United States Patent Office 3,694,187 Patented Sept. 26, 1972

3,694,187

PRODUCTION OF CARBONYL IRON

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No Drawing. Filed July 2, 1971, Ser. No. 159,472
Claims priority, application United Kingdom, July 7, 1970, 32,962/70
Int. Cl. B22f 9/00
U.S. Cl. 75—.5 AA 12 Claims

ABSTRACT OF THE DISCLOSURE

Thermal decomposition of iron carbonyl vapour to carbonyl iron powder is catalysed by carrying out the decomposition in the presence of nitric oxide (NO), nitrogen trioxide (N_2O_3) or nitrogen peroxide (NO_2). The presence of these gases also enables the carbon content of powder of a given particle size to be reduced.

The present invention relates to the production of metal powder, and more particularly to the production of metallic iron by the thermal decomposition of iron carbonyl vapour.

Vaporous iron carbonyl ($Fe(CO)_5$) has been thermally decomposed to metallic iron in various ways. Thus, decomposition of iron carbonyl in the hot free space of a decomposer leads to the formation of iron powder having variously shaped particles according to the conditions used. Another process is to decompose the carbonyl on the surface of hot solid particles, which can be of iron powder or of other materials that are to be coated with iron, in the form of a fluidized bed or a suspension of powder in a carbonyl containing gas.

In the production of carbonyl iron powder by the thermal decomposition of iron carbonyl vapour in the hot free space of a decomposer, carbonyl iron powder in the form of discrete particles is formed at relatively low temperatures, e.g., from 230° C. up to 280° C., but at higher decomposition temperatures carbonyl iron powder takes the form of filamentary aggregates of low bulk density, similar to the so-called "B" type carbonyl nickel powder.

The carbon content of carbonyl iron powder increases with increasing decomposition temperatures. Thus, if either a filamentary type carbonyl-iron powder or carbonyl iron powder of discrete particles having a specific size with low carbon contents is required, the powder must be decarburized. Likewise, if the size of carbonyl iron powder particles is not critical but high production rates and low carbon contents are required, either low production rates or subsequent decarburization must be resorted to.

It has now been discovered that carbonyl iron with low carbon contents can be produced at high throughput rates by thermally decomposing iron carbonyl vapour in the presence of special oxides of nitrogen.

It is an object of the present invention to decompose iron carbonyl vapour at high production rates.

Another object of the present invention to decompose iron carbonyl iron powder with low carbon contents.

Yet another object of the present invention is the production of carbonyl iron powder at high throughput rates.

An even further object of the present invention is to produce carbonyl iron powder with low carbon contents at high production rates.

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

Generally speaking the present invention contemplates thermally decomposing iron carbonyl in an iron-carbonyl-containing gas in the presence of at least one nitrogen oxide selected from the group consisting of nitric oxide (NO), nitrogen trioxide (N_2O_3) and nitrogen peroxide, the nitrogen oxide being present in small but effective amounts to increase the rate of the thermal decomposition of iron carbonyl.

In the production of carbonyl iron powder by the thermal decomposition of iron carbonyl vapour in the hot free space of a decomposer, the effect of the nitrogen oxide is shown by the reduction of the particle size (and, in most instances, a reduction of the carbon content) of the powder formed under given conditions of temperature and carbonyl concentration. At relatively low temperatures, e.g., from about 230° C. up to about 280° C., the powder is in the form of discrete particles, but at higher temperatures the product takes the form of filamentary aggregates of low bulk density, similar to the so-called "B" type nickel powder.

The process in accordance with the present invention can be carried on in the temperature range of about 230° C. to 290° C. Below about 230° C. so small a proportion of the carbonyl is decomposed to powder that the process is not practicable on an industrial scale. Above about 290° C. a high proportion of filamentary aggregates are formed. Advantageously, the process is conducted at temperatures above about 240° C. because the effects of the nitric oxide in increasing the production rate become more pronounced at temperatures above about 240° C.

The amount of the nitrogen oxide employed can vary within wide limits. However, in most instances, it is advantageous to employ only that amount or concentration that is effective in producing the required effect. Concentrations of nitric oxide as low as about 0.1% are effective in increasing the rate of iron carbonyl decomposition. Nitric oxide concentration as high as about 10% or higher can be employed if high nitrogen contents in the carbonyl iron powder can be tolerated. It should be noted that all gaseous compositions given herein are given on a volumetric basis while solid compositions are given on a weight basis.

The effects of nitric oxide in increasing production rates and in controlling the carbon content of carbonyl iron powder are illustrated by the results of tests carried out in a laboratory decomposer 10 inches in diameter, having mild-steel walls that are externally heated in use. In all the tests iron carbonyl vapour diluted with carbon monoxide to give a carbonyl concentration of 60% by volume was introduced through an inlet at the top at a rate of 250 litres/hour of the gas mixture (i.e., 150 litres/hour of carbonyl vapour). The nitric oxide, when used, was injected into the gas stream at a measured rate at room temperature. The temperature of the inlet to the decomposer was maintained at about 110° C. by air-cooling, and the temperature within the decomposer was measured mid-way between the axis and the wall and heating was carried out so as to maintain this temperature uniform in the region from 1 foot to 3 feet below the top of the decomposer.

In the test decomposer temperatures of 260° C., 290° C. and 310° C. were used and the concentration of the nitric oxide was varied. Table I below shows the decomposer temperature, the concentration of the nitric oxide by volume, the particle size of the powder as measured in the Fisher sub-sieve sizer, the tapped density of the powder, and the carbon and nitrogen contents of the powder. Tests A, B and C are given by way of comparison.

TABLE I

Test No.	Temp. (° C.)	NO concentration (percent)	Fisher size (microns)	Tapped density (g./cc.)	Composition C (percent)	Composition N (percent)
A	260	----------	8.1	4.3	0.62	<0.005
B	290	----------	4.92	3.92	0.91	<0.005
C	310	----------	3.9	3.3	1.03	<0.005
1	260	0.1	4.69	4.07	0.93	0.08
2	260	1.0	4.04	3.73	0.72	0.43
3	260	5.0	4.10	3.60	0.58	0.59
4	260	10.0	3.65	2.97	0.50	0.93
5	290	0.1	2.76	1.3	0.90	0.01

TABLE III

Powder	Fisher size (microns)	Tapped density (g./cc.)	Composition C (percent)	Composition N (percent)	Q value 20 mHz	Q value 50 mHz	Perm.
Grade ME	4.33	4.41	0.76	0.56	169	152	12.2
Test 2	3.98	4.16	0.72	0.43	166	163	12.1
Test 3	4.05	4.33	0.58	0.59	164	175	10.9

It is seen by comparison of Tests 1 to 4 with Test A that the introduction of even 0.1% of nitric oxide brings about a very marked reduction in the particle size, which continues as the nitric oxide concentration is increased up to 10%. At the same time the nitrogen content of the powder also progressively increases.

As the nitric oxide concentration is increased the carbon content of the powder at first increases and then decreases again. However in order to obtain powder of a particle size of about 5 microns without the addition of nitric oxide it is necessary to increase the temperature to about 290° C. The results of Test B show that at this temperature the product made without nitric oxide had a carbon content of 0.91%, while Test C shows that at 310° C. the carbon content of the product was increased to 1.03%. Thus, the addition of at least about 0.2%, and preferably at least about 0.5% or about 1%, of nitric oxide gives a powder having a substantially lower carbon content for a given particle size.

In Test 5 the decomposer temperature was increased to 290° C. and 0.1 NO was added. This led to the production of filamentary aggregate powder of low density, the bulk density being only 0.75 g./cc. Further increasing the temperature to 310° C. with 0.1% NO gave an extremely light and voluminous "cotton-wool" type powder.

The presence of nitric oxide during the formation of iron powder is also found to improve the electromagnetic properties of the powder in both the unmilled and the milled condition.

Table II gives the Q values at two frequencies and the magnetic permeability of the productions of Tests A, B and 1 to 4 both before and after milling for 2 hours in a laboratory end-runner mill. It will be seen that with only 0.1% NO the properties after milling are substantially improved over those of the Test A powder and in the unmilled state over those of the Test B powder, and this improvement becomes greater with higher NO concentration.

TABLE II

Test No.	Temp. (° C.)	No. concentration (percent)	Unmilled powder Q value 20 mHz.	Unmilled powder Q value 50 mHz.	Unmilled powder Perm.	Milled powder Q value 20 mHz.	Milled powder Q value 50 mHz.	Milled powder Perm.
A	260	----------	133	150	10.9	138	141	9.7
B	290	----------	<130	<130	11.0	----------	----------	----------
1	260	0.1	137	144	11.8	167	152	11.3
2	260	1.0	164	158	12.2	166	163	12.1
3	260	5.0	152	157	12.0	164	175	10.9
4	260	10.0	169	169	11.6	171	176	10.6

For purposes of comparison the properties of a standard commercial iron powder (grade ME) are compared in Table III with those of the powder produced in Test 2. This commercial powder is normally supplied in the milled condition.

It will be seen that at 20 megahertz (mHz.) the properties of the powders in this condition are substantially the same, while at 50 mHz. somewhat better properties can be obtained by the use of nitric oxide. An important advantage of the powder made with nitric oxide is that is has a substantially lower temperature coefficient of permeability than the ME powder, the coefficient for Test 3 powder after milling being only $+43\times10^{-6}/°$ C. compared with $+193\times10^{-6}/°$ C. for the Grade ME powder. The low value of the coefficient for the Test 3 powder may be due to the low decomposition temperature that was required in its production.

To determine the effect of nitric oxide under other decomposition conditions, tests were carried out in which a mixture of iorn carbonyl vapour and carbon monoxide, with and without the addition of nitric oxide, was blown into the bottom of a bed of iron powder in a fluidized bed decomposer so as to fluidize the bed. The decomposer consisted of a steel vessel 3 inches in diameter, externally heated by means of electrical heating coils, and the gas mixture was introduced at a rate of 3.5 cubic metres per hour at a temperature of 160° C. The initial weight of the bed was 2.5 kg., and it was heated by means of the heating coils to 290° C., 250° C. and 230° C. in three series of tests. The iron carbonyl in the inlet gases was decomposed both on the existing particles of iron powder and with the formation of new particles, with the result that the weight of the bed progressively increased. In each of the tests the concentration of iron carbonyl in the inlet gases was adjusted to give the maximum rate of decomposition at which the carbonyl was completely decomposed. The results are set forth in Table IV which shows the temperature of the bed, the concentration of nitric acid, the maximum rate of decomposition, expressed as kg. of iron deposited per hour, and the carbon content of the iron deposited. The carbonyl concentrations used were within the range 5 to 30% by volume.

TABLE IV

Bed temp. (° C.)	NO concentration (percent)	Max. rate of Fe deposition (kg./hr.)	C (percent)
290		1.63	1.12
290	0.3	[1] 2.02	1.07
250		0.594	1.74
250	0.3	0.926	0.74
230		0.33	2.5
230	0.3	0.327	1.15

[1] Rate of deposition restricted by maximum heat input.

These results show that at temperatures above 240° C. the addition of nitric oxide substantially increases the rate of decomposition of iron carbonyl to iron, and that at all the test temperatures used the carbon content of the deposited iron is lowered by the addition of nitric oxide.

It will be noted that although all the tests employed nitric oxide, similar results are obtained when nitrogen trioxide or nitrogen peroxide are used.

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.

I claim:

1. An improved process for decomposing iron carbonyl to produce metallic iron which comprises thermally decomposing iron carbonyl contained in an iron-carbonyl-containing gas in the presence of at least one nitrogen oxide selected from the group consisting of nitric oxide, nitrogen trioxide and nitrogen peroxide, the nitrogen oxide being present in small but effective amounts to increase the rate of iron carbonyl decomposition to metallic iron.

2. The improved process as described in claim 1 wherein iron carbonyl is decomposed at a temperature of at least about 230° C.

3. The improved process as described in claim 1 wherein the iron carbonyl is decomposed at a temperature between about 230° C. and 310° C.

4. The improved process as described in claim 3 wherein iron carbonyl is decomposed at a temperature of at least about 240° C.

5. The improved process as described in claim 4 wherein iron carbonyl is decomposed at a temperature below 290° C.

6. The improved process as described in claim 4 wherein the nitrogen oxide is added to the iron-carbonyl-containing gas in an amount of at least about 0.1%.

7. The improved process as described in claim 4 wherein the nitrogen oxide is added to the iron-carbonyl-containing gas in an amount of at least about 0.2% to provide carbonyl iron wtih lowered carbon contents.

8. The improved process as described in claim 4 wherein the nitrogen oxide is added to the iron-carbonyl-containing gas in an amount of at least about 0.5% to provide carbonyl iron with lowered carbon contents.

9. The improved process as described in claim 4 wherein the nitrogen oxide is added to the iron-carbonyl-containing gas in an amount of at least about 1.0% to provide carbonyl iron with lowered carbon contents.

10. The improved process as described in claim 4 wherein nitric oxide is added to the iron-carbonyl-containing gas in amounts between about 0.1% and 10%.

11. The improved process as described in claim 10 wherein the iron carbonyl is decomposed in the hot free space of a reactor.

12. The improved process as described in claim 2 wherein the iron-carbonyl-containing gas is fed to a fluidized bed of heated particles and nitric oxide is added to the iron-carbonyl-containing gas in amounts between about 0.1% and 10% to increase the rate of metallic iron deposition on the heated particles by decomposition of iron carbonyl.

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