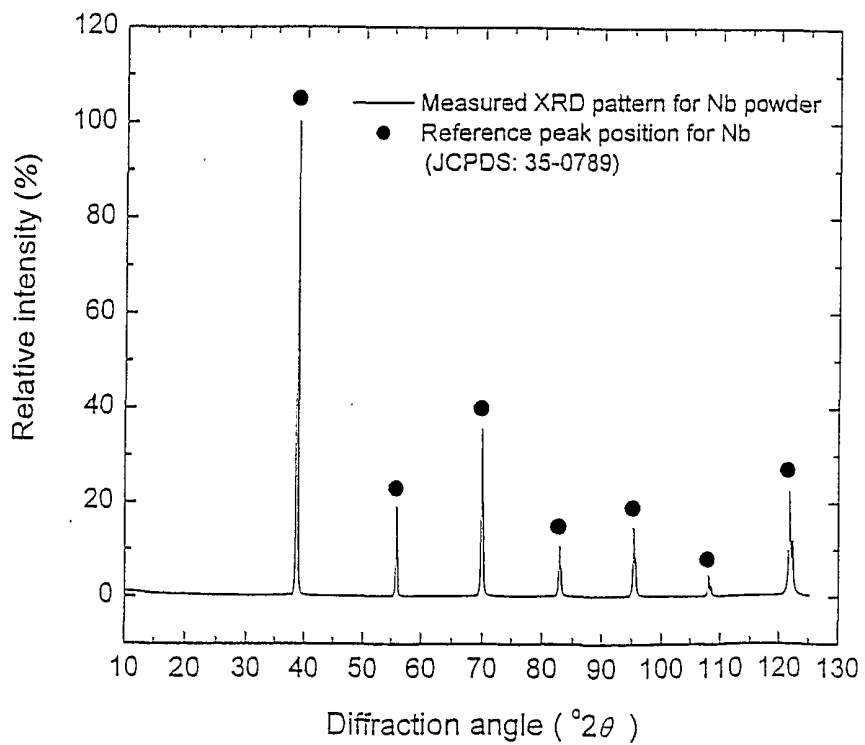


FIGURE 12