A method of producing a fine, low bulk density nickel powder, comprising a) charging particles of at least one reducible nickel salt within a furnace so as to form a moving bed of furnace charge, and b) reducing the furnace charge with a H₂ containing gas at a temperature ranging from about 300°C to about 500°C, the bed of furnace charge being moved gently so as to minimise formation of hard agglomerates and obtaining a fine, low bulk density nickel powder. A similar method, wherein the furnace charge is static and contained within a shallow bed.
METHOD FOR PRODUCING FINE, LOW BULK DENSITY, METALLIC NICKEL POWDER

FIELD OF THE INVENTION

[0001] The present invention relates to a method for producing a fine, low bulk density, metallic nickel powder.

BACKGROUND OF THE INVENTION

[0002] Canadian application No. 2,418,063 teaches how to produce an active nickel powder by reducing a nickel chloride containing salt having a high surface area with hydrogen gas at a temperature above 300° C., and how to rapidly convert such active powder to nickel carbonyl. However, this patent application does not address the deleterious issue of particle agglomeration during the production of active nickel powder.

[0003] Indeed, it is known that freshly reduced metallic nickel particles exhibit a great affinity for each other and for the inner surfaces of the furnace, and can readily form growing agglomerates. These agglomerates thwart attempts at producing a fine, low bulk density, metallic nickel powder.

[0004] Prior art teaches several methods said to limit agglomeration of nickel particles during reduction.

[0005] U.S. Pat. No. 5,914,124 teaches the use of at least one additive selected from the group consisting of "calcium oxide, magnesia or compounds that are heat decomposable thereto" (abstract), to create an anti-agglomerating coating on a substantial portion of the particles to minimise sticking while reducing nickel oxide. However, the process disclosed requires very high temperatures to assure a low volatile impurity content.

[0006] Canadian Patent 2,204,525 teaches the use of an organic dispersant such as gelatin and/or bone glue as an anti-agglomerating agent, as well as of a spheroid-promotion agent such as anthraquinone. However, the process disclosed results in the formation of a high density nickel powder, as opposed to low density nickel powder.

[0007] The use of fluidized beds has also been suggested (GB Patent No. 769099) but has not helped to avoid agglomeration since such beds tend to collapse when the reduction of nickel containing compounds to metallic nickel powder exceeds 70% and particles begin to agglomerate.

[0008] U.S. Pat. No. 2,948,525 teaches the use of a kiln with a continuously operating oxide film, such as aluminum oxide, which is irreducible at the temperature used for reduction of nickel compounds, so as to eliminate sticking of the nickel powder to the kiln walls. However, this patent does not solve the problem of inter-particles sticking and agglomerating.

[0009] It is also known that when reducing a furnace charge of solid particles with a gas, it is desirable to maximize the contact between each particle and the reducing gas. This is often achieved by moving the furnace charge during the reduction phase, for example, in a rotating kiln or a fluidized bed. However, it has been found that reducing a nickel containing charge in a rotating kiln operating at a typical rotation rate of about 10 rpm, results in a coarse agglomerate containing some hard agglomerate lumps, exceeding 1.3 cm in diameter. Such an end product does not have enough reactivity for a possible further chemical treatment, for example, to produce nickel carbonyl. Moreover, it has been observed that in a rotating kiln, for example, the formation of agglomerates and lumps increases as the rate of kiln rotation increases.

[0010] Thus, vigorous agitation during reduction results in production of hard agglomerates, which cannot subsequently be crushed to powder. In attempts to break-up the agglomerates of nickel powder during reduction, it was found that the addition of ceramic or metallic balls to the kiln charge was not successful. The balls become rapidly hard-coated with nickel powder and continue to grow in size.

[0011] As noted above, prior art processes fail to solve the difficulty of making fine, low bulk density, nickel powder. Thus there remains a need for a method for preparing fine, low bulk density nickel powder while minimising non-friable particle agglomerates.

[0012] The present invention seeks to meet this and other needs.

[0013] The present description refers to a number of documents, the content of which is herein incorporated by reference in their entirety.

SUMMARY OF THE INVENTION

[0014] It has been found that a fine, low bulk density, metallic nickel powder can be produced by treating reducible nickel salts with a hydrogen containing gas, at temperatures ranging from about 300° C. to about 500° C., while the extent of movement and the average kinetic energy of the freshly produced metallic nickel particles are minimised. This method has been found to significantly reduce formation of nickel agglomerates.

[0015] It has also been found that during reduction, soft agglomerates can be produced when gentle agitation is used. In contrast to the hard agglomerates produced by some of the prior art processes, these soft agglomerates are friable and can subsequently be crushed quite easily to powder and mostly break up during product screening.

[0016] More specifically, the present invention relates to a method of producing a fine, low bulk density nickel powder, comprising:

[0017] a) charging particles of at least one reducible nickel salt within a furnace so as to form a moving bed of furnace charge; and

[0018] b) reducing the furnace charge with a H₂ containing gas at a temperature ranging from about 300° C. to about 500° C., the bed of furnace charge being moved gently so as to minimise formation of hard agglomerates and thereby obtaining a fine, low bulk density nickel powder.

[0019] The present invention also relates to a method of producing a fine, low bulk density nickel powder, comprising:

[0020] a) charging particles of at least one reducible nickel salt within a furnace so as to form a static, shallow bed of furnace charge; and

[0021] b) reducing the furnace charge with a H₂ containing gas at a temperature ranging from about 300° C.
to about 500° C.; the static bed of furnace charge being shallow so as to allow penetration of reducing gas into the bed and minimise formation of hard agglomerates, thereby obtaining a fine, low bulk density nickel powder.

[0022] Other objects, advantages and features of the present invention will become more apparent upon reading of the following nonrestrictive description of preferred embodiments thereof, given by way of example only with reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] In the appended drawings:

[0024] FIG. 1 is a graph illustrating the effect of reducing the rotation rate of a kiln having an internal diameter of 10.2 cm on the quantity of metallic nickel powder passing various screens (size fractions are indicated in microns);

[0025] FIG. 2 is a graph illustrating the effect of varying the rotation rate of a kiln having an internal diameter of 10.2 cm on the quantity of metallic nickel powder passing through a 65 mesh screen (210 microns);

[0026] FIG. 3 is a graph illustrating the effect of varying the rotation rate of a kiln having an internal diameter of 10.2 cm on the quantity of metallic nickel powder passing through a 100 mesh screen (149 microns);

[0027] FIG. 4 is a flowchart of a preferred embodiment of the present invention;

[0028] FIG. 5 is an electronmicrograph of a dry free-flowing powder of nickel carbonate and nickel hydroxide used as a feed in Example 1, and as typically used in the method of the present invention (AMRAY Scanning electron microscope, ×500 magnification); and

[0029] FIG. 6 is an electronmicrograph of a fine, low bulk density metallic nickel powder as obtained according to the method of the present invention (AMRAY Scanning electron microscope, ×500 magnification).

DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0030] The present invention is illustrated in further details by the following non-limiting examples.

[0031] In general terms, the present invention relates to a method for producing a fine, low bulk density, unagglomerated or friable, metallic nickel powder by reducing, in a hydrogen containing gas, a furnace charge that is either static or moved gently so as to minimise the average kinetic energy of these freshly reduced particles.

[0032] As used herein when referring to either a feed or a product, the term “particle” designate any small piece or part of a flowable material, such as a powder.

[0033] As used herein, the term “agglomerate” refers to a group of individual particles sticking together to form either a soft or hard lump.

[0034] As used herein when referring to a nickel powder, the term “fine” means that at least about 45% of the powder would pass through a 100 mesh (149 microns) screen, with essentially no remaining hard agglomerates in the +100 mesh fraction.

[0035] As used herein when referring to a nickel powder obtained by the method of the present invention, the term “low bulk density” means a bulk density of 4 g/cc or less. Preferably, nickel powders obtained by the method of the present invention have a bulk density between about 0.5 and about 2 g/cc. Most preferably, nickel powders obtained by the method of the present invention have a bulk density between about 0.5 and about 1.6 g/cc.

[0036] As used herein when referring to a static bed of furnace charge, the term “shallow” defines a depth of powder charge that would allow the penetration of reducing gas into the bed. Usually, such static shallow bed is about 2.5 cm deep or less.

[0037] As used herein when referring to numerical values or percentages, the term “about” includes variations due to the methods used to determine the values or percentages, statistical variance and human error. Moreover, each numerical parameter in this application should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0038] It is quite counter-intuitive to minimise the rotation rate of a kiln when searching to achieve an acceptable reduction rate and an acceptable reduction product, since this action limits both the gas-solid interaction and the rate of charge throughput.

[0039] However, it was unexpectedly discovered that reducing the rotation rate of the kiln, thus reducing the peripheral speed of the kiln during reduction, resulted in less agglomeration and increased the amount of fine nickel powder product. The effect of lowering the rotation rate of a kiln having an internal diameter of 10.2 cm on the amounts of nickel powder product passing various screens is illustrated in FIG. 1. For example: reducing the rotation rate from 2 rpm to 0.8 rpm reduces the proportion of the fraction above 150 microns in diameter (+100 mesh) from about 72% to about 53%; and reducing the rotation rate from 2 rpm to 0.2 rpm allows reducing the proportion of +100 mesh fraction from about 72% to about 48%.

[0040] Similar data can be seen from another angle in FIGS. 2 and 3, illustrating the effects of varying the rotation rate of a kiln having an internal diameter of 10.2 cm on the amounts of nickel powder passing through a 65- and a 100-mesh screen, respectively.

[0041] The screening measures referred to in this application were performed on a well-known Ro-Target™ machine, in which the screens are shaken and tapped. The screening period used was usually 20 min.

[0042] The method according to the present invention utilizes either a static or slowly moving furnace charge.

[0043] The method itself can be performed either continuously or batch-wise.

[0044] The reduction temperature ranges from about 300° C. to about 500° C., preferably from about 350° C. to about 450° C.

[0045] In a particular embodiment, the reducing gas contains at least 20% hydrogen in volume.

[0046] In another particular embodiment, the hydrogen containing gas is preheated before entering the kiln.
In still another particular embodiment, the feed of reducible nickel salt is calcinated in a nitrogen or other inert gas atmosphere at a temperature ranging from about 300 to about 350°C. This is done in either the first compartment of the furnace or in a separate furnace.

Such calcination of the feed drives off carbon dioxide gas from the nickel carbonate in the feed and thus allows separate scrubbing and removal of carbon dioxide. This simplifies the cleaning of the off-gas from the reduction step and allows the recycling of unused hydrogen.

It is to be understood that both the preheating of the gas and the calcination can occur within the same particular embodiment of the method according to the present invention.

One of the preferred embodiments of the present invention is illustrated on FIG. 4. The dry free flowing powder of reducible nickel salt (1) is calcinated in a first furnace in presence of nitrogen gas (2). The off-gas of calcination (4) essentially contains CO₂, CO, H₂O and N₂. The hot calcine (3) is then transferred into a second furnace, namely the reduction kiln, so as to form a bed of furnace charge. H₂ gas (5) is advantageously passed into the static or slowly moving bed of furnace charge, and an excess of H₂ is advantageously used. Such a process allows obtaining a fine, low bulk density nickel powder (6). Thanks to the separate calcination step, the off-gas of the reduction kiln only contains H₂ and H₂O, which allows an easy H₂ recycling.

The exact composition of the feed of reducible nickel salt used in the method of the present invention may of course influence the final bulk density and fineness of the nickel powder product.

Indeed, it has been found that the bulk density of the nickel powder product increased as the total amount of inert impurities in the feed material decreased. Inert impurities are typically various amounts of carbonate/chloride/sulphate salts of sodium/magnesium/calcium. This is illustrated in Table 1 below. Thus, the bulk density of nickel powder product decreased from 1.2 g/cc to 0.5 g/cc as the total amount of inert impurities increased from about 10 wt % (well-washed nickel carbonate) to about 30 wt % (poorly washed nickel carbonate).

<table>
<thead>
<tr>
<th>Degree of washing</th>
<th>RPM of kiln</th>
<th>wt % passing through a 65 mesh screen</th>
<th>wt % passing through a 100 mesh screen</th>
</tr>
</thead>
<tbody>
<tr>
<td>well-washed feed</td>
<td>0.2</td>
<td>53.6</td>
<td>45.7</td>
</tr>
<tr>
<td>regularly washed</td>
<td>0.2</td>
<td>59.6</td>
<td>51.3</td>
</tr>
<tr>
<td>poorly washed</td>
<td>0.2</td>
<td>99.7</td>
<td>99.5</td>
</tr>
</tbody>
</table>

Table 2 shows that, as the degree of washing of the nickel carbonate decreases, and therefore the inert impurity content increases, the nickel powder obtained according to the process of the present invention becomes much finer. Indeed, at least 99% of the final product obtained from a poorly washed nickel carbonate feed (about 30 wt % inert impurities) passes through a 100 mesh screen.

The reducible nickel salts used in the method of the present invention are preferably nickel carbonate, nickel oxide, nickel hydroxide, nickel oxalate. Those skilled in the art will appreciate that any other fine, low density nickel compound that is reduced to a metallic state in hydrogen gas below 500°C can also be used. For example, nickel chloride may be used. However, nickel chloride, either hydrated or not, or other reducible nickel salts that happen to melt or become sticky below 500°C, can be used as feed in the method of the present invention only when used in combination with at least another reducible nickel salt of the above category, such as the preferred cited salts.

It is to be understood that many other operating parameters and processing conditions can be easily varied by a person skilled in the art without departing from the method of the present invention. Such parameters and conditions are (but not limited to): reducing gas flow rate and composition, co-current or counter-current kiln operation, kiln length and furnace charge residence time and back mixing of nickel powder product with fresh feed.

EXAMPLE 1

Fine, low bulk density nickel powders were prepared according to the method of the present invention in a rotating kiln with an internal diameter of about 10.2 cm (4 inches). In a batch process, charges of 300 to 500 g of nickel carbonate were used. The reduction temperature was 450°C and a hydrogen gas flow at 2 lpm was provided to the feed
in a kiln rotating at 0.2 rpm, corresponding to a peripheral velocity of 6.4 cm/min (see formula below). The residence time of the feed in the kiln was 3% to 4 hours.

Peripheral velocity = internal diameter \times \pi \times rotation rate (cm/min)

**Example 2**

Fine, low bulk density nickel powders were prepared according to the method of the present invention in a rotating kiln with an internal diameter of about 30.5 cm (12 inches). In a batch process, charges of 3.5 kg of nickel carbonate were used. The reduction temperature was 450°C, and a hydrogen gas flow at 3 lpm was provided to the feed in a kiln rotating at 0.07 rpm, corresponding to a peripheral velocity of 6.7 cm/min. The residence time of the feed in the kiln was 6 to 7 hours.

**Example 3**

Fine, low bulk density nickel powders were prepared according to the method of the present invention in a rotating kiln with an internal diameter of about 61 cm (24 inches). In a continuous process, 7 to 8 kg per hour of nickel carbonate were fed to the kiln. The reduction temperature was 350 to 400°C in the first half of the kiln and 450°C in the second half of the kiln. Hydrogen and nitrogen gases were fed at 8.5 and 42.5 lpm, respectively, in the kiln rotating at 0.125 rpm, corresponding to a peripheral velocity of 23.9 cm/min. The residence time of the feed in the kiln was about 20 hours.

**Table 3**

<table>
<thead>
<tr>
<th>Test</th>
<th>Weight g</th>
<th>Volume cc</th>
<th>Bulk Density g/cc</th>
<th>Average bulk Density g/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.883</td>
<td>7.2</td>
<td>1.09</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6.247</td>
<td>5.5</td>
<td>1.14</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>9.789</td>
<td>7.1</td>
<td>1.38</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>6.649</td>
<td>11.034</td>
<td>1.33</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3.557</td>
<td>3.904</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2.833</td>
<td>10.895</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>9.843</td>
<td>11.938</td>
<td>1.27</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>8.8</td>
<td>9.35</td>
<td>1.28</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>5.4</td>
<td>5.45</td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>8</td>
<td>3.35</td>
<td>1.65</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>6.7</td>
<td>7.7</td>
<td>0.87</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>7.2</td>
<td>7.2</td>
<td>0.87</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>5.5</td>
<td>6.6</td>
<td>0.87</td>
<td></td>
</tr>
</tbody>
</table>

**What is claimed is:**

1. A method of producing a fine, low bulk density nickel powder, said method comprising:
   a) charging particles of at least one reducible nickel salt within a furnace so as to form a moving bed of furnace charge; and
   b) reducing said furnace charge with a H₂ containing gas at a temperature ranging from about 300° C. to about 500° C., said bed of furnace charge being moved gently so as to minimise formation of hard agglomerates and thereby obtaining a fine, low bulk density nickel powder.

2. The method according to claim 1, further comprising:
   c) collecting said fine, low bulk density nickel powder; and
   d) screening said fine, low bulk density nickel powder, thereby producing an essentially unagglomerated, low bulk density nickel powder.

3. The method according to claim 1, wherein said furnace is a rotating kiln operating with a peripheral velocity of less than about 25 cm per minute.

4. The method according to claim 1, employing a continuous production of said fine, low bulk density nickel powder.

5. The method according to claim 1, employing a batch-wise production of said fine, low bulk density nickel powder.

6. The method according to claim 1, wherein said hydrogen containing gas contains at least 20 volume percent hydrogen.

7. The method according to claim 1, wherein said hydrogen containing gas is in excess during the reduction step.

8. The method according to claim 1, wherein said reducible nickel salts are in form of a dry powder.

9. The method according to claim 1, wherein said reducible nickel salts are calcinated in nitrogen or another inert gas in either a first compartment of the furnace or in a separate furnace.

10. The method according to claim 1, wherein said hydrogen containing gas is preheated before the reduction step.

11. The method according to claim 9, wherein said calcination is made at a temperature ranging from about 300° to about 350° C.

**Illustration of nickel carbonate feed as used and of nickel powder as produced in this Example is provided in the electromicrographs of Figs. 5 and 6, respectively.**

**The bulk densities of nickel powders produced in the rotating kiln used in this example varied between 0.46 and 1.58 g/cc, as shown in Table 3 below.**
12. The method according to claim 10, wherein said preheating is made at a temperature ranging from about 300 to about 350°C.

13. The method according to claim 8, wherein said reducible nickel salts are calcined in nitrogen or another inert gas in either a first compartment of the furnace or in a separate furnace.

14. The method according to claim 8, wherein said hydrogen containing gas is preheated before the reduction step.

15. The method according to claim 9, wherein said hydrogen containing gas is preheated before the reduction step.

16. The method according to claim 13, wherein said calcination is made at a temperature ranging from about 300 to about 350°C.

17. The method according to claim 14, wherein said preheating is made at a temperature ranging from about 300 to about 350°C.

18. The method according to claim 1, wherein said reducible nickel salts include nickel carbonate.

19. The method according to claim 1, wherein said reducible nickel salt includes salts selected from the group consisting of nickel oxide, nickel hydroxide and nickel oxalate.

20. The method according to claim 1, wherein said reduction temperature ranges from about 350 to about 450°C.

21. The method according to claim 2, wherein said screening is performed onto a 100-mesh screen.

22. A method of producing a fine, low bulk density nickel powder, comprising:
   a) charging particles of at least one reducible nickel salt within a furnace so as to form a static, shallow bed of furnace charge;
   b) reducing said furnace charge with a H₂ containing gas at a temperature ranging from about 300°C to about 500°C, said static bed of furnace charge being shallow so as to allow penetration of reducing gas into the bed and minimise formation of hard agglomerates, thereby obtaining a fine, low bulk density nickel powder.

23. The method according to claim 22, further comprising:
   c) collecting said fine, low bulk density nickel powder;
   d) screening said fine, low bulk density nickel powder, thereby producing an essentially unagglomerated, low bulk density nickel powder.

24. The method according to claim 23, wherein said screening is performed onto a 100-mesh screen.

25. The method according to claim 22, wherein said hydrogen containing gas is in excess during the reduction step.

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