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Description

The present invention relates to the production of cobalt metal powder by hydrogen reduction from a cobalt containing solution.

Hydrogen-reduced elemental cobalt powder is an article of commerce. One presently available product of this type is known to be produced by hydogen reduction of aqueous cobalt ammine ammonium sulphate solutions using a catalyst, for example sodium sulphite-sodium cyanide. The nucleation of cobalt powder in this system is irregular, resulting in production of powder having an apparent density of 0.6 to 1 grams/cubic centimeter (g/cc). In order to provide a denser commercial product, repeated densification cycles are employed which deposit further cobalt upon the initially formed powder from fresh cobalt-containing solution. In this manner the particle size is increased such that possibly about 60% of the product will have a particle size greater than 200 mesh (0.075 mm) on a Tyler screen scale, and the apparent density of the product increases to approximately 3.2 g/cc. The cobalt bite per reduction cycle is of the order of about 40 g/l. About 30% of the cobalt metal produced is recycled and redissolved in a step in which cobaltic ions are reduced to cobaltous ions in a feed cobaltic ammine ammonium sulphate solution in order to obtain the starting solution for the hydrogen reduction stage. The average hydrogen reduction cycle is reported to require about 30 minutes. The final cobalt powder particles have an irregular shape with a rough pebbly surface. In many instances the powder is dark grey to black in colour. The cobalt powder produced must be handled carefully and exposure to air should be avoided until the powder product is cool. Drying of the washed cobalt powder is usually conducted in an atmosphere of hydrogen or nitrogen.

The prior art in this field is exemplified by the nickel preferential reduction scheme which is set forth in a paper by Schaufelberger and Roy entitled "Separation of Copper, Nickel and Cobalt by Selective Reductions from Aqueous Solution", *Transactions of the Institute of Mining and Metallurgy*, London, Vol. 64, 1954—1955, pages 375—393 and in U.S. Patents 2,694,005 and 2,694,006. A scheme involving soluble cobaltic ammine is disclosed in U.S. Patents 2,767,055 and 2,767,054. US—A—2749235 discloses a process wherein hydrogen reduction is carried out in acidic conditions with addition of ammonia. Another hydrogen reduction process wherein a leach solution is made alkaline with ammonia, is described in a paper by Mitchell entitled "Cobalt Pressure Leaching and Reduction at Garfield", which appeared in *Journal of Metals*, March 1957 on pages 343—345. Direct gaseous reduction of cobaltous oxide or hydroxide aqueous slurries to cobalt metal has been reported in the literature, for example, Schaufelberger U.S. Patent 2,805,149 and papers by R. Soubirous et al which appeared in *C. R. Acid. Sc.*, Paris, t. 270, pages 1595—1597 and by Dobrokhotov et al which appeared in *Cvetn. Metally*, 35, 1962, page 44. In many of the processes the starting material is cobaltic hydroxide which must be converted to the cobaltous form. The dissolution of cobaltic hydroxide with an organic reductant such as methanol has been disclosed in U.S. Patent 4,151,258 and in an article by L. Syper entitled "Oxidation of Some Organic Compounds by Cobalt (III) Hydroxide", *Roczniki Chemii*, Vol. 47, No. 1, pages 43—48, (1973). The use of nucleating agents in hydrogen reduction processes is disclosed in U.S. Patents Nos. 2,767,081, 2,767,082 and 2,767,083.

It would be desirable to produce a cobalt powder having a higher apparent density than the product presently available and the present invention is based on the appreciation that such cobalt powder can be obtained by reducing a cobalt solution with hydrogen under certain conditions. Thus, according to the present invention there is provided a process of making dense cobalt powder of coarse, relatively uniform particle size which comprises subjecting a portion of a cobaltous sulphate solution to hydrogen reduction at a hydrogen partial pressure of at least one megapascal and a temperature of at least 180°C in the presence of seed cobalt powder in the form of fine, discrete particles while maintaining the pH of the solution not greater than 4 by introducing a solution of an alkali metal hydroxide at a rate not substantially exceeding the molar equivalent of the rate of sulphuric acid production due to hydrogen reduction, continuing the hydrogen reduction to reduce a substantial part of the cobalt content of said portion to produce an end reduction solution and cobalt powder, and repeating said hydrogen reduction cyclically with fresh successive portions of cobaltous sulphate solution with each successive reduction being performed in the presence of the cobalt powder formed in the previous cycle to provide a densified cobalt powder product.

The cobalt sulphate solution should generally contain between about 50 and 100 grams per litre of cobalt and the hydrogen reduction is preferably stopped when about 80 to 95% of the cobalt has been reduced. The cobalt bite per reduction cycle can be as high as 90 grams/litre.

By means of the invention a product can be obtained consisting of coarse cobalt particles having smooth surfaces and having a density in the range of about 4.5 to 5.5 grams/cc. At this density, the cobalt powder is found to be densified such that 98% or more of the particles exceed 200 mesh (0.075 mm) Tyler screen size. The particles have a uniform spherical shape and appear bright to the eye. The number of densification steps, i.e. hydrogen reduction steps, employed is not important, the process being operated until the desired particle size and powder density is obtained.

The product can be washed and dried in the presence of air. The end reduction liquor contains no ammonium sulphate and the residual dissolved cobalt can be recovered by simple hydrolysis. The average reduction cycle duration can be as low as 30 minutes.

The seed cobalt powder employed to initiate the precipitation of cobalt during hydrogen reduction must be in the form of fine, discrete particles, which should not exceed 20 micrometers in average size. It is preferred to use fine, discrete seed powder having a particle size of about 1 to 5 micrometers on the average. For example, extra fine cobalt powder having an average particle size in the range of 1 to 20 micrometers, known in the trade as "Afrimet" ® powder, may be employed. Alternatively, cobalt powder produced by the thermal decomposition of cobalt oxalate, for example by heating cobalt oxalate at 500°C under nitrogen for 15 minutes, may be employed. The very small needle-shaped particles and large surface area which characterise the "Afrimet" cobalt powder render it a preferred starting material. Thermal decomposition of cobalt oxalate also produces fine needle-shaped particles but not as fine as the Afrimet product.

In contrast to these powders, cobalt powder produced by nucleation with sodium cyanide and sodium sulphide as catalysts is irregularly shaped and of large particle size. Cobalt powder formed by self-nucleation during the hydrogen reduction is in the form of large porous particles. Whereas the finely divided needle-shaped initiating powders permit densification by growth of individual particles or aggregates of particles during reduction, with the porous types of cobalt powder seed there is a tendency for the hydrogen reduced cobalt to deposit in the void space of the large particles, leading to an overall reduction in the available surface area on which cobalt may be deposited in subsequent densification steps. Great care is then required in the subsequent densification steps not to add too much base, and generally the amount of base added in one densification step should be less than that added in the preceding step in order to compensate for the lower rate of cobalt reduction (and hence sulphuric acid production) caused by the smaller surface area on which fresh cobalt can be deposited. Even so the product powders have a lower apparent density than products seeded with fine, discrete cobalt powder.

It will be appreciated that in carrying out the process of the invention that one mole of sulphuric acid is formed for each mole of cobalt sulphate that is reduced. It is important that the rate of addition of alkali metal hydroxide does not exceed that required to neutralize the sulphuric acid as it forms. Thus, for example, if sulphuric acid is produced at the rate of 200 grams per hour (2.04 moles per hour), sodium hydroxide should be added at a rate not substantially greater than 164 grams (4.1 moles) per hour. If the addition rate of sodium hydroxide exceeds that necessary to neutralize the sulphuric acid formed, cobaltous hydroxide can form, which has a tendency to provide self-nucleated cobalt powder and which interferes with densification of the cobalt powder already present. In order to minimise the risk of cobaltous hydroxide precipitating, the pH of the solution is maintained not greater than 4 during any of the hydrogen reduction steps.

To avoid dilution of the solution, the alkali metal hydroxide is preferably added as a saturated solution of NaOH or KOH. The use of an alkali metal hydroxide instead of ammonia as previously proposed in US—A—2749235 avoids problems in separating ammonium sulphate from the solution remaining after the hydrogen-reduction.

The source of the cobalt sulphate feed solution treated in accordance with the invention is immaterial. Desirably the feed solution should be substantially free of impurities which co-reduce or co-precipitate with cobalt during hydrogen reduction. Thus the contents of nickel, copper, iron and lead should be as low as possible. In addition, species such as chloride ions should be very low, e.g. less than 100 parts per million (ppm), since such ions tends to be corrosive toward the autoclave. In addition, unsaturated sulphur species, i.e. all sulphur compounds except sulphate, which can lead to sulphur contamination of the cobalt product, e.g. dithionate ion, should be removed.

The invention may advantageously be used for the recovery of cobalt from cobaltic oxide hydrate obtained by oxidation-precipitation of cobalt from process leach solutions using sodium hypochlorite and a base. Treatment of cobaltic hydrate to provide cobalt sulphate feed solution suitable for recovery of a cobalt as cobalt powder according to the invention may comprise the following steps:

1) treat $Co(OH)_3$ with H_2SO_4 and water at 60°C for 30 minutes, with suitable agitation and aeration to eliminate the soluble Cl^- as Cl_2 according to the reaction:

$$2Co(OH)_3+6H^++2Cl^-\rightarrow 2Co^{++}+Cl_2+6H_2O$$

(The reaction is only favourable at $pH \leq 1.5$, preferably pH 0.5—1.0).

2) add methanol to the dechlorinated slurry in the presence of sufficient H_2SO_4 (already added in step 1) to solubilize the Co^{+++} as Co^{++} at 60°C, according to the reaction:

$$6Co(OH)_3+6H_2SO_4+CH_3OH\rightarrow 6CoSO_4+CO_2+17H_2O$$

(This reaction however, does not go to completion unless large excesses of H_2SO_4 and CO_3OH are added. In the presence of the stoichiometric amount of H_2SO_4 and 1.2 times the stoichiometric amount of CH_3OH, 85 to 90% of the Co is dissolved (i.e., at least about 80%) in one hour at 60°C with a final pH reading of 1.5 to 2.0).

3) add a small amount of H_2O_2 to the leach slurry to complete the dissolution of $Co(OH)_3$ according to the reaction:

$$2Co(OH)_3+2H_2SO_4+H_2O_2\rightarrow 2CoSO_4+6H_2O+O_2$$

Complete dissolution of the $Co(OH)_3$ is obtained by keeping the pH below about 2.5.

4) add 0.5 to 1.0 g/l of $BaCO_3$ to precipitate Pb, at 60°C and a pH of about 2.5.

5) neutralize the excess H_2SO_4 with $CoCO_3$ or Na_2CO_3 to pH 5.5. In this step Fe and Cu are precipitated as their hydroxides.

6) separate the leach liquor from the leach residue, which contains Pb, Fe and Cu, by filtration.

7) treat the leach solution through a Cu, Ni selective ion exchange resin (such as XF-4195®—by Dow Chemical Company) to remove the residual Cu and the required amount of Ni.

8) recover Co in the elemental form from the purified leach solution by the process of the invention.

The process of the present invention will now be described in greater detail, by way of example only, with reference to the accompanying photomicrographs in which:

Figure 1 is a photomicrograph taken at 200 diameters of a fine, commercial cobalt powder of a kind useful as seed particles in the process in accordance with the invention;

Figure 2 is a photomicrograph taken at 200 diameters of a powder made by a process in accordance with the present invention after 2 densifications using the seed powder shown in Figure 1;

Figure 3 is a photomicrograph taken at 200 diameters of a powder made by a process in accordance with the invention after 4 densifications starting initially from the seed powder of Figure 1;

Figure 4 is a photomicrograph taken at 200 diameters of a powder produced by a process in accordance with the invention after 6 densifications starting initially with the seed powder of Figure 1;

Figure 5 is a photomicrograph taken at 200 diameters of a cobalt powder obtained as a result of self-nucleation; and

Figure 6 is a photomicrograph taken at 200 diameters of a product powder obtained after 6 densifications using as seed powder the powder of Figure 5 by a process not in accordance with the present invention.

Example I

6.3 kg of wet $Co(OH)_3$ cake analyzing in weight percent Co 27.6, Ni 0.48, Fe 0.06, Cu 0.003, Zn 0.001 and Cl 0.2, were slurried with water and 3 kg of concentrated H_2SO_4 to a volume of 15 litres. The slurry was heated to 60°C and stirred while air was sparged through it for 30 minutes to remove the chloride ion content as gaseous chlorine. At this point the slurry pH was at 0.1 and less than 5% of the cobalt in the cake was dissolved.

The dechlorinated slurry was then subjected to a reductive leach by introducing a pure methanol solution into it at a rate of 600 ml/h for 15 minutes. The progress of the leach was followed by monitoring the pH which increased from 0.1 to 1.5 in one hour. At pH 1.5 about 85% of the feed $Co(OH)_3$ had been dissolved and further dissolution of $Co(OH)_3$ was very slow due to lack of H_2SO_4 and methanol. Complete reaction with methanol would require not only excess of methanol, but a large excess of H_2SO_4 (pH of not greater than 1 in the end dissolution liquor) which must be neutralized with base. This operation would be costly.

Methanol was therefore substituted by H_2O_2 which reacts with $Co(OH)_3$ as a reducing agent below pH 4. A 30% H_2O_2 solution was added into the leach slurry at a rate of 75 ml/h for 140 minutes. At this point completion of the leach was evidenced by a sharp change in colour from black to pink. During the completion of the leach the pH was kept at 1.5 with H_2SO_4 when required. This pH is preferred for the subsequent Pb removal operation. Lead was removed from solution by the addition of 0.5 g of $BaCO_3$ per litre of solution. After 30 minutes at 60°C, the solution was neutralized to pH 5.5 using a 100 g/l Co containing $CoCo_3$ slurry. After filtration the liquor was passed through a Ni selective ion-exchange resin for Ni removal. The final purified solution contained 96 g/l Co and 0.038 g/l Ni, and in mg/l Cu 1, Pb<0.3, Fe 1, Zn 5 and Cl^- 30.

Leach solution prepared in the aforedescribed manner and containing 92.2 g/l Co, 1.3 g/l Ni, 0.3 mg/l Cu, 0.3 mg/l Pb and 0.6 mg/l Fe was treated for cobalt recovery in the elemental powder form as follows: 0.8 litres of leach solution and 10 g of fine, discrete Co powder having an apparent density of 0.6 gm/cc were placed and sealed in a 2 litre capacity Parr all Ti autoclave provided with a twin propellor agitator which was rotated in all runs at 1000 revolutions per minute (rpm). The suspension was heated to 200°C and H_2 was admitted to the autoclave at a partial pressure of 1.3 MPa (a total pressure of 3 MPa). A 9.4 N NaOH solution was then pumped into the autoclave at a rate of 150 ml/h for 90 minutes, representing an NaOH addition rate of 1.1 mole per mole of cobalt per hour. The pH of the solution during NaOH addition was between 2.0 and 3.0. The reduction was continued after NaOH addition for 20 minutes to ensure complete elimination of $Co(OH)_2$. The end reduction solution was cooled to 80°C and withdrawn from the autoclave through a carbon filter, leaving the Co powder inside the autoclave. About 100 ml of end reduction liquor was left in the autoclave.

0.8 Litres of fresh feed $CoSO_4$ leach solution was pumped into the autoclave and the H_2 reduction cycle was repeated as above. After 6 cycles (or densifications), the total amount of Co powder was washed and dried in air at room temperature. The final powder contained 97% cobalt, 2% nickel, and in ppm, <15 copper, <40 iron, 14 zinc, 170 sulphur and 590 carbon. Table I illustrates the densification achieved over the 6 cycles.

TABLE I
Cobalt powder

Reduction cycle	% S	Apparent density (g/cc)	Co Reduced (g)	Co reduced / Co seed (g/g)
1	0.058	2.0	56	5.6
2	0.024	4.1	104	10.4
4	0.019	5.2	209	20.9
6	0.017	5.5	300	30.0

The structure of the finely-divided cobalt seed powder employed in this Example is shown in Figure 1 and of the product powder after 2, 4 and 6 densifications is shown in Figures 2, 3 and 4, all at 200 diameters. The correlation between density and particle size is marked.

Example II

The H_2 reduction procedure used in Example I was repeated but using feed leach solution containing 85.5 g/l Co, 0.13 g/l Ni, 0.2 mg/l Cu, 0.3 mg/l Pb and 0.9 mg/l Fe. After 8 reduction cycles the cobalt powder was washed and dried in air. The cobalt powder product contained 99% by weight cobalt, 0.32% nickel and, in ppm, 7 copper, 20 iron, <10 lead, <5 zinc, 280 sulphur and 630 carbon. Table II illustrates the densification achieved during the 8 cycles.

TABLE II
Cobalt powder

Reduction cycle	% S	Apparent specific gravity (g/cc)	Co Reduced (g)	Co reduced / Co seed (g/g)
2	0.024	2.35	77.9	7.8
4	0.025	4.59	156.1	15.6
6	0.027	5.48	218.0	21.8
8	0.028	5.50	273.5	27.4

Example III

Leach solution containing 96 g/l Co, 0.038 g/l Ni, 0.3 mg/l Cu, 0.2 mg/l Pb, 1.3 mg/l Fe and 5 mg/l Zn was treated for Co recovery in the elemental powder form as follows: 0.8 litres of leach solution and 40 g of fine, discrete cobalt powder (Afrimet) were placed in a 2 litre capacity Parr Ti autoclave. The suspension was heated with stirring to 200°C and H_2 was introduced into the vessel at a partial pressure of 1.2 MPa (total pressure of 3 MPa). A 9.4 N NaOH solution was pumped into the autoclave at a rate of 780 ml/h (5.5 moles NaOH per mole of cobalt per hour) for 18 minutes and 20 seconds. The pH of the solution during NaOH addition was between 2 and 3. The reduction was continued thereafter for another 11 minutes and 40 seconds (total time 30 minutes). The end reduction liquor was cooled and withdrawn from the autoclave through a Ti inlet tube equipped with a carbon filter. About 100 ml of end reduction liquor and the reduced Co powder were left in the autoclave.

0.8 Litres of fresh feed $CoSO_4$ leach solution were pumped in the autoclave and the hydrogen reduction cycle was repeated under the conditions mentioned above. After 11 such cycles, the total amount of Co powder was withdrawn, washed and dried in air at room temperature. The powder contained 99% cobalt and 0.042% nickel by weight, and, in ppm, 5 copper, 33 iron, 2 lead, 2 zinc and 210 sulphur.

Results are shown in Table III. Again the S content was decreased and the apparent density of the Co powder was increased with increasing number of cycles.

TABLE III

Cobalt powder

Reduction cycle	% S	Apparent density (g/cc)	Co Reduced (g)	Co reduced / Co seed (g/g)
1	0.083	0.8	51	1.3
3	0.040	1.9	160	4.0
6	0.018	3.8	310	7.8
8	0.026	4.3	420	10.5
11	0.021	4.7	560	14.0

Example IV

Feed $CoSO_4$ leach solution prepared by the method described in Example I and containing 92 g/l Co, 0.035 g/l Ni, <0.1 mg/l Cu, 1.1 mg/l Fe, 0.25 mg/l Pb, and 2 mg/l Zn was treated for Co recovery by H_2 reduction in the following manner: 0.8 litres of $CoSO_4$ leach solution and 30 g of Co powder, made by decomposition of cobalt oxalate crystals at 500°C under N_2 atmosphere for 15 minutes, were placed in a 2 litre capacity Parr Ti autoclave. The suspension was heated to about 200°C and H_2 was introduced into the autoclave at a partial pressure of 1.3 PMa (total pressure of 3 MPa). A 9.95 N NaOH solution was then pumped into the autoclave at a rate of 150 ml/h for 90 minutes. The pH of the solution during NaOH addition was between 2.5 and 3.5. The reduction was carried out thereafter for another 30 minutes during which the pH of the solution decreased to 2.5. The end reduction liquor was cooled to 80°C and withdrawn from the autoclave through a Ti inlet tube equipped with a carbon filter. 0.8 litres of fresh $CoSO_4$ solution was fed to the autoclave and the H_2 reduction cycles was repeated as above 11 times. At the end of 11 cycles, the Co powder was washed and dried in air. The cobalt powder contained, by weight, 99% cobalt and 0.089% nickel and, in ppm, 12 copper, 32 iron, 9 lead, 4 zinc and 518 sulphur.

The satisfactory densification achieved is illustrated in Table IV.

TABLE IV

Cobalt powder

Reduction cycle	% S	Apparent density (g/cc)	Co Reduced (g)	Co reduced / Co seed (g/g)
3	—	3.3	155	5.2
6	—	4.3	271	9.0
11	0.05	4.7	518	17.3

In order to illustrate the unsatisfactory results obtained when sodium hydroxide is introduced during reduction at a rate substantially exceeding the rate of sulphuric acid production, the following three Examples are given:

Example A

Feed $CoSO_4$ leach solution containing 86 g/l Co, 0.046 g/l Ni, 0.3 mg/l Cu, 0.4 mg/l Pb and 2 mg/l Fe was treated for Co recovery by H_2 reduction in the following manner: 0.7 litres of $CoSO_4$ leach solution and 10 g of Afrimet Co powder were placed in a 2 litre capacity Parr Ti autoclave. The suspension was heated to 200°C and H_2 was introduced into the vessel at a partial pressure of 1.3 MPa (total pressure of 3 MPa). A 10 N NaOH solution was then pumped into the autoclave at a rate of 1.44 litres per hour (12 moles NaOH per mole of cobalt per hour) for 7 minutes and 30 seconds. The pH of the solution during NaOH addition increased from 2.0 to 7.0. The reduction was carried on thereafter until the pH in the solution was below about 3. This took about 110 minutes. The end reduction liquor was cooled to 80°C and withdrawn from the autoclave through a Ti inlet tube equipped with a carbon filter. 0.7 litres of fresh $CoSO_4$ solution was fed into the autoclave and the H_2 reduction cycle was repeated as above 8 times. At the end of 8 cycles, the produced Co powder was washed and dried in air. The Co powder was light and porous. About 3% of the Co was plastered onto the autoclave internals. The powder contained 99% cobalt and 0.05% nickel and, in ppm, 5 copper, 30 iron, <5 lead, 6 zinc, 1,000 sulphur and 500 carbon.

Results are shown in Table A. Evidently with a fast NaOH addition rate and only 10 g of Afrimet seed powder, the apparent density of the Co powder was much lower than in the tests described in the preceding Examples.

TABLE A

Reduction cycle	Cobalt powder % S	Apparent density (g/cc)	Co Reduced (g)	Co reduced / Co seed (g/g)
8	0.10	1.7	413	41.3

Example B

Leach solution containing 96 g/l Co, 0.038 g/l Ni, <0.3 mg/l Cu, <0.3 mg/l Pb, 1.3 mg/l Fe and 5 mg/l Zn was treated for cobalt powder recovery as follows: 0.7 litres of leach solution was sealed in a 2 litre Ti autoclave and heated to 200°C. A 1.3 MPa partial pressure of H_2 was admitted to the autoclave and 0.1 litres of solution containing 20 g/l NaCN and 2 g/l Na_2S was pumped in. This was followed by the addition of a 9.4 N NaOH solution at a rate of 780 ml/h for 18 minutes and 36 seconds. The reduction was continued after NaOH addition for about 12 minutes. The autoclave contents were cooled to 80°C and the solution was withdrawn from the vessel through a Ti inlet tube equipped with a carbon filter.

0.7 litres of fresh feed $CoSO_4$ leach solution was pumped in the autoclave, heated to 200°C and pressurized with H_2 to a total pressure of 3 MPa (gauge). A 9.4 N NaOH solution was pumped in a rate of 780 ml/h for 16 minutes and the reduction was carried out for a total time of 30 minutes. After cooling and solution withdrawal, the reduction cycle was repeated 5 times. The pH of the solution during NaOH addition was between 2.5 and 3.0. After 5 cycles, the Co powder was washed and dried in air. The powder contained 99% cobalt and 0.05% nickel, by weight, and in ppm, 4 copper, 150 iron, <10 lead, <10 zinc and 450 sulphur.

Densification results are shown in Table B.

TABLE B

Reduction cycle	Cobalt powder % S	Apparent density (g/cc)	Co Reduced (g)	Co reduced / Co nucleated (g/g)
0 nucleation	—	—	63	—
2	0.152	1.15	155	2.46
5	0.045	2.50	274	4.35

Example C

A leach solution containing 92 g/l Co, 0.032 g/l Ni, <0.1 mg/l Cu, 1 mg/l Fe, <0.25 mg/l Pb and 2 mg/l Zn was treated for cobalt powder recovery as follows: 0.8 litres of $CoSO_4$ leach solution was heated in autoclave to 200°C and H_2 was admitted at 1.3 MPa partial pressure. A 9.4 N NaOH solution was pumped in at a rate of 1.2 litres per hour for 15 minutes (equivalent to 99% of the Co as $Co(OH)_2$) and the reduction was continued thereafter for another 35 minutes. After cooling the end reduction liquor was pumped out and 0.8 litres of fresh feed $CoSO_4$ solution was pumped in. After heating to 200°C, H_2 was admitted at 1.3 MPa partial pressure (3 MPa total pressure) and a 9.4 N NaOH solution was pumped in at 0.7 litres per hour for 17 minutes. During NaOH addition, the pH of the reduction liquor varied between 2.7 and 3.9. The end reduction liquor was cooled and removed through a Ti inlet tube equipped with a carbon filter. After adding 0.8 litres of fresh feed $CoSO_4$ solution the reduction cycle was repeated under the same conditions. After 6 cycles, the Co powder was removed, washed and dried in air. The powder contained 99% cobalt, 0.09% nickel, by weight, and, in ppm, 240 copper, 240 iron, <10 lead, <10 zinc, 1,000 sulphur.

Densification results are given in Table C.

TABLE C

Cobalt powder

Reduction cycle	% S	Apparent specific gravity (g/cc)	Co Reduced (g)	Co reduced / Co nucleated (g/g)
0 nucleation	—	—	72	—
3	0.046	3.6	220	3.0
6	0.100	3.6	350	5.0

The structure of the seed powder at 200 diameters is shown in Figure 5. A large amount of void space is evident. The powder structure obtained after 6 densifications is shown in Figure 6. The powder is still porous and the tendency to deposit reduced cobalt in the void space of the seed particles is illustrated. The density of the product is notably low. We believe that the reason why the powder produced in Examples B and C is not particularly dense is that the seed particles are large and porous. Cobalt is deposited in the voids in such particles, and that results in a reduction in the surface area available for cobalt deposition in subsequent steps. This situation can be contrasted with the processes described earlier in which the surface area increases in each successive densification when small compact seed particles are used. The addition of sodium hydroxide at the same rate in all steps when using porous seed cobalt leads to an excessive addition in the later steps because the rate of sulphuric acid generation in these later steps is lower than in the earlier steps as a result of the slower reaction rate caused by the reduction of surface area of crystallized cobalt on which new cobalt can be deposited. When the porous seed powder of Figure 5 is subjected to a light grind, as in a ball mill, fine discrete powder particles are produced which are satisfactory as seed powder for the production of a dense cobalt powder product after a number of densifications carried out in accordance with the present invention.

Claims

1. A process of making dense cobalt powder of coarse, relatively uniform particle size by reduction of a cobalt-containing solution with hydrogen under pressure in the presence of cobalt powder and then reducing further amounts of the solution in the presence of the cobalt powder produced, characterised by the steps of subjecting a portion of a cobaltous sulphate solution to hydrogen reduction at a hydrogen partial pressure of at least one megapascal and a temperature of at least 180°C in the presence of seed cobalt powder in the form of fine, discrete particles not exceeding 20 micrometers in average size while maintaining the pH of the solution not greater than 4 by introducing a solution of an alkali metal hydroxide at a rate not substantially exceeding the molar equivalent of the rate of sulphuric acid production due to hydrogen reduction, continuing the hydrogen reduction to reduce a substantial part of the cobalt content of said portion to produce an end reduction solution and cobalt powder, and repeating said hydrogen reduction cyclically with fresh successive portions of cobaltous sulphate solution with each successive reduction being performed in the presence of the cobalt powder formed in the previous cycle to provide a densified cobalt powder product.

2. A process according to claim 1 in which the seed cobalt powder has an average particle size in the range from 1 to 5 micrometers.

3. A process according to claim 1 or claim 2 in which the seed cobalt powder is in the form of needle-shaped particles.

4. A process according to any preceding claim in which the cobalt sulphate solution contains from 50 to 100 g/l of cobalt.

5. A process according to any preceding claim in which the hydrogen reduction is stopped when from 80 to 95% of the cobalt in the solution has been reduced.

Patentansprüche

1. Ein Verfahren zur Herstellung eines dichten Kobaltpulvers mit grober, relativ gleichmäßiger Partikelgröße durch Reduktion einer kobalthaltigen Lösung mit Wasserstoff unter Druck in Gegenwart von Kobaltpulver, wobei anschließend weitere Mengen der Lösung in Gegenwart des so hergestellten Kobaltpulvers reduziert werden und dieser Vorgang dadurch gekennzeichnet ist, daß ein Teil einer Kobalt(II)sulfatlösung mit Wasserstoff reduziert wird, und zwar bei einem Wasserstoff-Partialdruck von mindestens einem Megapascal und einer Temperatur von mindestens 180°C in Gegenwart von Impfkobaltpulver in Form feiner Einzelpartikel von maximal 20 µm, wobei der pH-Wert der Lösung bei maximal 4 gehalten wird durch Zugabe einer Lösung eines Alkalimetallhydroxids, wobei die Zugaberate

nicht wesentlich größer ist als das Moläquivalent der durch die Wasserstoffreduktion enstehenden Schwefelsäure und die Wasserstoffreduktion fortgesetzt wird, um einen wesentlichen Teil des Kobaltgehaltes des besagten Anteils zu reduzieren und damit eine Endreduktionslösung und Kobaltpulver zu erhalten, wobei die Wasserstoffreduktion zyklisch durch sukzessive Zugabe frischer Kobalt(II)-sulfatlösung fortgesetzt und jede Stufenreduktion in Gegenwart des im jeweils vorangegangenen Zyklus enstandenen Kobaltpulvers durchgeführt wird, um ein verdichtetes Kobaltpulver zu erhalten.

2. Ein Verfahren nach Anspruch 1, wobei das Impfkobaltpulver eine durchschnittliche Partikelgröße von 1 bis 5 µm aufweist.

3. Ein Verfahren nach Anspruch 1 oder 2, wobei das Impfkobaltpulver in Form nadelförmiger Partikel vorliegt.

4. Ein Verfahren nach einem der vorgenannten Ansprüche, wobei die Kobaltsulfatlösung 50 bis 100 g/l Kobalt enthält.

5. Ein Verfahren nach einem der vorgenannten Ansprüche, wobei die Wasserstoffreduktion gestoppt wird, sobald 80 bis 95% des Kobalts in der Lösung reduziert worden sind.

Revendications

1. Procédé de préparation de poudre de cobalt dense de taille particulaire grossière et relativement uniforme par réduction d'une solution contenant du cobalt avec de l'hydrogène sous pression en présence de poudre de cobalt puis réduction de quantités supplémentaires de la solution en présence de la poudre de cobalt produite, caractérisé par les étapes consistant à soumettre une fraction d'une solution de sulfate cobalteux à une réduction par l'hydrogène à une pression partielle d'hydrogène d'au moins 1 mégapascal et une température d'au moins 180°C en présence de poudre de cobalt d'ensemencement sous forme de particules discrètes et fines n'excédant pas 20 micromètres de taille tout en maintenant le pH de la solution à au plus 4 en introduisant une solution d'un hydroxyde de métal alcalin à une vitesse ne dépassant pas substantiellement l'équivalent molaire de la vitesse de production d'acide sulfurique due à la réduction par l'hydrogène, à continuer la réduction par l'hydrogène pour réduire une partie substantielle de la teneur en cobalt de ladite fraction pour produire une solution de réduction finale et une poudre de cobalt, et à répéter ladite réduction par l'hydrogène de façon cyclique avec des fractions successives fraîches de solution de sulfate cobalteux, chaque réduction successive étant conduite en présence de la poudre de cobalt formée dans le cycle antérieur pour fournir un produit de poudre de cobalt densifié.

2. Procédé selon la revendication 1 où la poudre de cobalt d'ensemencement a une taille particulaire moyenne située dans un intervalle allant de 1 à 5 micromètres.

3. Procédé selon les revendications 1 et 2 où la poudre de cobalt d'ensemencement est sous forme de particules en forme d'aiguilles.

4. Procédé selon l'une quelconque des revendications précédentes où la solution de sulfate de cobalt contient de 50 à 100 g/l de cobalt.

5. Procédé selon l'une quelconque des revendications précédentes où la réduction par l'hydrogène est arrêtée lorsque de 80 à 95% du cobalt dans la solution a été réduit.

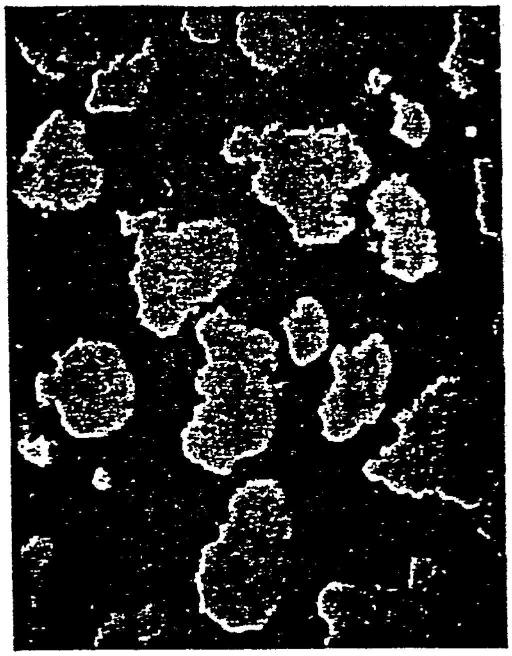
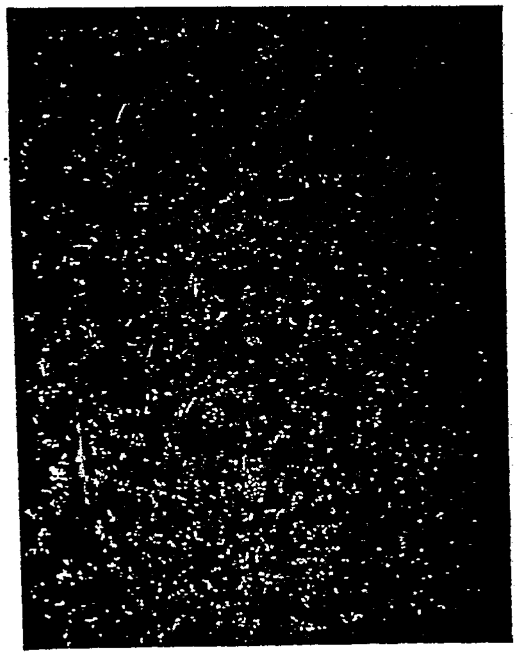


Fig.~~1~~, 2



Fig~~2~~, 1

Fig.3.

Fig.4.

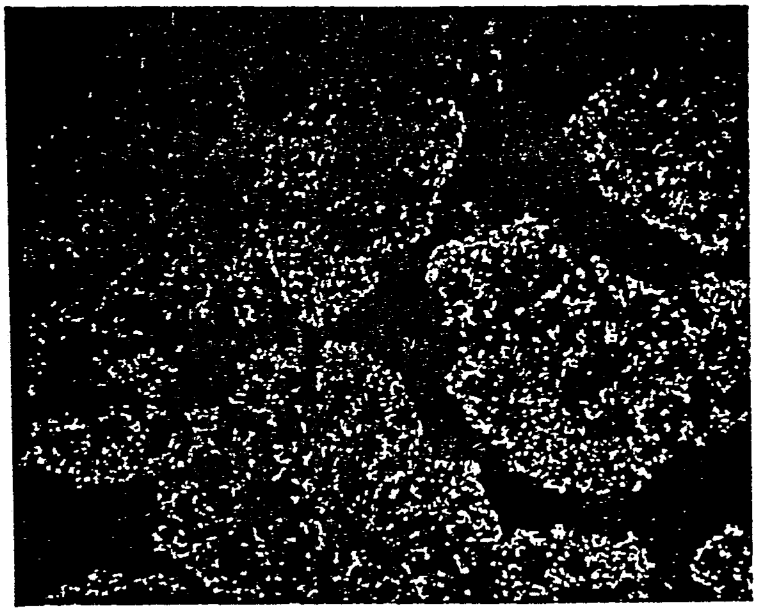


Fig.5.

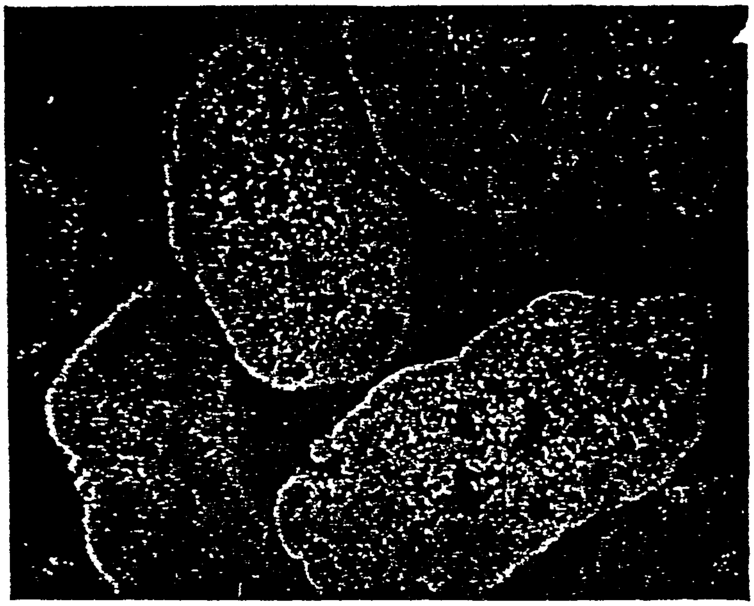


Fig.6.