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(54) Nickel powder comprising ultra-fine spherical particles and method of producing the same.

(57) A method of continuously manufacturing an ultrafine spherical nickel powder containing 99.5% or more by weight of nickel in which chemical reaction of nickel chloride vapor and hydrogen is caused by introducing an inert gas into the reaction and controlling the nickel chloride vapor density to about 0.05 to 0.3 in the inert gas while controlling the reaction temperature to about 1,004°C (1,277K) to 1,453°C (1,726K). The ultrafine spherical nickel powder produced is formed of substantially spherical particles having a particle size of about 0.1 to 3 μm, and contains about 99.5% or more by weight of nickel.

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This invention relates to a high-purity ultrafine spherical powder of nickel suitable for making a conductive paste filler for use in electronic parts or the like. The invention also relates to a novel method of making the new nickel powder.

Ultrafine metallic powders according to this invention consist of spherical particles having limited dispersion of particle size, i.e. having an average particle size in the range of about 0.1 to several microns. The expression "particle size", as used herein, is intended to mean the average diameter determined by the specific surface area of the particles. Ultrafine metallic powders according to this invention have improved paste properties and, when used to form conductors in an electronic circuit, enable formation of fine conductor patterns and also enable reduction in the thicknesses of conductor layers. Such powders are therefore in much demand.

Laminated ceramic capacitors used as electronic circuit components are generally manufactured in such a manner that layers of ceramic dielectric are alternately layered with internal electrodes and the resulting layered structure is pressed and fired so as to be integrally combined. In this case it is necessary to use, as an internal electrode material, a precious metal such as Pt or Pd which does not melt at the temperature at which the dielectric ceramic is sintered, and which is not oxidized by firing in an atmosphere having a high oxygen partial pressure which does not decompose or reduce the dielectric ceramic. Where such an expensive material is used, it is difficult to manufacture a large-capacity low-price capacitor.

In an effort to solve this problem a ceramic has been developed which enables use of a base metal as the internal electrodes. The ceramic is not changed into a semi-conductor by firing in an atmosphere of low oxygen partial pressure or in a reducing atmosphere, in order to maintain the metallic state of the base metal and the ceramic has excellent dielectric characteristics and a specific resistance which is sufficient for use as a dielectric for capacitors.

With recent progress of the development of small large-capacity electronic parts, a need for reduction of thickness and of resistance of the internal electrodes has arisen.

The thickness of the internal electrode is limited by the particle size of the filler used in the paste. This thickness cannot be smaller than the particle size itself. Accordingly, a filler powder having a smaller particle size may be used to afford reduction of thickness. However, there is a practical limit to the available extent of reduction of particle size, because the filling properties of the filler deteriorate if the particles are too small.

A method of manufacturing an ultrafine nickel powder is disclosed in Japanese Patent Publication No.59-7765. Nuclei of the metal generated in interface unstable regions are grown to form ultrafine particles by controlling differences between the flow rates of a metal halide gas and a reducing gas and by utilizing the difference between the specific gravities of the gases to form an ultrafine nickel powder. In this case particles having a crystal habit such as a cubic shape (noted in Table 1 of the reference) are formed into a nickel powder. Such particles, while less expensive than precious metal powders, cause a problem of filling when the powder is used as a paste filler.

A similar method of obtaining an ultrafine nickel powder utilizes a vapor phase hydrogen reduction reaction of nickel chloride. Such method is disclosed in the thesis "Manufacture of ultrafine particles of nickel, cobalt or iron by vapor phase hydrogen reduction of chloride" (Nihon Kagaku Kaishi, 1984, (6), pp 869 to 878) authored by Kenichi Ohtsuka et al. In this method, reaction is effected at a temperature of 750 to 950°C and a chloride vapor density of 0.02 or lower to obtain an ultrafine powder having a particle size of 0.1 μm or smaller. This method also entails a serious problem because of formation of particles having undesirable crystal habits.

Japanese Patent Publication No.2-49364 discloses a method in which a reducing agent such as sodium boron hydride is added to an aqueous solution containing nickel ions to reduce and precipitate nickel. This method entails problems including a need for various reducing agents, complicated manufacturing conditions, and a need to use an expensive high-purity reducing agent for obtaining a high-purity product. This reducing precipitation method uses a batch type process which is difficult to practise as a continuous process.

The so-called carbonyl method is known among other methods for manufacturing very fine powders of nickel and iron. However, this method cannot satisfy demands for finer or thinner conductor patterns because the particle size attained by this method is too large.

Japanese Patent Laid-Open Nos.62-63604 and 62-188709 disclose methods for manufacturing powders of copper and silver. According to these methods a metal halide is vaporized, the vapor of the metal halide is supplied to a reaction section by its vapor pressure or by an inert gas carrier, and the metal halide vapor and a reducing gas (such as hydrogen gas) are brought into contact and mixed with each other in the reaction section. Particles of the metal are thereby immediately reduced and separated out in the gas and are discharged through an outlet together with the gas. It is thus possible to continuously supply the raw-material metal halide and to continuously collect the formed powder.

In comparison with the copper powder in Japanese Patent Laid Open No. 62-63604 and the silver powder in Japanese Patent Laid Open No. 62-

188709, nickel powders formed by conventional methods include particles having cubic, octahedral and other crystal habits, which crystal habits create a major problem in terms of filling when the powder is used as a paste filler.

Accordingly, it has been a serious drawback that fine nickel powders manufactured by conventional methods include particles having undesirable crystal habits when the particle size is reduced to about 1 μm or smaller. The filling properties and performance of the resulting fillers at the time of internal electrode paste printing have been found to be unsatisfactory. Serious problems of low filler density, large amounts of voids formed by firing, and increase in electrical resistance have accordingly been encountered. There is also an increased possibility of delamination of the resulting layered structure at the time of firing. No nickel powder has heretofore been provided which has a particle size of 3 μm or smaller and has a satisfactorily high purity. Known nickel powder fillers used as components of electronic parts cannot be improved to provide a reduction in the resistance of the electrodes or by preventing undesirable influences on the dielectric.

In view of these problems, an object of the present invention is to provide a method of manufacturing, at a low cost, an ultrafine high-purity nickel powder consisting of spherical particles having a particle size of 0.05 to 3 μm, having a high filler density, and useful as a filler.

Another object is to provide a novel ultrafine high-purity nickel powder overcoming the problems of the prior art and highly useful as a filler for electronic parts.

For a better understanding of the invention and to show how the same may be carried into effect, reference will be made to the following figures, in which:

Fig. 1 is a schematic diagram of a reactor suitably used to carry out the method according to this invention;

Fig. 2 is an electron micrograph of the structure of particles of a fine nickel powder manufactured by a method of the present invention in accordance with Example 1;

Fig. 3 is an electron micrograph of the structure of particles of a fine nickel powder manufactured by a method of the present invention in accordance with Example 2;

Fig. 4 is an electron micrograph of the structure of particles of a fine nickel powder manufactured in accordance with Comparative Example 1; and

Fig. 5 is a graph of the relationship between nickel chloride vapor density and reaction temperature in reactions forming nickel powder.

According to a first aspect of the present invention there is provided an ultra-fine nickel powder characterised in that the powder comprises substantially spherical particles having a particle size in the range of from 0,1 μm to 3 μm and comprising not less than about 99.5% of nickel.

According to a second aspect of the present invention there is provided a method of producing an ultra-fine substantially spherical nickel powder characterised in that the method comprises reacting nickel chloride vapour with hydrogen at a temperature within the range of from about 1004°C to about 1453°C wherein the vapour density of the nickel chloride is within the range of from about 0.05 to 0.3.

The invention further provides a laminated ceramic capacitor including the ultrafine spherical nickel powder of the invention.

To manufacture an ultrafine nickel powder by chemical vapor phase reaction, nickel chloride vapor, which may be diluted with inert gas, such as argon, is brought into contact with and mixed with hydrogen and is reacted. Ultrafine nickel powder thereby formed passes through a cooling section together with the resulting gas and is thereafter collected.

A remarkable phenomenon is believed to take place in nickel particles in this process. It is believed that when the nickel chloride and the reducing gas are brought into reactive contact with each other, atoms of the resulting nickel or clusters of a monomer are generated, and that ultrafine nickel particles are formed by collision and coalescence of the monomer. The nickel particles are believed to grow by further collision and coalescence.

Ordinarily, ultrafine powders of copper or silver are not to be compared to nickel because they normally consist of spherical particles. In contrast, nickel powders generally consist of polyhedral particles. With respect to the comparatively large particle sizes, the proportion of surface energy to internal energy is reduced so that the powder tends to develop and possess undesirable crystal habits. In particular, in the case of nickel, particles having distinct cubic or octahedral crystal habits strongly tend to be formed if the particle size is greater than about 0.1 μm. Therefore, it is surprising that the method of this invention is capable of producing a finely divided nickel powder having substantially completely spherical particles even when the particle size is substantially greater than 0.1 μm.

After having fully examined the reaction and generation of fine nickel powders, it has been found that a substantially completely spherical powder can be obtained by reacting the nickel chloride with hydrogen if the nickel chloride vapor density (partial pressure in the supplied gas except for hydrogen) is in the range of about 0.05 to 0.3, and if the reaction/powder generation temperature is within a range from about 0.74 times as high as the melting point of nickel (1,726K) in terms of absolute temperature to the nickel melting point, i.e., a range of about 1,004°C (1,277K) to 1,453°C (1,726K). The

present invention has been achieved based on this finding.

An important reason for the limitation of the nickel chloride vapor density in the supplied gas to about 0.05 to 0.3 is as described below.

It has been found by experiment that if the nickel chloride vapor density in the supplied gas such as argon is lower than about 0,05, undesirable crystal habits are developed and it is not possible to obtain a spherical powder. This may be because the particles grow at a comparatively low speed. If the nickel chloride vapor density exceeds about 0.3, the nickel particles are excessively large and it is not possible to obtain a powder having a desired particle size. Also, if the particle size is excessive,undesirable crystal habits readily occur.

Most preferably, the nickel chloride vapor density in the supplied gas is about 0.06 to 0.15.

The reason for the limitation of the reaction temperature to about 1,004°C to 1,453°C is as described below.

If the reaction temperature is lower than about 1,004°C, crystal habit particles are mixed and the reaction rate is reduced. The upper limit of the reaction temperature is, preferably, equal to or lower than about the melting point of nickel, i.e., 1,453°C (1,716K). If the reaction temperature is substantially higher than the melting point, generated particles exist in a liquid state, so that the probability of particles growing to a very large size is high, the particle size distribution is extended, and the amount of nickel attached to the reactor wall is increased.

Most preferably, the reaction temperature is about 1,010°C to about 1,100°C.

It is believed that this temperature dependency of the particle shape relates to the influence of the temperature upon the reaction rate, i.e., the rate of generation of atoms or monomer clusters, that is, the particle growth speed influences the particle shape. It is explained that if the reaction temperature is higher, the anisotropy of the particle growth is reduced so that the particles tend to grow into spherical bodies. It is considered that the density dependency of the particle shape relates to the influence of the density upon the homogeneous nuclei formation speed. In this case, it is also believed that the particle shape depends upon the particle growth speed as in the case of the temperature dependency.

In a case where the reaction is carried out in a reaction tube heated in an electric furnace, since this reaction is an exothermic reaction, spherical nickel particles can be attained even if the set temperature of the electric furnace is lower than the predetermined temperature mentioned above, provided that the set temperature is high enough to be supported by the exothermic reaction. That is because it is important to control the temperature at which the nickel particles grow by formation, collision and coalescence of metallic monomers during reaction.

Further, according to the present invention, the nickel content in the nickel powder is controlled to about 99.5% or more by weight, the lower limit of the particle size thereof is about 0.05 μm, the upper limit of the same is smaller than about 3 μm, and the shape of the particles is substantially limited to a spherical shape.

If the nickel content is less than about 99.5% by weight, the desired resistance of electrodes or the desired reliability of electronic parts cannot be achieved owing to undesirable influence upon dielectric characteristics. The nickel content is therefore about 99.5% to about 100% by weight.

Particles having a particle size smaller than about 0.05 μm tend to agglomerate easily. If such particles are used as a paste to be printed as internal electrodes of a laminated ceramic capacitor or the like, the filling performance of the filler is very poor so that the electrode layers after being fired are porous, have a high electrical resistance and are reduced in strength of bonding to the dielectric layer, resulting in delamination. In the case of particles having a particle size greater than about 3 μm, it is impossible as a practical matter to reduce the thickness of the electrode layers for physical reasons.

If the particles are spherical the resulting structure achieves a degree of filling close to optimum density filling when printing internal electrodes, and high-quality electrodes can be obtained by firing which are uniform, in which the amount of voids is small and which electrodes have low resistance. It is also possible to limit the shrinkage of the electrode layers at the time of firing and, hence, to prevent occurrence of cracks in the dielectric layer and delamination.

EXAMPLES

The following examples are intended to be illustrative and not to define or to limit the scope of the invention, which is defined in the appended claims.

Example 1

A reactor 1 such as that shown in Fig. 1 was used and 10 g of raw-material nickel chloride was placed in a quartz boat 3 in a vaporization section and was vaporized in argon gas 4 supplied at 2 liter/min so that the density (partial pressure) of the vaporized nickel chloride was 5.0×10^{-2}. The raw-material gas thereby formed was introduced into a reaction section 5 controlled at 1,050°C (0.77 times as high as the melting point of nickel in terms of absolute temperature), and was brought into contact and mixed with hydrogen supplied at a rate of 1 liter/min. through a central reaction nozzle 6. The temperature measured by a thermocouple 8 protected with a

quartz tube was increased up to 1,090°C (0.79 times as high as the melting point of nickel). The nickel powder produced was collected by a cylindrical filter paper after passing through a cooling section 9 together with the gas. The specific surface area of the produced powder was 3.5 m^2/g which was a spherical powder having a particle size of 0.2 μm as observed with an electron microscope.

Fig. 2 shows an electron microscope photograph of the nickel powder obtained in accordance with this example. As can be seen in this photograph, the shape of nickel powder particles obtained is nearly perfectly spherical.

Example 2

A nickel powder was manufactured under the same conditions as Example 1 except that the reaction temperature was 960°C (0.714 times as high as the melting point of nickel in terms of absolute temperature). The temperature measured by thermocouple 8 was increased up to 1,004°C (0.74 times as high as the melting point of nickel). The specific surface area of the produced powder was 3.7 m^2/g and the product was a spherical powder having a particle size of 0.18 μm as observed with an electron microscope.

Fig. 3 shows an electron microscope photograph of the nickel powder obtained in accordance with this example.

Example 3

A nickel powder was manufactured under the same conditions as Example 1 except that the reaction temperature was 960°C (0.714 times as high as the melting point of nickel in terms of absolute temperature), and that the density (partial pressure) was set to 8.0×10^{-2}. The temperature measured by thermocouple 8 was increased up to 1,006°C (0.74 times as high as the melting point of nickel). The specific surface area of the produced powder was 3.0 m^2/g and the product was a spherical powder having a particle size of 0.22 μm as observed with an electron microscope.

Example 4

A nickel powder was manufactured under the same conditions as Example 1 except that the reaction temperature was controlled at 1,000°C (0.74 times as high as the melting point of nickel in terms of absolute temperature), and that the density (partial pressure) was controlled at 8.5×10^{-2}. The temperature measured by thermocouple 8 was increased up to 1,053°C (0.77 times as high as the melting point of nickel). The specific surface area of the produced powder was 2.9 m^2/g and the product was a spherical powder having a particle size of 0.23 μm as observed with an electron microscope.

Example 5

A nickel powder was manufactured under the same conditions as Example 1 except that the reaction temperature was controlled at 1,050°C (0.767 times as high as the melting point of nickel in terms of absolute temperature), and that the density (partial pressure) was set to 3.0×10^{-1}. The temperature measured by thermocouple 8 was increased up to 1,120°C (0.81 times as high as the melting point of nickel). The specific surface area of the produced powder was 0.9 m^2/g and the product was a spherical powder having a particle size of 0.8 μm as observed with an electron microscope.

Comparative Example 1

A nickel powder was manufactured under the same conditions as Example 1 except that the reaction temperature was set at 950°C (0.71 times as high as the melting point of nickel in terms of absolute temperature), and that the density (partial pressure) was 4.5×10^{-2}. The temperature measured by thermocouple 8 was increased up to 993°C (0.73 times as high as the melting point of nickel). The specific surface area of the produced powder was 3.6 m^2/g and the powder was observed with an electron microscope as having a particle size of 0.2 μm and having cubic, octahedral and other crystal habits as shown in Fig. 4.

Comparative Example 2

A nickel powder was manufactured under the same conditions as Example 1 except that the reaction temperature was 950°C (0.71 times as high as the melting point of nickel in terms of absolute temperature), and that the density (partial pressure) was 8.0×10^{-2}. The temperature measured by thermocouple 8 was increased up to 998°C (0.73 times as high as the melting point of nickel). The specific surface area of the produced powder was 3.4 m^2/g and the product was observed with an electron microscope as a powder having a particle size of 0.2 μm and having cubic, octahedral and other crystal habits.

Comparative Example 3

A nickel powder was manufactured under the same conditions as Example 1 except that the reaction temperature was 1,000°C (0.74 times as high as the melting point of nickel in terms of absolute temperature), and that the density (partial pressure) was 4.5×10^{-2}. The temperature measured by

thermocouple 8 was increased up to 1,042°C (0.76 times as high as the melting point of nickel). The specific surface area of the produced powder was 3.4 m^2/g and the product was observed with an electron microscope as a powder having a particle size of 0.2 μm and having cubic, octahedral and other crystal habits.

Comparative Example 4

A nickel powder was manufactured under the same conditions as Example 1 except that the reaction temperature was 1,100°C (0.795 time as high as the melting point of nickel in terms of absolute temperature), and that the density (partial pressure) was 3.6×10^{-1}. The temperature measured by thermocouple 8 was increased up to 1,160°C (0.83 times as high as the melting point of nickel). The specific surface area of the produced powder was 1.0 m^2/g and the product was observed with an electron microscope as a powder having a particle size of 0.8 μm and having cubic, octahedral and other crystal habits.

Fig. 5 collectively shows the relationships between various nickel chloride vapor densities and reaction temperatures with respect to each of Examples and Comparative Examples described above.

The present invention makes it possible to continuously produce, at a low manufacturing cost, an ultrafine nickel powder which consists of spherical particles having a particle size of about 0.05 to 3 μm highly superior for use as a conductive paste filler, and which contains about 99.5% or more by weight of nickel.

Although the invention has been described with respect to particular reactors, powders and reaction gases and gas mixtures, it will be appreciated that many variations may be made without departing from the spirit and scope of the invention as defined in the appended claims.

Claims

1. An ultra-fine nickel powder characterised in that the powder comprises substantially spherical particles having a particle size in the range of from 0.1 μm to 3 μm and comprising not less than about 99.5% of nickel.

2. A method of producing an ultra-fine substantially spherical nickel powder characterised in that the method comprises reacting nickel chloride vapour with hydrogen at a temperature within the range of from about 1004°C to about 1453°C wherein the vapour density of the nickel chloride is within the range of from about 0.05 to 0.3.

3. A method as claimed in claim 2 wherein the nickel chloride vapour is supplied by means of a carrier gas and wherein the vapour density of the nickel chloride is measured independently of the hydrogen.

4. A method as claimed in claim 2 or 3 wherein the reaction temperature is in the range of from about 0.74 to 1.00 times the melting point of nickel, when the said temperature and melting point are expressed in terms of absolute temperature.

5. A method as claimed in claim 2, 3 or 4 wherein the vapour density of the nickel chloride is in the range of from 0.06 to 0.15.

6. A method as claimed in any of claims 2 to 5 wherein the reaction temperature is in the range of from 1010°C to 1100°C.

7. A method as claimed in any of claims 3 to 6 wherein the carrier gas is an inert gas.

8. A method as claimed in claim 7 wherein the carrier gas is Argon.

9. A laminated ceramic capacitor including the nickel powder of claim 1.

FIG. 1

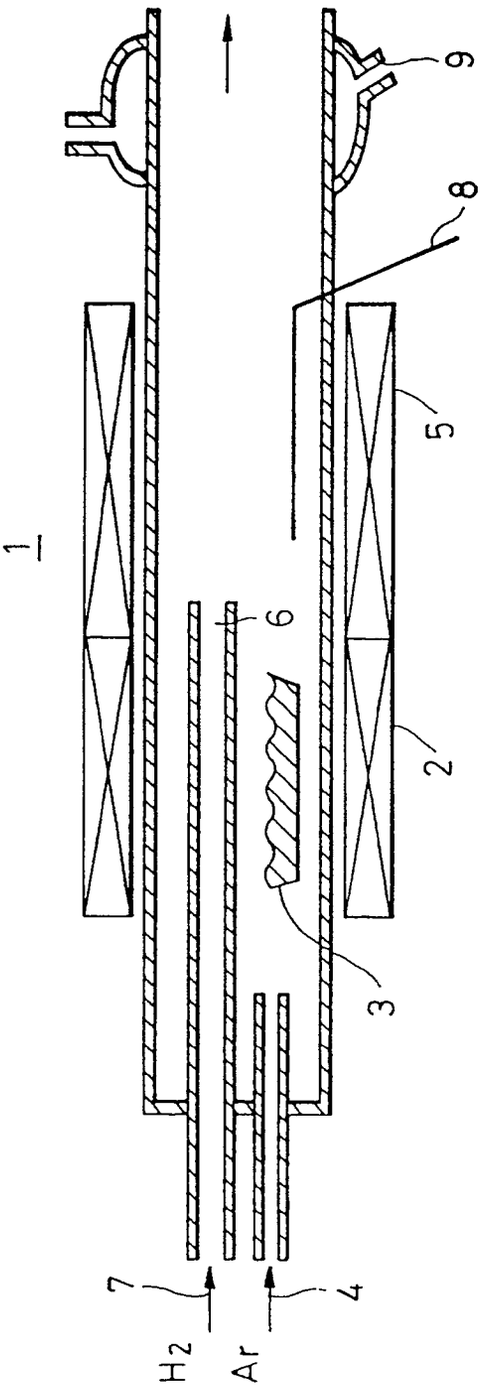
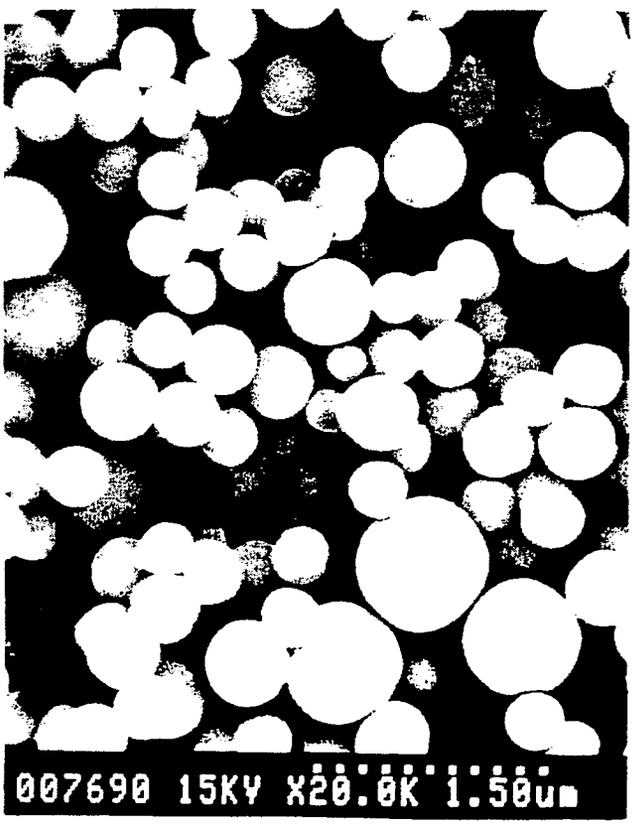
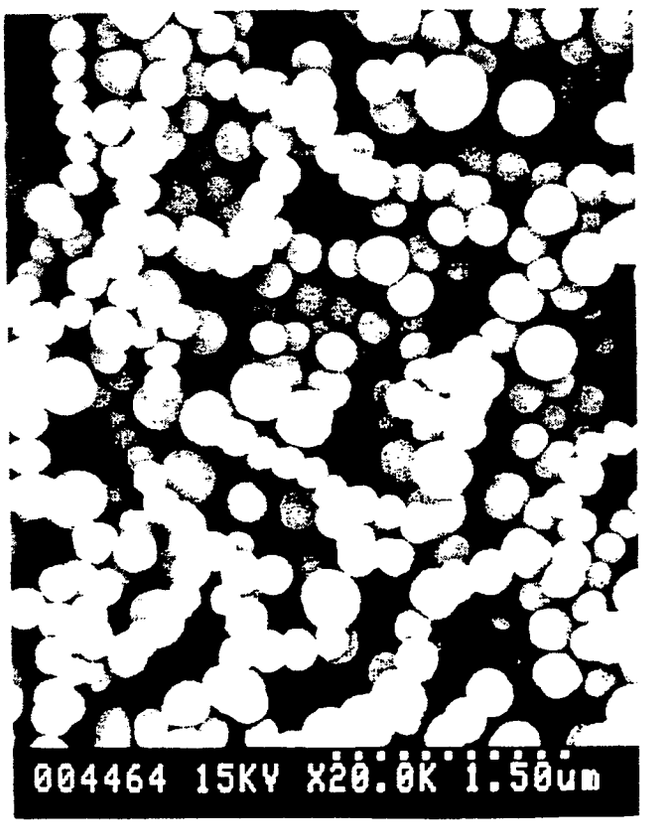


FIG. 2



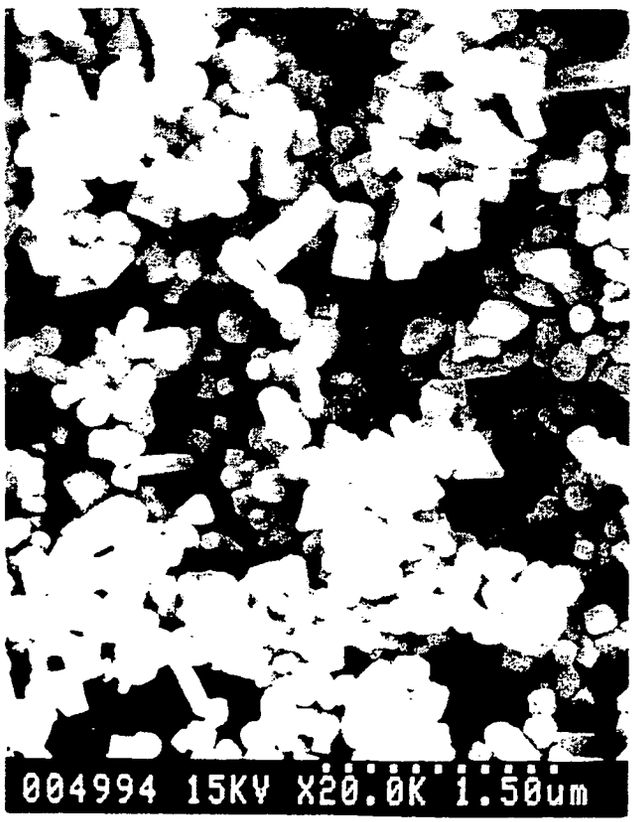
EXAMPLE 1

FIG. 3



EXAMPLE 2

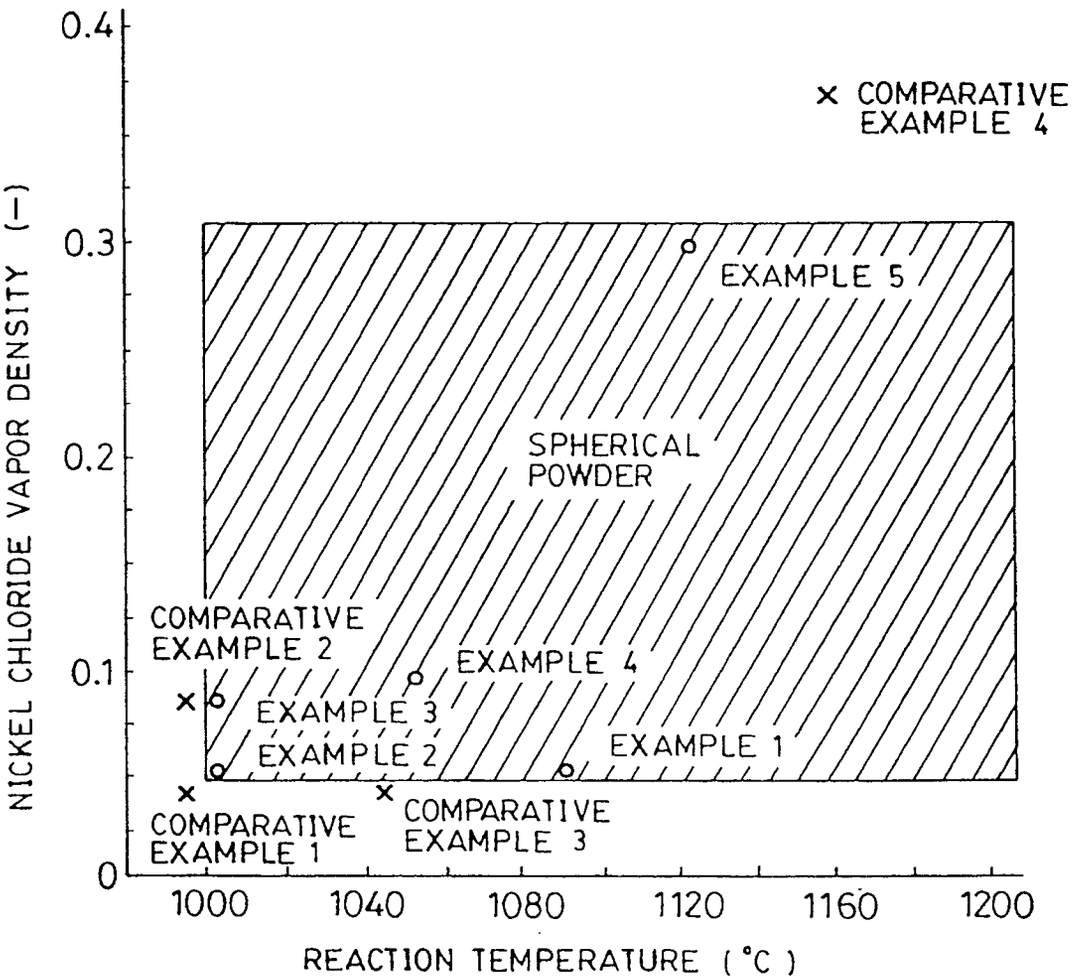
FIG. 4



1 μm

COMPARATIVE EXAMPLE 1

FIG. 5


0.4
0.3
0.2
0.1
0
NICKEL CHLORIDE VAPOR DENSITY (−)
× COMPARATIVE EXAMPLE 4
EXAMPLE 5
SPHERICAL POWDER
COMPARATIVE EXAMPLE 2
EXAMPLE 4
EXAMPLE 3
EXAMPLE 2
EXAMPLE 1
COMPARATIVE EXAMPLE 1
COMPARATIVE EXAMPLE 3
1000
1040
1080
1120
1160
1200
REACTION TEMPERATURE (°C)