CARBONYL NICKEL POWDER AND PRODUCTION THEREOF

Filed July 2, 1971 3 Sheets-Sheet 1

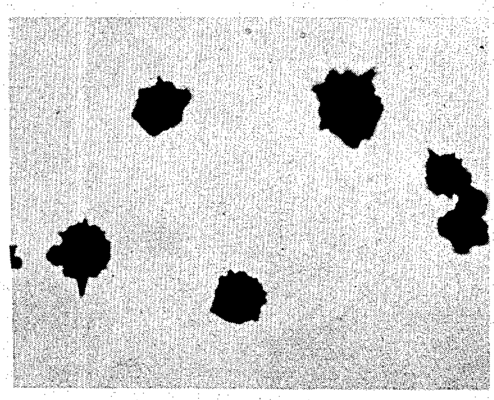

FIG.1

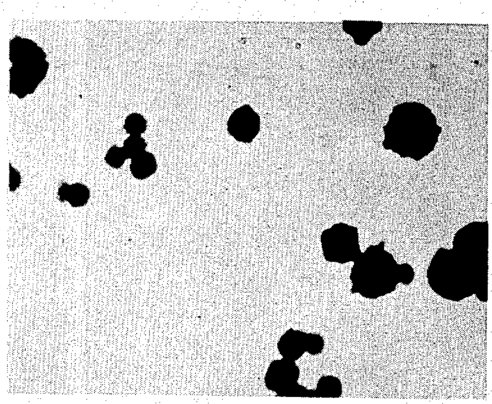

FIG.2

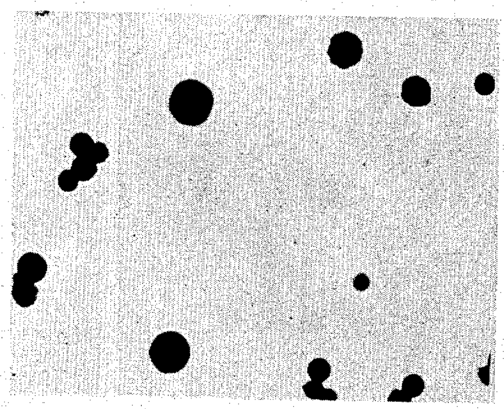

FIG. 3

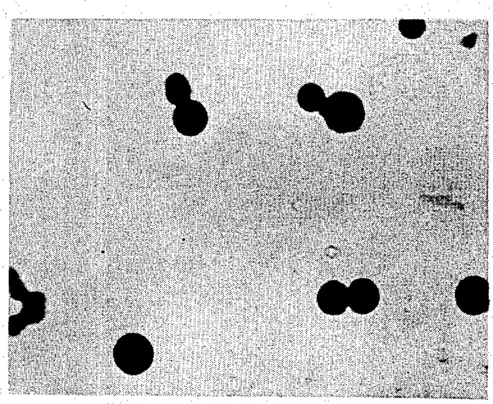

FIG. 4

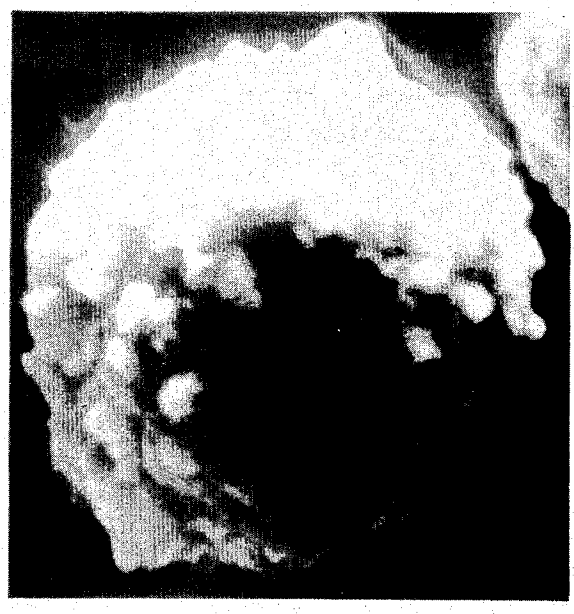

FIG. 5 PRIOR ART

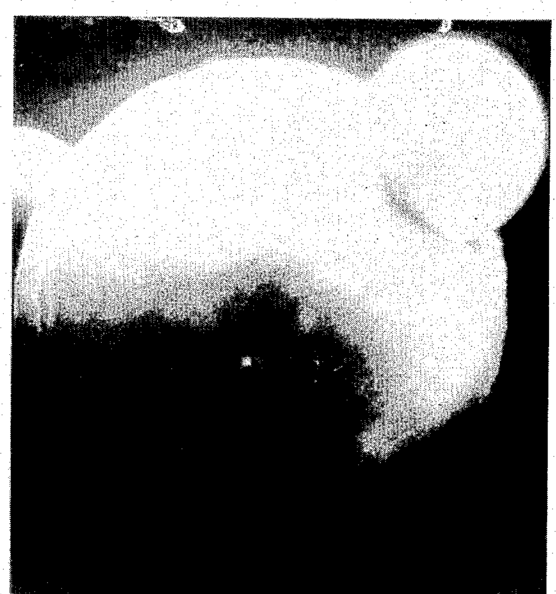

FIG. 6

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3,702,761

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CARBONYL NICKEL POWDER AND PRODUCTION THEREOF

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U.S. Cl. 75—.5 AA 8 Claims

ABSTRACT OF THE DISCLOSURE

Nickel carbonyl is thermally decomposed to nickel powder or pellets in the presence of nitric oxide, nitrogen trioxide or nitrogen peroxide in concentrations of 1–5000 p.p.m. or more. By suitable choice of gas concentrations and temperatures in the range 230–350° C. the powder can be produced with substantially spherical particles or with low carbon content or both.

The present invention relates to the production of metallic nickel and more particularly to the production of metallic nickel by the thermal decomposition of nickel carbonyl.

Nickel carbonyl has been decomposed in various ways. For example, nickel carbonyl is passed over nickel pellets heated above the decomposition temperature of the carbonyl to deposit nickel on the surface of the pellets so that they increase in size. Nickel carbonyl has also been decomposed in the hot free space of a decomposer to produce nickel powder having variously shaped particles according to the temperatures employed. Nickel carbonyl has also been decomposed on the surface of hot powder particles, which can be nickel or other materials, that are to be coated with nickel, in the form of a fludized bed or a suspension of powder in the stream of carbonyl-containing gas.

One of the problems encountered in decomposing nickel carbonyl is contamination of the metal product, particularly nickel powder, with carbon. The carbon is produced by the disproportionation of carbon monoxide, and the amount produced increases with increasing temperatures. In U.S. Patent No. 3,367,767, a process for decomposing nickel carbonyl in a steel reactor having nitrided walls and in the presence of controlled amounts of ammonia and oxygen to produce nickel powder with low carbon contents is disclosed. U.S. Patent No. 3,367,768 discloses a process for decomposing nickel carbonyl to spherical nickel powders by decomposing nickel carbonyl in the presence of controlled amounts of ammonia and oxygen to incorporate at least about 0.01% nitrogen in the powder to insure that the powder assumes a spherical shape. These processes work reasonably well, but in practice the off-gases, primarily carbon monoxide, must be treated to separate the ammonia and oxygen from the carbon monoxide. Although attempts have been made to avoid the foregoing problems, none, as far as I am aware was entirely successful when carried into practice commercially on an industrial scale.

It has now been discovered that nickel carbonyl can be decomposed to metallic nickel having low carbon contents at increased rates by adding special oxides of nitrogen to the decomposer. If added in sufficient quantities the special oxides of nitrogen are also effective in producing spherical nickel powder.

It is an object of the present invention to provide a process for thermally decomposing nickel carbonyl at increased rates.

Another object of the present invention is to thermally decompose nickel carbonyl to produce a metallic nickel product that contains minimum amounts of carbon.

The invention also contemplates providing a process for thermally decomposing nickel carbonyl to produce spherical nickel powder.

An even further object of the present invention is to provide spherical carbonyl nickel powder having smooth surfaces.

Other objects and advantages will become apparent from the following description taken in conjunction with the accompanying figures in which:

FIGS. 1 to 4 are representations of photomicrographs of carbonyl nickel powder having increasing nitrogen contents from FIG. 1 to FIG. 4 taken by transmitted light at a magnification of 1,000 times.

FIG. 5 is a scanning electron micrograph of prior art spherical carbonyl nickel powder at a magnification of 10,000 times, and

FIG. 6 is a scanning electron micrograph of spherical carbonyl nickel powder in accordance with the present invention at a magnification of 10,000 times.

Generally speaking, the present invention contemplates a process for thermally decomposing nickel carbonyl. A nickel carbonyl decomposing zone is established and is heated to a temperature high enough to decompose nickel carbonyl but below the temperature at which carbon formation will occur during the decomposition of nickel carbonyl. At least one nitrogen oxide selected from the group consisting of nitric oxide, nitrogen trioxide and nitrogen peroxide in small but effective amounts to increase the rate of nickel carbonyl decomposition and nickel carbonyl-containing gas are fed to the decomposing zone to decompose the nickel carbonyl to metallic nickel.

The present invention is based on the discovery that the rate of thermal decomposition of nickel carbonyl under otherwise similar conditions of temperature and carbonyl concentration is increased by the presence of at least one nitrogen oxide selected from the group consisting of nitric oxide (NO), nitrogen trioxide (N_2O_3) or nitrogen peroxide (NO_2), and according to the present invention nickel is produced by the thermal decomposition of nickel carbonyl in the presence of one of these gases.

The amount of the oxides of nitrogen employed can vary widely, and these gases have been found to be effective in concentrations ranging from 1 to 1,000 parts per million of the carbonyl-containing gases. Even higher concentrations can be used, but the presence of the oxide of nitrogen during the decomposition introduces nitrogen into the nickel produced, and as the concentration increases so does the nitrogen content of the product. Very high concentrations, e.g. up to 2,000 or 3,000 or even 5,000 p.p.m., can therefore only be employed when relatively high nitrogen contents in spherical powders can be tolerated.

It should be noted that all gaseous compositions or additions are given on a volumetric basis unless otherwise stated while solid compositions are given on a weight basis.

The use of nitrogen oxides will now be described in more detail in relation to the production of carbonyl nickel powder, that is to say powder made by the thermal decomposition of nickel carbonyl vapour in the hot free space of a decomposer.

When nitric oxide, nitrogen peroxide or nitrogen trioxide is used in place of ammonia or ammonia and oxygen as described in U.S. Pat. No. 3,367,767, it is found that powder consisting of discrete particles can be produced at an increased rate in a vessel of given size. The optimum conditions vary with the properties required in the powder, but broadly for the production of powder of given properties the temperature (and therefore the rate) of decomposition can be higher than when ammonia and oxygen are added, and, moreover, the concentration of oxide of nitrogen required is less than that of ammonia.

It is advantageous to use nitric oxide, which is more effective than the other two oxides. To achieve equivalent results greater amounts of nitrogen trioxide or nitrogen peroxide are required than when nitric oxide is employed.

The production of powder can be carried on in the temperature range of 230 to 350° C. Below 230° C. so small a proportion of the carbonyl is decomposed to powder that the process is not practicable on an industrial scale. Above 350° C. a high proportion of filamentary aggregates are formed. A very suitable temperature is 290° C.

The amount of oxide of nitrogen required varies with the temperature, decreasing as the temperature decreases. Considering nitric oxide, and assuming that low carbon content is required, some reduction in the carbon content is obtained with very small amounts of nitric oxide, that is to say, as little as 1 part per million, particularly if the vessel walls have previously been nitrided and the process is operated continuously. When a steel reactor is employed, the walls of the reactor can be initially nitrided by introducing ammonia into the reactor and heating the reactor to nitriding temperatures, e.g., 500° C., for at least one hour, e.g., 3 hours. It is found that as the concentration of nitric oxide increases, the carbon content falls and then rises again. Typically the nickel carbonyl is introduced into the decomposer, as a gas mixture of carbon monoxides containing 8% nickel carbonyl, and at this concentration and at 290° C. the concentration of nitric oxide should be from 50 p.p.m. to 200 p.p.m. Above 250 p.p.m. the carbon content of the powder can actually be higher than if no nitric oxide is added.

Converted into percentage of the carbonyl by volume, at 290° C. the nitric oxide should be from about 0.06% to about 0.25% of the carbonyl, whatever the concentration of the carbonyl.

In controlling the carbon content of the carbonyl nickel powder, at lower temperatures the nitrogen oxide concentration in the gaseous mixture is correspondingly lowered, being from 25 to 100 p.p.m., i.e. 0.03% to 0.12%, at 230° C., and at higher temperatures it is correspondingly increased, being from 100 to 300 p.p.m., i.e. 0.12% to 0.4% at 320° C.

When the object is to produce spherical powder, the concentration of nitric oxide at 290° C. should be at least 0.09% of that of the carbonyl. If the temperature is lower, this minimum can be correspondingly reduced, but at 230° C. should be at least 0.012%. Likewise at higher temperatures the minimum concentration of nitric oxide must be higher, being at least 0.2% at 320° C.

If low carbon content is not important, the concentration of nitric oxide can be considerably higher, but so far as the production of spherical powder is concerned there is no advantage in exceeding 1.25% or even 0.625% of the carbonyl concentration.

It is clear that the shape of the powder depends on the incorporation of nitrogen into the powder, but the mechanism by which this occurs is unclear. Whatever the mechanism is, nitrogen peroxide is less effective than nitric oxide, and nitrogen trioxide is still less effective. It is therefore necessary to use increased quantities of these gases in order to obtain results equivalent to those obtained with nitric oxide.

The way in which the process can be controlled to produce powders of different properties is shown by the results of a large number of tests. All these were carried out in an externally heated decomposer having a diameter of 10 inches and mild steel walls, which are nitrided as a result of use in numerous processes in which ammonia has been added. In all the tests carbon monoxide gas containing from 7% to 9% of nickel carbonyl was fed into the decomposer through an inlet at the top at a rate (unless otherwise stated) of 2,000 litres per hour. The oxide of nitrogen, when used, was injected into the gas stream at a measured rate at room temperature. The temperature at the inlet to the decomposer was maintained at about 50° C. by water cooling.

The particles obtained varied in shape as shown in the accompanying figures, and were classified as follows:

FIG. 1—spiky
FIG. 2—angular, the spikes becoming rounded
FIG. 3—nearly spherical
FIG. 4—spherical

Spherical powder made by the process of the invention has also been examined using the scanning electron microscope at a magnification of ×5000 and ×10000 and it is surprisingly found that the surface of these powders is smoother than powders made by the use of ammonia and oxygen which have a similar appearance under the optical microscope. The difference in surface characteristics of spherical carbonyl nickel powder produced by decomposing nickel carbonyl in the presence of ammonia and oxygen, as taught in U.S. Pat. No. 3,367,768, and in the presence of nitric oxide is shown in FIGS. 5 and 6. FIG. 6 dramatically confirms that spherical carbonyl nickel powder produced by decomposing nickel carbonyl in the presence of nitric oxide and containing at least about 0.01% nitrogen has smooth surfaces as compared with the rough surface of spherical carbonyl nickel powder produced by decomposing nickel carbonyl in the presence of ammonia and oxygen.

In the first set of tests the decomposer temperature was maintained at 290° C., nitric oxide was used and the concentration of the nitric oxide was varied. Table I below shows the concentration of the carbonyl by volume, the amount of nitric oxide introduced (in parts per million), the particle size of the powder as measured in the Fisher apparatus, the bulk density of the powder, the carbon and nitrogen contents of the powder and the particle shape. The first three tests, A, B and C, are given by way of comparison. Test A, which is in fact the test numbered 1 in U.S. Pat. No. 3,367,767, and Test B were carried out in the decomposer before its walls were nitrided. Test C was carried out at a time when the walls of the decomposer were nitrided.

TABLE I

Test	Carbonyl concn., percent	Nitric oxide, p.p.m.	Fisher value, microns	Bulk density, gms./cc.	Chemical characteristics, percent C	Chemical characteristics, percent N	Particle shape
A	9.0		4.47	2.47	.057	<.001	Spiky.
C	8.0		4.37	2.41	.029	<.001	Do.
B	7.0		3.66	1.99	.039	<.001	Do.
1	8.5	1,000	4.96	3.21	.069	.17	Spherical.
2	8.5	500	5.25	3.23	.056	.08	Do.
3	8.5	250	5.95	3.71	.023	.024	Do.
4	8.0	125	5.76	3.60	.022	.014	Do.
5	8.0	62	6.73	3.29	.017	.008	Nearly spherical.
6	8.0	31	6.74	3.03	.020	.005	Angular and irregular.

This table shows an optimum concentration of nitric oxide to be 62 p.p.m. at 290° C. and nickel carbonyl concentrations between 8% and 8.5% when powder of low carbon content is required. It also shows that, as when ammonia and oxygen are added, a minimum of 0.01% nitrogen is required in the powder to produce a spherical particle shape.

In the next series of tests a nitric oxide concentration of 62.5 p.p.m. was maintained and the decomposer temperature was varied, with the following results:

Table IV shows that the addition of nitric oxide always increases the particle size and bulk density, lowers the carbon content and introduces a small amount of nitrogen into the powder, and that, despite doubling the gas flow rate for tests 13 and 14, the powder characteristics were maintained, particularly the low carbon content.

Test D demonstrates how in the absence of nitric oxide bulk densities were low, and in fact the powder had some "B" Type characteristics.

TABLE II

Test	Decomposition temp., ° C.	Carbonyl concn., percent	Fisher value, microns	Bulk density, gms./cc.	Chemical characteristics, percent C	N	Powder shape
7	320	8.0	4.43	2.66	.032	.006	Angular.
5	290	8.0	6.73	3.29	.017	.008	Nearly spherical.
8	260	8.5	7.80	3.11	.018	.011	Spherical.
9	230	9.0	9.02	3.75	.014	.038	Do.

In the next series of tests the concentration of nitric oxide was increased to 125 p.p.m., and the decomposer temperature was again varied, with the following results:

Finally Table V shows comparative results obtained with the same oxides of nitrogen under identical conditions, namely a decomposer temperature of 260° C. and a concentration of the oxide of nitrogen that equalled 1.25% by volume of the carbonyl.

TABLE III

Test	Decomposition temp., ° C.	Carbonyl concn., percent	Fisher value, microns	Bulk density, gms./cc.	Chemical characteristics, percent C	N	Powder shape
10	320	9.0	4.56	2.86	.021	.008	Angular.
4	290	8.0	5.76	3.60	.022	.014	Spherical.
11	260	9.0	7.49	3.75	.014	.025	Do.
12	230	9.0	8.06	3.85	.018	.051	Do.

Tables II and III clearly indicate that the highest nitriding efficiency, leading to spherical particles and low carbon contents, is obtained at low decomposer temperatures. Further, the particle shape can be modified by varying the decomposer temperature while maintaining a constant addition of nitric oxide.

Test 7 shows that even at high decomposition temperatures, powders of low carbon content can be produced with the normal particle size and bulk density of Type A powder (discrete, angular particles). In contrast, with optimum ammonia and oxygen concentration (2,000 p.p.m. ammonia and 1,500 p.p.m. oxygen) under the same conditions of temperature, rate of gas flow and carbonyl concentration Type B powder (agglomerates of interlocking spiky filaments) containing 0.12% carbon was produced.

In all the tests (except A and B) the free carbon content of the powders was negligible. Even at high inlet concentrations nitric oxide was not detected in the outlet gas by chromatograph.

The advantage that the output can be increased by increasing the rate of gas flow is shown by two further tests, reported in Table IV below, in which Test 7 is reproduced by way of comparison and a further experiment (D) carried out in the nitrided decomposer but in the absence of nitric oxide is also reported

TABLE V

Test	Gas additive	Fisher value, microns	Bulk density, gms./cc.	Percent C	N
15	NO	7.92	4.22	.026	.12
16	N_3O_2	4.45	3.07	.036	.11
17	NO_2	3.38	2.43	.036	.08

Although the present invention has been described in conjunction with the production of nickel powder, it may also be used in the production of nickel pellets, for which the decomposition temperature will generally be less than 230° C., e.g. 180–220° C.

It is to be understood that other modifications and variations may also be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

I claim:

1. A process for decomposing nickel carbonyl to metallic nickel which comprises establishing a nickel carbonyl decomposing zone, heating the decomposing zone to a temperature high enough to decompose nickel carbonyl

TABLE IV

Test	Decomposition temp., ° C.	Gas flow, $M.^3$/hr.	Carbonyl concentration (percent)	Nitric oxide, p.p.m.	Fisher value, microns	Bulk density, gms./cc.	Percent C	N	Ni in outlet gas
D	320	2	8.5	----------	2.75	1.67	.048	<.001	Nil.
7	320	2	8.0	62	4.43	2.66	.032	.006	Nil.
13	320	3	8.5	62	3.8	2.26	.035	.006	Trace.
14	320	4	8.5	62	4.69	2.67	.027	.008	Do.

but below the temperature at which carbon formation will occur during the decomposition of nickel carbonyl, feeding to the decomposing zone a nitrogen oxide selected from the group consisting of nitric oxide, nitrogen trioxide, and nitrogen peroxide in small but effective amounts to increase the rate of nickel carbonyl decomposition and nickel carbonyl-containing gas, to decompose the nickel carbonyl to metallic nickel at an increased rate.

2. The process as described in claim 1 wherein the decomposing zone is the free space of a reactor and the free space is maintained at a temperature between about 230° C. and 350° C. to produce carbonyl nickel powder.

3. The process as described in claim 2 wherein the free space of the reactor is bounded by nitrided mild steel walls.

4. The process as described in claim 1 wherein the nitrogen oxide is nitric oxide.

5. The process as described in claim 1 wherein the concentration of nitrogen oxide in the carbonyl-containing gas is between about 1 part per million and 5,000 parts per million.

6. The process as described in claim 4 wherein the carbonyl-containing gas contains between about 50 parts per million and 200 parts per million nitrogen oxide to produce carbonyl nickel powder with low carbon contents.

7. The process as described in claim 4 wherein the nickel carbonyl is decomposed at a temperature between about 230° C. and 330° C. and the nitric oxide is present in amounts between about 25 parts per million and 100 parts per million at 230° C. and is correspondingly increased with temperature to 100 parts per million and 300 parts per million at 320° C. to produce carbonyl nickel powders with low carbon contents.

8. The process as described in claim 4 wherein the nitric oxide is added to the nickel carbonyl-containing gas in amounts equivalent to at least about 0.012% of the nickel carbonyl at 230° C. and increasing to at least about 0.2% of the nickel carbonyl at 320° C. to produce spherical carbonyl nickel powders with smooth surfaces.

References Cited

UNITED STATES PATENTS

2,844,456 7/1958 Llewelyn et al. ----- 75—.5 AA

WAYLAND W. STALLARD, Primary Examiner