Feb. 6, 1968 DE WITT H. WEST ET AL 3,367,768

NICKEL POWDER

Filed Aug. 16, 1965 2 Sheets-Sheet 1

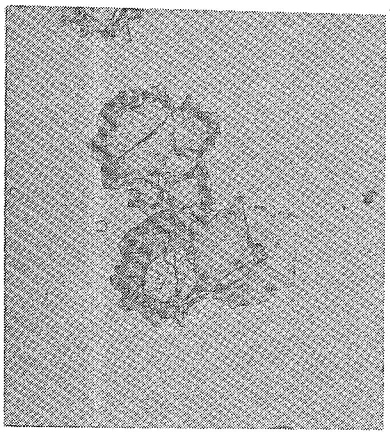

Fig.1.

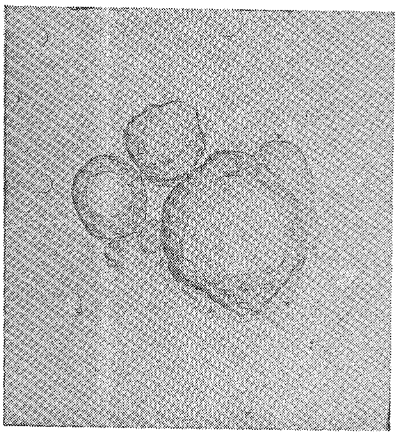

Fig.2.

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NICKEL POWDER

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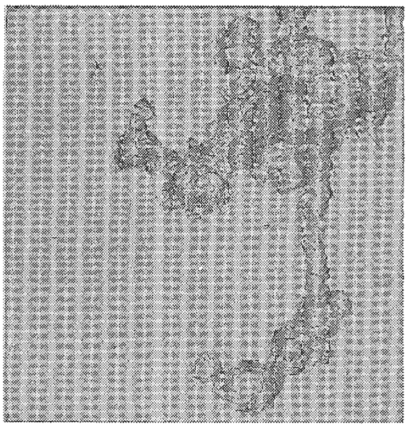

Fig. 3.

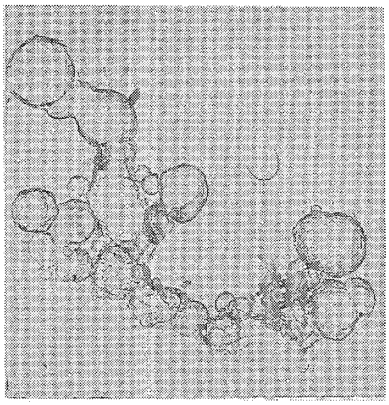

Fig. 4.

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NICKEL POWDER

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ABSTRACT OF THE DISCLOSURE

Nickel carbonyl is decomposed in the hot free space of a decomposer and small amounts of ammonia and oxygen are mixed with the nickel carbonyl to produce substantially spherical carbonyl nickel powder.

This invention relates to 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.

The production of carbonyl nickel powder in this way has been carried out on an industrial scale for many years, and it is well-established that according to the conditions of temperature, the concentration of carbonyl, and the presence or absence of diluent gases, e.g. carbon monoxide, the powder produced may assume one of two forms. These are the so-called "A" carbonyl nickel powder, which consists of discrete particles with an irregular spiky surface, and the so-called "B" powder, which consists of agglomerates of interlocking filaments or chains of interconnected (aggregated) particles which again are individually irregular. Type "B" powder has a low bulk density and has a microscopic appearance of small spongy flakes. The size of the aggregates of particles making up the chains can vary widely.

For many powder-metallurgical uses the irregularity of the powder particles is a disadvantage, since it impairs the flow properties of the powder, making it difficult to fill the angles of mould. It also leads to lack of uniformity in the size and distribution of the pores in sintered products. Nevertheless the high purity of carbonyl nickel powder renders it very desirable. Although attempts have been made to provide more satisfactory powders, none, so far as we are aware, was entirely successful when carried into practice commercially on an industrial scale.

It has now been discovered that by means of special control of the decomposition of nickel carbonyl in the hot free space of a decomposer, carbonyl nickel powder can be provided which exhibits an advantageous combination of physical characteristics.

It is an object of the present invention to provide a novel carbonyl nickel powder for use in powder metallurgy.

Another object of the invention is to provide a novel carbonyl nickel powder having a regular particle shape and high purity.

A further object of the invention is to provide a process of producing carbonyl nickel powder of regular particle shape by the thermal decomposition of nickel carbonyl.

Other objects and advantages will become apparent from the following description.

The present invention is based on the discovery that when the decomposition of nickel carbonyl to nickel powder is carried out in the presence of a source of active or nascent nitrogen, that is to say, nitrogen formed in situ in the decomposer, so as to introduce at least 0.01% by weight of nitrogen into the powder, a remarkable and wholly unexpected change occurs in the form of the individual particles of nickel produced, which become substantially spherical.

Thus under conditions of decomposition which would normally produce "A" type powder, the discrete particles produced in the presence of active nitrogen are no longer irregular and spiky, but are smooth and substantially spherical. A similar change in the shape of the individual nickel particles occurs when the decomposition conditions are such as to lead, in the absence of active nitrogen, to the production of normal type "B" powder. The product still consists of interlocking chains or filaments of particles, but when examined under very high magnification, for example by means of the electron microscope, these chains have the appearance of more or less branched linear aggregates of intergrown spheres.

So far as we are aware carbonyl nickel powder has not hitherto been produced in the form of spherical particles, and the invention includes as novel products both the discrete and aggregated forms of carbonyl nickel powder having substantially spherical particles.

The invention will now be described in more detail in conjunction with the accompanying drawings, which are electron micrographs of carbon replicas of typical prior art carbonyl nickel powders and of novel powders of the invention, and which illustrate the changes of form brought about by the introduction of nitrogen into the powder. In these drawings:

FIGURE 1 represents, at a magnification of ×4000, a cluster of separate particles of conventional type "A" powder;

FIGURE 2 represents, at the same magnification, a similar cluster of nitrogen-containing particles of type "A" nickel powder according to the invention;

FIGURE 3 represents, at a magnification of ×4500, part of a single aggregate of conventional type "B" powder particles; and

FIGURE 4 represents, at a magnification of ×6000, a similar type "B" aggregate from nitrogen-containing powder according to the invention.

The powders shown in FIGURES 1 and 3 each contained less than 0.01% nitrogen. The type "A" powder of the invention shown in FIGURE 2 contained 0.016% nitrogen and had a bulk density of 2.97 g./cc., and a Fisher value of 5.5 microns, while the type "B" powder of the invention shown in FIGURE 4 contained 0.08% nitrogen, had a bulk density of 0.69 g./cc. and had a Fisher value of 2.6 microns.

To ensure that the form of the powder particles is spherical it is necessary to introduce at least 0.01% by weight of nitrogen into the powder. Some modification of the normal irregular, spiky shape of the particles occurs with even lower introgen contents, and as the nitrogen content is increased the particles become progressively more rounded until at a nitrogen content of 0.01% they are substantially spherical. The nitrogen content may be as high as 0.2% or 0.3% or even higher, but increasing it above 0.01% does not materially change the shape of the individual particles.

The nitrogen contents in this specification refer to the powders in bulk.

Owing to the nature of the endothermic reaction taking place, the conditions in an externally-heated carbonyl decomposer are not uniform throughout the hot free space. Hence it will be appreciated that a nickel powder product of the present process which has spherical particles and in which the nitrogen content of the product as a whole is at least 0.01%, will generally contain individual particles or aggregates of particles having nitrogen contents higher or lower than the average. We find in particular that if the powder product is separated into a coarser aggregate fraction and a fine fraction, e g. by sieving on a 150 mesh BSS sieve, the nitrogen content of the coarse material is lower than that of the finer material and may even be below 0.01%. The particles forming the coarser aggregates are generally still of spherical form, and it is believed that they have adhered to the hot walls of the decomposer and have lost nitrogen owing to the resulting excessive heating.

The invention also includes the process of producing the novel nickel powder in which a mixture of ammonia and oxygen is employed as the source of active or nascent nitrogen during the decomposition. These gases are believed to react in the decomposer in the presence of the decomposing carbonyl and newly-formed nickel particles, according to the equation

$$4NH_3+3O_2=6H_2O+4N$$

If the nitrogen is to be active it is important that it should be formed in the decomposer. Thus the introduction of gaseous molecular nitrogen into the decomposer is quite ineffective, and it is also ineffective to introduce ammonia alone. When using ammonia and oxygen, the oxygen may be introduced in any convenient form, e.g. as air.

The operating conditions under which "A" and "B" type nickel powders are obtained in a carbonyl decomposer are now well understood. In general, conditions in which the rate of nucleation is high lead to the formation of type "B" powder, while a low rate of nucleation leads to the formation of "A" type powder. A high rate of nucleation is favoured by high temperature, high carbonyl concentration and high throughput, while a low nucleation rate is favoured by low temperature, low carbonyl concentration and low throughput. These same considerations apply when the decomposition is carried out in the presence of ammonia and oxygen, and broadly speaking the process may be carried out using decomposer temperatures in the range of about 230° C. to about 350° C. For type "A" powder the temperature should be less than about 300° C. or 310° C. and for type "B" powder it should be above this temperature.

The nitrogen content of the powder increases as the concentration of ammonia in the decomposer increases. Generally speaking at least 0.2% by volume is needed to introduce 0.01% nitrogen into the powder and preferably the ammonia concentration is at least 0.3%. Powder having spherical particles is formed at ammonia concentrations as high as 1% or even higher, but the use of such high concentrations is wasteful. The oxygen concentration is preferably at least 0.15% by volume. The ratio of ammonia to oxygen may be varied within wide limits, but is preferably from 3:4 to 4:1 by volume. The greatest nitriding efficiency, and hence the greatest economy of expensive ammonia, is obtained with an ammonia: oxygen ratio of 4:3 by volume. High concentrations of ammonia and oxygen, above about 0.5% of each, should also be avoided if it is desired to produce powder of low carbon content, since the water vapour formed by the reaction of ammonia and oxygen in the decomposer favours the carburization of the powders. For this reason the gases fed to the decomposer should not contain more than traces of water vapour if low-carbon powder is required.

Numerous tests have been carried out to show the effect of changes in the process variables on the properties of the powder produced, and the results of these are set out in Tables I to IV below. In these tests carbon monoxide gas containing 7% by volume of nickel carbonyl (175 grams nickel per cubic metre) was fed into an externally heated 10 inch diameter decomposer having mild steel walls at the rate of 2000 litres per hour through an inlet at the top. Dry ammonia gas and oxygen were injected into the inlet gas stream in the amounts indicated in the tables. The temperature was measured at a point halfway between the wall and the axis and one-quarter of the distance down from the top.

The results in Table I show the effect of varying the proportion of the combined addition of ammonia and oxygen to carbonyl at an ammonia:oxygen ratio of 4:3 by volume, using a decomposer temperature of 290° C. All the powders produced were of "A" type. The nitrogen content of the powders decreased as the proportion of the ammonia-oxygen mixture was decreased. The four powders, Nos. 1–4, with the highest nitrogen contents, all consisted of smooth spherical particles in accordance with the invention. The other three powders all had nitrogen contents below the critical minimum of 0.01%. The particles of Powder No. 5, with 0.009% nitrogen had a rough surface, those of No. 6 with 0.002% nitrogen were irregular but less spiky than ordinary "A" powder, and No. 7 made in the absence of ammonia and oxygen, was a typically irregular and spiky "A" powder.

TABLE I

Expt. No.	Flow in litres per hour		Concentration, percent by volume		Properties of powder product			
					Fisher value, microns	Bulk Density, gms./cc.	Chemical Composition	
	NH_3	O_2	NH_3	O_2			Percent C	Percent N
1	20	15	1	0.75	4.10	2.12	.075	.13
2	16	12	0.8	0.6	4.56	2.21	.047	.14
3	12	9	0.6	0.45	5.10	2.8	.034	.065
4	8	6	0.4	0.3	5.28	3.09	.029	.035
5	4	3	0.2	0.15	5.20	2.87	.033	.009
6	1.6	1.2	0.08	0.06	4.36	2.39	.035	.002
7	----------	----------	----------	----------	3.66	1.99	.039	<.001

Increasing the decomposer temperature leads to the formation of "B" type powder. This is shown in Table II for flow rates of ammonia and oxygen of 4 and 3 litres/hour respectively, and in Table III for twice these rates (8 l./hr. NH_3 and 6 l./hr. oxygen). In each case there is a sharp transition from "A" to "B" type powder between 290° C. and 320° C. The nitrogen contents of the powders in Table II were too low to be in accordance with the invention, and the particles irregular, though not spiky, but the powders in Table III all had smooth, spherical particles, and were in accordance with the invention.

TABLE II

Expt. No.	Decomposer Temp., ° C	Properties of powder product				
		Fisher value, microns	Bulk Density, grams/cc.	Chemical Composition		
				Type	Percent C	Percent N_2
8	320	2.35	0.65	“B”	.12	.007
5	290	5.20	2.87	“A”	.033	.009
9	260	5.70	2.81	“A”	.031	.005
10	230	6.04	2.19	“A”	.050	.006

TABLE III

Expt. No.	Decomposer Temp., ° C	Properties of powder product				
		Fisher value, microns	Bulk Density, grams/cc.	Chemical Composition		
				Type	Percent C	Pereent N_2
11	320	1.55	0.31	“B”	.072	.02
4	290	5.28	3.09	“A”	.029	.035
12	260	6.12	3.26	“A	.031	.06
13	230	6.22	3.29	“A”	.028	.026

The results in Table IV illustrate the effects of varying the ratio of ammonia to oxygen at a constant temperature of 290° C.

TABLE IV

Expt. No.	Flow rate l.p.h.		Ratio $NH_3:O_2$	Properties of powder product			
	NH_3	O_2		Fisher value, microns	Bulk Density, grms./cc.	Chemical Composition	
						Percent C	Percent N_2
14	0	2	0	3.02	1.19	0.062	<0.001
15	8	12	2:3	4.22	2.51	.033	.031
4	8	6	4:3	5.28	3.09	.029	.035
16	24	6	4:1	4.04	2.29	.032	.026
17	36	6	6:1	4.26	2.60	.027	.032
18	48	6	8:1	3.59	2.09	.033	.031
19	8	0	0	4.2	2.42	.035	.002

In this series of experiments, Nos. 14 and 19 both yielded ordinary irregular, spiky Type ‘A” powder, substantially free from nitrogen, showing that additions of either ammonia or oxygen alone are ineffective. The other powders were all spherical “A” powders according to the invention, showing that the ammonia:oxygen ratio can be varied within wide limits.

Provided they are made with the use of only such small amounts of ammonia and oxygen that no significant amount of water vapour is formed, the powders of the invention have lower contents of combined carbon than nickel powder made under the same conditions in the absence of ammonia which usually contain from 0.05 to 0.08% carbon. Carbonyl nickel powder is also commonly contaminated with a very small proportion, generally less than 0.01% by weight, of particles of very high carbon content, which are highly undesirable and have to be removed, e.g. by sieving. The formation of such carbonaceous particles may be avoided in the present process by carrying out the decomposition in a decomposer of which the steel internal surfaces have been nitrided, e.g. by heating them in contact with ammonia gas at 500° C. for 3 hours. Operating the decomposer for the production of nickel powder with the addition of ammonia also results in the internal surfaces becoming nitrided, and all the tests reported in Tables I and IV were performed in a decomposer which had previously been nitrided in this way.

The use of a decomposer that has been conditioned as just described for the production of non-spherical nickel powder is the subject of a separate application.

Besides the spherical form of their particles and their nitrogen content of at least 0.01%, the novel carbonyl powders of the invention are characterized by very high purity, in particular very low contents of sulphur and of cobalt. Thus both the type “A” powder shown in FIGURE 2 of the drawings and the type “B” powder shown in FIGURE 4 contained less than 0.0002% sulphur and less than 0.002% colbalt. In general the powders of the invention contain less than 0.0007% sulphur and less than 0.002% cobalt.

The spherical powders of the invention, both of type “A” and of type “B”, are particularly useful for powder-metallurgical purposes, since they have improved sintering properties compared with ordinary nickel powders of the same type. For example, spherical type “A” powder is found to sinter more readily to give bodies which have a very narrow range of pore sizes and are of interest for making electrodes for fuel cells and filters. Thus a spherical powder made as described with reference to the tables above using a temperature of 290° C., 20 litres/hour of ammonia and 4 litres/hour of oxygen, and having a Fisher size of 5.5 microns, a bulk density of 2.96 grams/cc., and containing 0.03% carbon and 0.015 nitrogen, was sintered in a loose layer 0.187 inch thick at 1100° C. for 15 minutes. The resulting sintered plate had a porosity of 28%, compared with 51% for an ordinary type “A” powder.

Spherical type “B” powder is particularly useful for making battery electrodes and other shaped centered bodies, since it has better flow properties than ordinary type “B” powder.

Nitrogen may readily be removed from the spherical powder of the invention by heating it at a moderate temperature, e.g. 250° C., and substantially nitrogen-free spherical powder of either type “A” or type “B” may be produced in this way.

As an example of the way the nitrogen content of individual particles of spherical nickel powder may vary, a powder having an average nitrogen content of 0.013% and containing 0.022% carbon was made by the process of the invention using a decomposer temperature of 240° C. and an ammonia:oxygen ratio of 4:3. The product was divided into fine and coarse fractions by sieving on a 150-mesh sieve, and a small proportion (less than 1%)

of very coarse material that was retained on a 30-mesh sieve was discarded. The fine fraction, which amounted to 70% of the whole, had a bulk density of 3.42 g./cc. and contained 0.016% nitrogen and 0.022% carbon, while the coarse fraction (about 30% of the whole) had a bulk density of 1.87 g./cc. and contained only 0.005% nitrogen and 0.022% carbon.

The nickel particles in both fractions were spherical. In the course fraction, the particles were highly-aggregated into dense clusters and had very good flow properties. This material is particularly useful for powder-metallurgical purposes, since its carbon content is no higher than the average for the whole of the powder, whereas the coarse fraction separated from ordinary nickel powder has an undesirably high carbon content.

It will be understood that the proportions of relatively fine and coarse material will vary according to the decomposition conditions. The low temperature used in the present example led to the formation of an unusually large proportion of coarse powder.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may 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.

We claim:

1. Carbonyl nickel powder having substantially spherical particles and containing at least 0.01% nitrogen.

2. Carbonyl nickel powder according to claim **1** in the form of discrete, substantially spherical particles containing at least 0.01% nitrogen.

3. Carbonyl nickel powder according to claim **1** in the form of chains of intergrown substantially spherical particles containing at least 0.01% nitrogen.

4. A process of producing nickel powder having substantially spherical particles by the decomposition of nickel carbonyl vapour in the hot free space of a decomposer, comprising introducing nickel carbonyl into the hot free space of a decomposer and mixing the nickel carbonyl with ammonia and oxygen, said ammonia and oxygen being added in small but effective amounts to introduce at least about 0.01% nitrogen into the powder formed.

5. A process according to claim **4**, characterised in that the ratio of ammonia to oxygen is from 3:4 to 4:1 by volume.

6. A process according to claim **4**, characterised in that the ratio of ammonia to oxygen is 4:3 by volume.

7. A process according to claim **4**, carried out in a decomposer of which the steel inner surfaces have been nitrided.

8. A process according to claim **4** in which the powder is divided into fractions and a coarse fraction of low nitrogen content is recovered.

9. A process according to claim **4** in which the powder is heated to expel nitrogen.

10. A process according to claim **5** wherein the concentration of ammonia in the decomposer is at least about 0.2% by volume.

11. A process according to claim **5** wherein the concentration of ammonia in the decomposer is at least about 0.3% by volume.

12. A process for producing substantially spherical nickel powder by the decomposition of nickel carbonyl vapor in the hot free space of a decomposer which comprises introducing nickel carbonyl into the hot free space of the decomposer and mixing the nickel carbonyl with ammonia and oxygen, said ammonia and oxygen being added in small but effective amounts to form spherical nickel carbonyl powder.

13. A process according to claim **12** wherein the ratio of ammonia to oxygen is from about 3:4 to 4:1 by volume.

14. A process according to claim **12** carried out in a decomposer of which the steel inner surfaces have been nitrided.

15. A process according to claim **13** wherein the concentration of ammonia in the decomposer is at least about 0.2% by volume.

16. A process according to claim **13** wherein the concentration of ammonia in the decomposer is at least about 0.3% by volume.

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