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PRODUCTION OF COBALT POWDERS FOR CEMENTED CARBIDE AND DIAMOND TOOL INDUSTRIES

OTRZYMYWANIE PROSZKÓW KOBALTU PRZEZNACZONYCH DO PRODUKCJI WĘGLIKÓW SPIEKANYCH ORAZ NARZĘDZI METALICZNO-DIAMENTOWYCH

A current review of the most widely used production methods for fine cobalt powders, which find application as a binder in the manufacture of cemented carbides and diamond impregnated cutting tools, is provided. Emphasis has been placed on the powder's chemical, physical and technological characteristics specific to each production route.

Nowadays, the majority of cobalt powder grades are made by chemical methods, such as thermal decomposition of cobalt oxalate, reduction of oxides, and hydrometallurgical processing of aqueous solutions, although an atomised material, used mainly in the thermal spray and surface coating field, is also applied in the diamond tool industry.

The bulk of the industrially important cobalt powder passes through the 37μm (400 mesh) standard sieve. Therefore it has become customary to classify the commercial powders into *ultrafine* (or *sub-micron*), extrafine and *mesh* grades, which are characterised by an average particle size of 0.5–1μm, 1–3.5μm and 3.5–6μm respectively, as determined by the Fisher method [1].

W artykule zaprezentowano główne sposoby otrzymywania proszków kobaltu, które znajdują zastosowanie w procesie produkcji węglików spiekanych oraz kompozytowych, metaliczno-diamentowych materiałów narzędziowych. Szczególną uwagę zwrócono na sposób w jaki metoda produkcji proszku wpływa na jego chemiczne, fizyczne oraz technologiczne własności.

W chwili obecnej proszki kobaltu otrzymuje się głównie poprzez wykorzystanie rozmaitych metod fizykochemicznych, takich jak: termiczny rozkład szczawianu kobaltawego, redukcja tlenków kobaltu wodorem oraz redukcja wodnych roztworów związków kobaltu wodorem pod ciśnieniem. Ponadto, przy produkcji narzędzi diamentowych zastosowanie znajdują również proszki rozpylane, których głównym przeznaczeniem pozostaje jednak produkcja różnego rodzaju powłok ochronnych. Przemysłowe zastosowanie znajdują głównie proszki drobnoziarniste o wielkości cząstek nie przekraczającej 37μm (400 mesh). Dla bliższego scharakteryzowania poszczególnych gatunków

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proszku pod względem średniej wielkości cząstek zmierzonej przy użyciu aparatu Fishera [1], powszechnie stosuje się określenia ultrafine lub sub-micron (0.5–1μm), extrafine (1–3.5μm) oraz mesh (3.5–6μm).

1. Thermal decomposition of cobalt oxalate

The simplified flow chart for the oxalate decomposition process is shown in Fig 1.

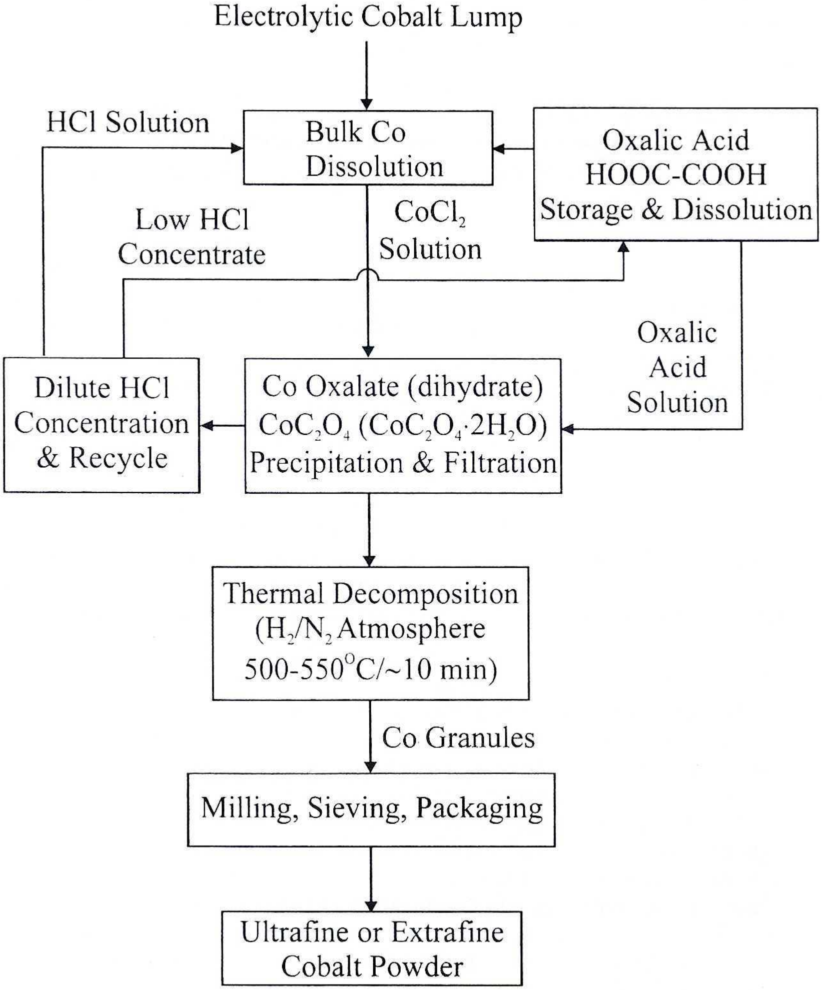

Fig. 1. Cobalt powder production by means of thermal decomposition of cobalt oxalate

A typical precursor material for the thermal decomposition process is cobalt chloride obtained by dissolution of the metal in hydrochloric acid. An intermediate processing step, which consists in introducing oxalic acid to the solution, converts this precursor into a cobalt oxalate. It is extremely important that the oxalate precipitation conditions ensure that the final product has desired crystal form and size. It has been well documented that the morphologies of the cobalt oxalate (dihydrate) and cobalt metal powder are interrelated [2].

Cobalt oxalate decomposes directly to cobalt metal without the need of a reducing atmosphere, but a hydrogen containing atmosphere is normally used to minimise the presence of oxides in the final product. The decomposition temperature typically lies between 500 and 550°C and, discounting the influence of the cobalt oxalate characteristics, has an effect on the particle size of the powder; whereas 10 minutes hold at temperature is normally long enough for the process to be completed [2].

Fig. 2. SEM micrograph of extrafine cobalt powder with fibre shaped structure

As illustrated in Fig 2, the *oxalate route* powder consists of loosely agglomerated, elongated particles. Their shape, which facilitate mechanical interlocking of the particles, contribute to the powder's excellent mixing and green strength properties. Taking no account of oxygen, the cobalt content amounts to 99.85% or more, which value is difficult to achieve by other methods [3]. The oxygen content in fresh (as-delivered) state ranges between 0.2–0.8% depending mainly on the particle size (specific surface area).

2. Reduction of oxides

The flow diagram for the oxide reduction process is shown in Fig 3.

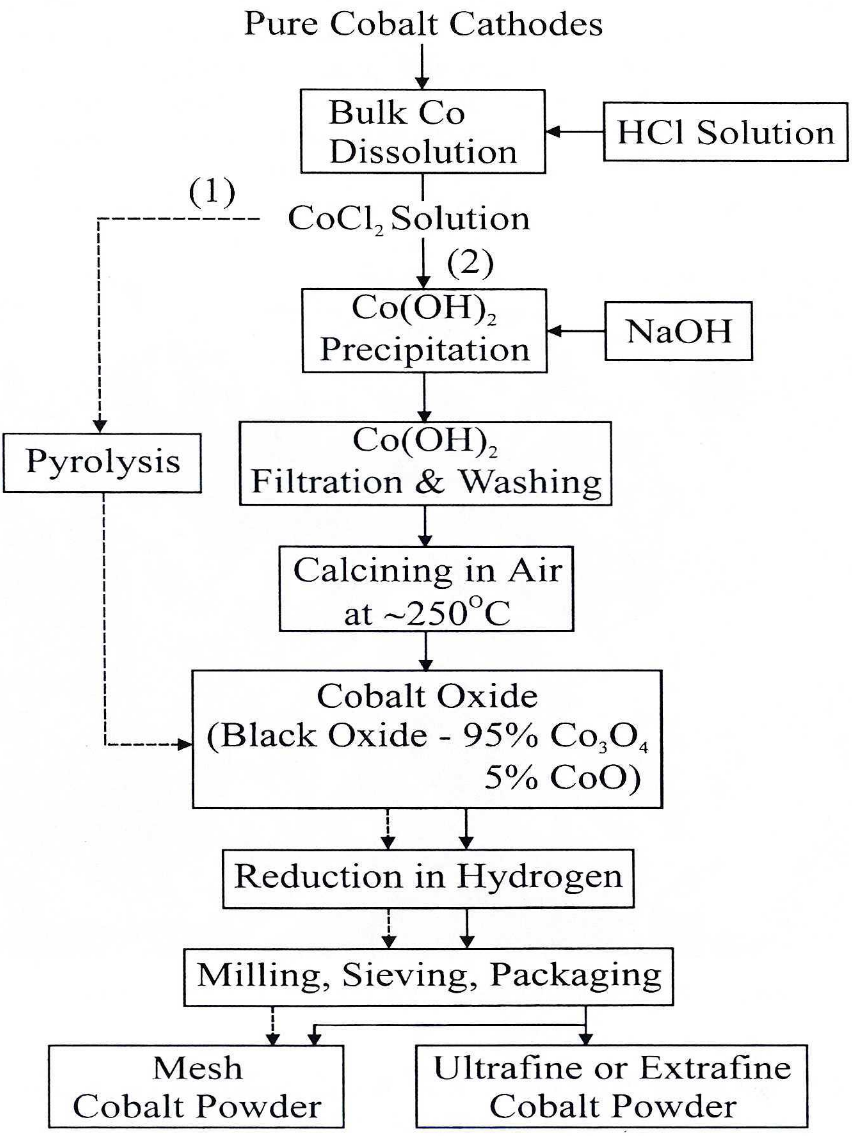

Fig. 3. Cobalt powder production by means of reduction of cobalt oxides

As in the *oxalate process*, the precursor material for the thermal reduction route is predominantly cobalt chloride, which may be either directly converted into the black oxide or neutralised with sodium hydroxide to precipitate cobalt hydroxide. The hydroxide is subsequently calcined in air and the oxide is then, in either case, reduced to metal powder in a hydrogen atmosphere. The reduction takes place at between 700°C [4] and 850°C [5], but processing at higher temperatures reaching 1100°C has also been reported [6].

The pyrolytic decomposition of cobalt chloride is mainly used in the manufacture of mesh powders, whereas the *hydroxide* route enables production of finer powders as well. Excepting the reduction temperature, the metal particle size is mainly affected by the size of the oxide particles which in turn is controlled by the characteristics of the cobalt hydroxide precipitate.

Compared to oxalate material, which tends to be elongated, oxide reduced powders are more spherical. Scanning electron images of typical oxide sourced powders are shown in Figs 4 and 5.

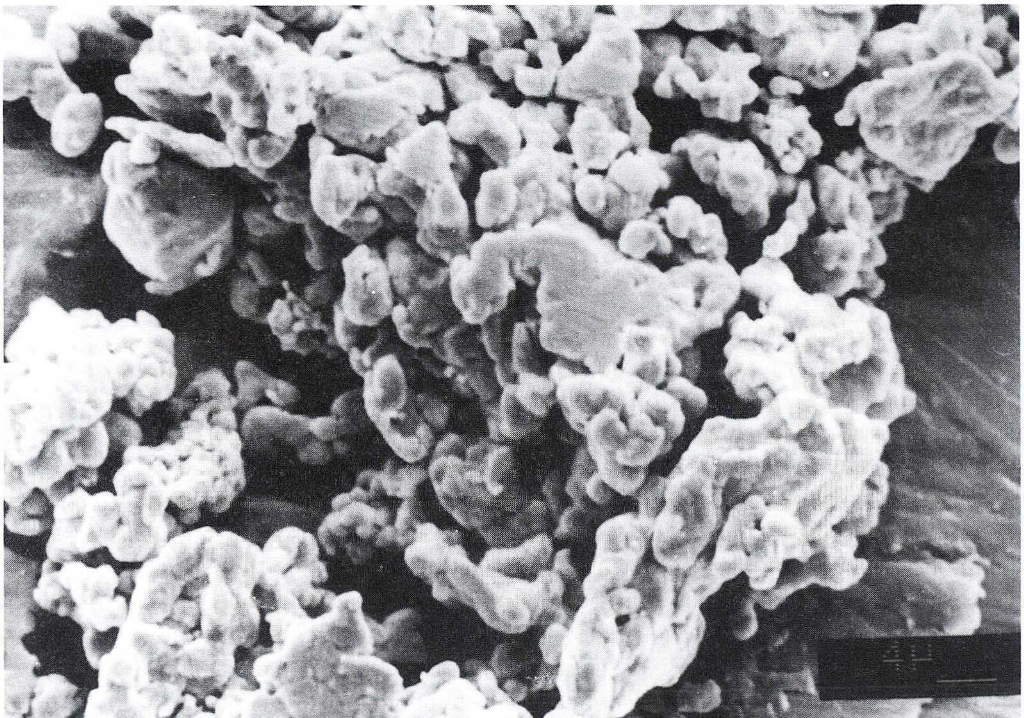

Fig. 4. SEM micrograph of irregularly shaped mesh cobalt powder

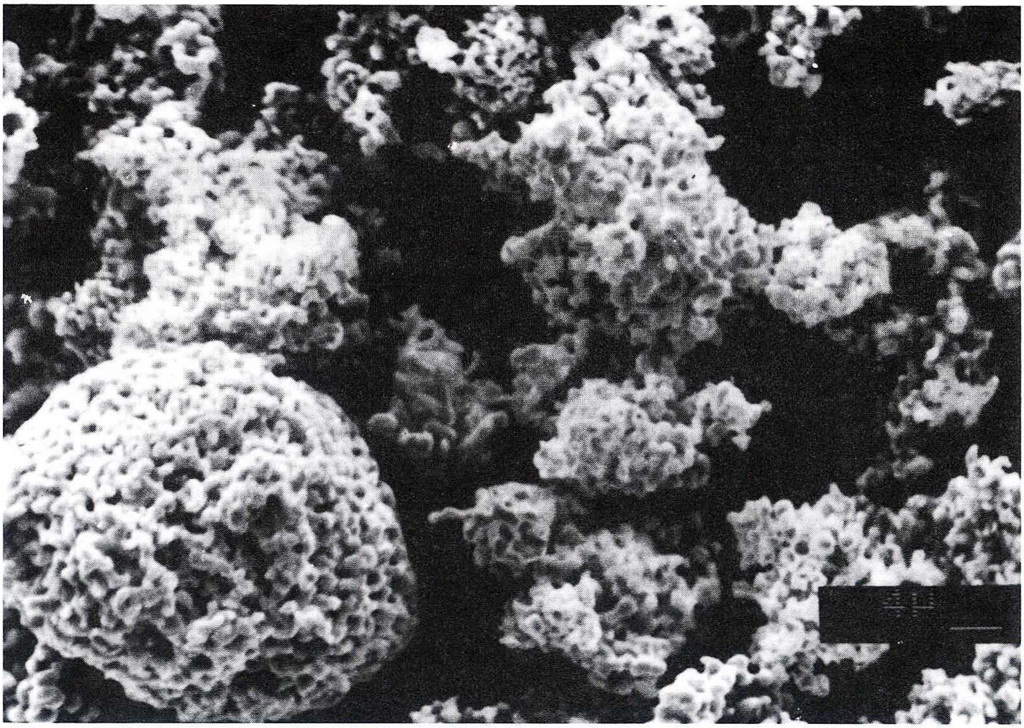

Fig. 5. SEM micrograph of slightly agglomerated extrafine cobalt powder

3. Hydrometallurgy

Cobalt powder was traditionally produced through the hydrogen reduction of aqueous solutions under pressure [7,8]. The precipitate, however, was coarse and widely varying in particle size [8,9]. The hydrometallurgical process has recently been modified to produce very fine cobalt powder characterised with a narrow size range [10–12]. Its diagrammatic representation is given in Fig 6.

The first step consists in generating a cobaltous sulphate solution by dissolving metallic cobalt feed in sulphuric acid. Aqueous ammonia is then added to produce cobaltous ammine sulphate but attention is paid so that some basic cobalt sulphate has also been obtained. The supersaturated solution of cobaltous sulphate is then transferred to an autoclave to precipitate ultrafine or extrafine cobalt particles by adding hydrogen at a pressure of about 3.5 MPa. To produce ultrafine cobalt powder, the nucleation and reduction steps take less than 20 minutes at a temperature of about 180°C. A soluble silver salt, preferably silver sulphate or silver nitrate, is always present to serve as a nucleation catalyst although the basic cobalt sulphate is also believed to provide surface on which the cobalt particles nucleate. Organic compounds are added to prevent growth and agglomeration of the cobalt particles. At the completion of the reduction process the powder is filtered, washed, and dried, then packaged.

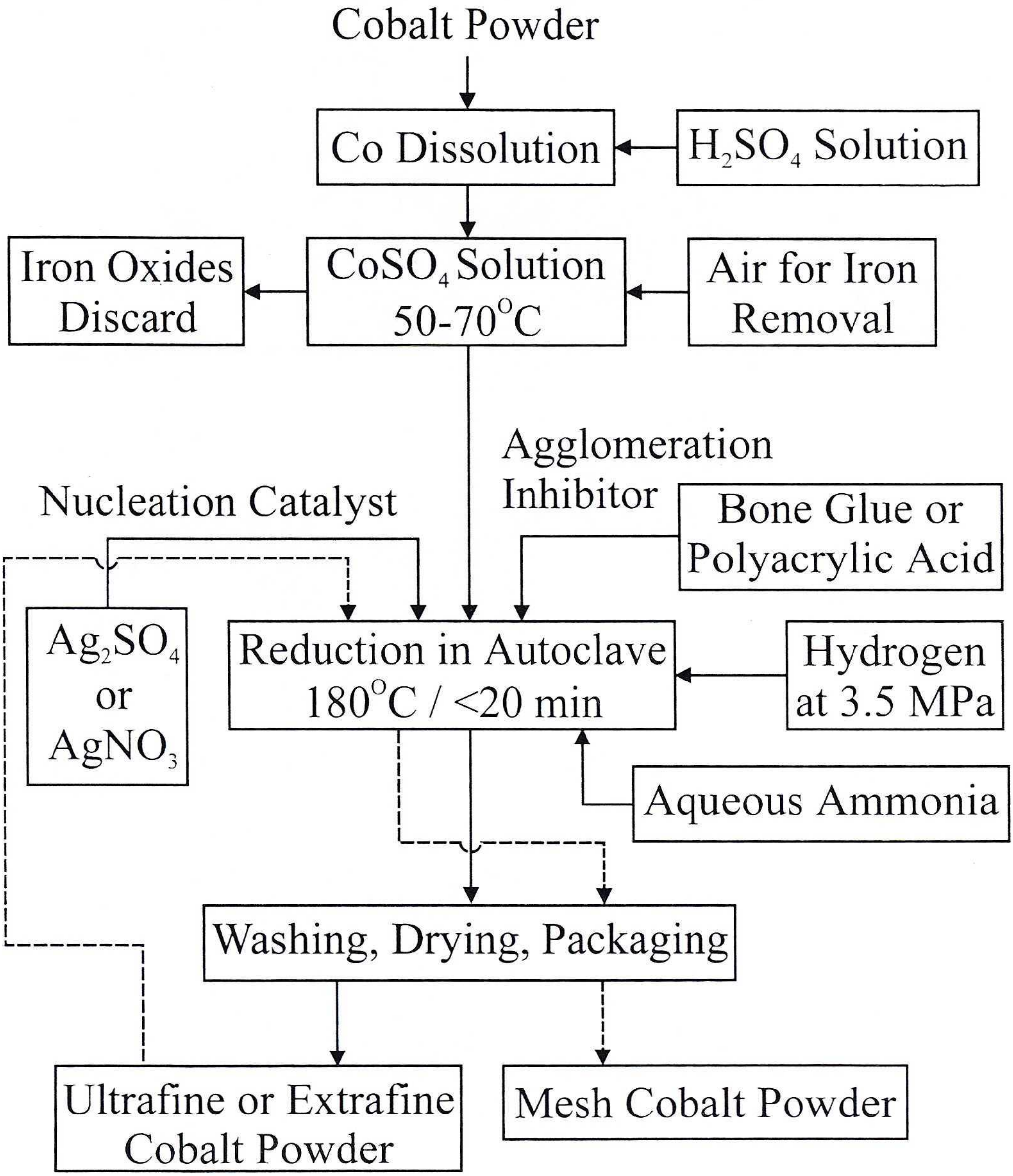

Fig. 6. Cobalt powder production by means of a hydrometallurgical process

As shown in Fig 7, the hydrometallurgical powder consists of loosely agglomerated spherical crystallites.

The reduction of mesh cobalt from solution is carried out in a similar manner to that described for fine powder, the nucleation seed in this case being ultrafine cobalt powder from a previous cycle. Fine cobalt particles grow in size by a combination of

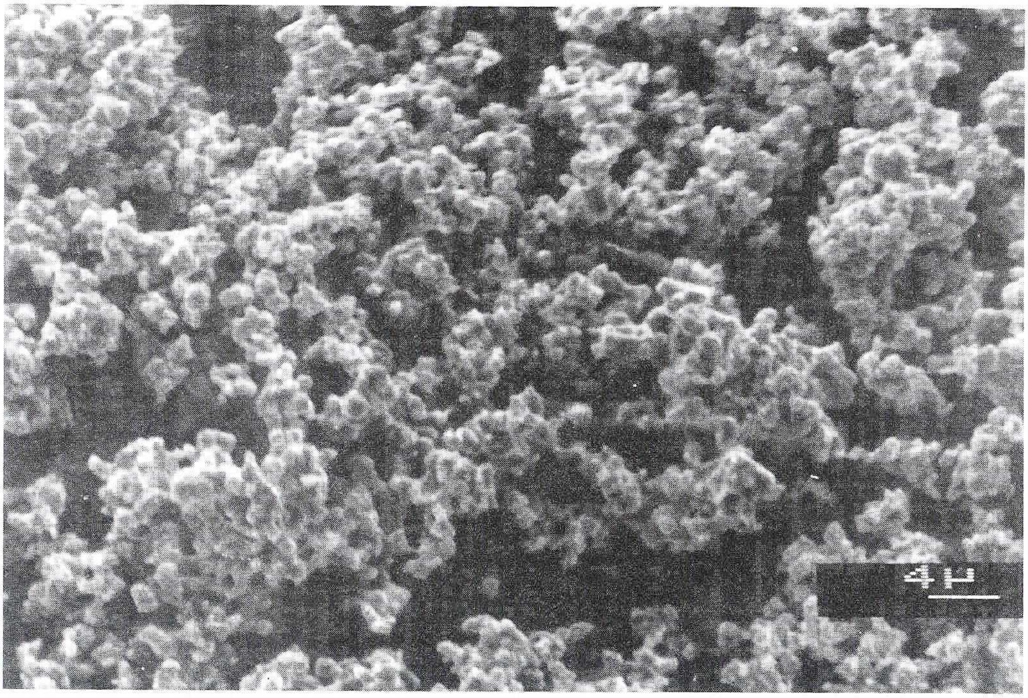

Fig. 7. SEM micrograph of hydrometallurgical extrafine cobalt powder

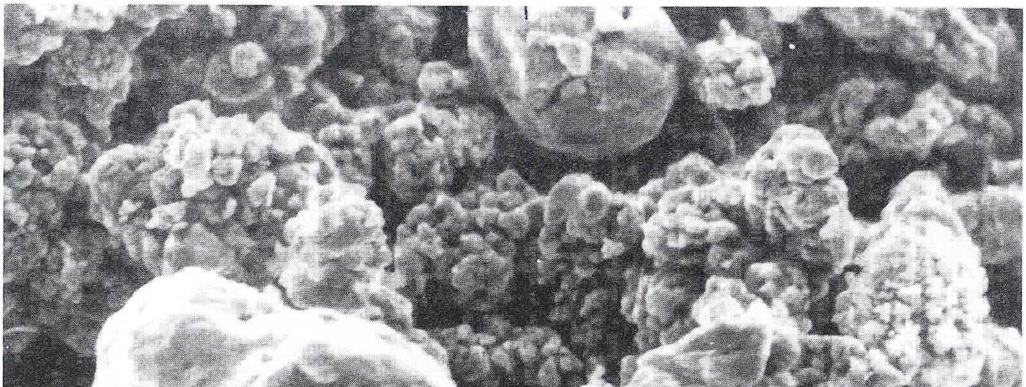

Fig. 8. SEM micrograph of hydrometallurgical mesh cobalt powder

agglomeration and coating with newly reduced metal from solution. In such multiple densifications way relatively porous particles (see Fig 8) with high specific surface area ranging from 1.0 to 1.5 m^2/g (compared to about 0.5 m^2/g obtained with thermally reduced powder) and sizes bigger than 4μm can easily be produced [3].

Particles nucleated from cobaltous sulphate solution always retain residual amounts of organic material wherein most of the oxygen and almost all of the carbon is present. This organic material forms a layer on the particle surface that minimises formation of metal oxides when the powder is stored in contact with air [13]. Therefore the hydrometallurgical powders, unlike their thermally decomposed counterparts, purify themselves during hot pressing to yield material virtually free from oxygen and carbon.

Results of thermogravimetric and evolved gas analyses are presented in Figs 9 and 10 respectively to contrast the response to temperature of a hydrometallurgical powder with a thermally decomposed material.

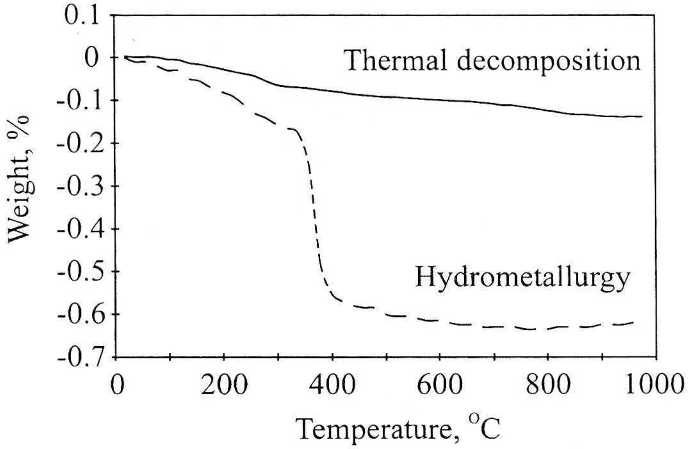

Fig. 9. Thermogravimetric analysis of hydrometallurgical and thermally decomposed extrafine cobalt powders [14]

Other impurities, closely related to the selection of precursor materials and nucleation catalysts, such as silver and sulphur are less volatile and remain as residuals in the product. The latter is always present at levels of at least 50 ppm [15] (compared to less than 10ppm in the *oxalate* material [16]), which value is conceived of as the embrittlement threshold in cobalt [17].

Typical impurity levels characteristic of cobalt powders manufactured by means of the hither presented chemical processes are given in Table 1.

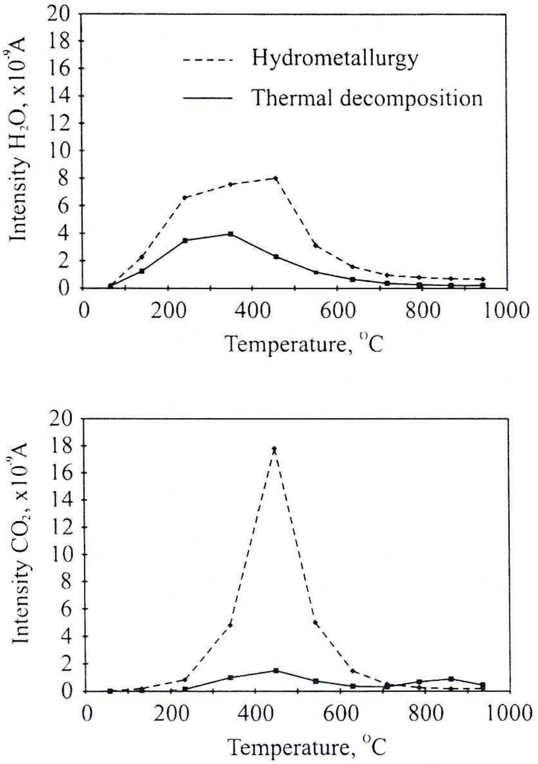

Fig. 10. QMS analysis of hydrometallurgical and thermally decomposed extrafine cobalt powders [14]

TABLE 1

Main impurities (in ppm) characteristic of cobalt powders obtained from various manufacturing routes [3,18]

Element	Thermal decomposition of cobalt oxalate	Reduction of oxides		Hydrometallurgy	
		$CoCl_2$ precursor	$Co(OH)_2$ precursor	Ultrafine powder	Mesh powder
Fe	<200	100	80	<200	30
Ni	<500	700	250	<3000	2000
Si	<300	400	150	<50	30
Na	<10	100	250	<100	20
Ca	<40	400	150	<20	<5
Mg	<10	200	250	<10	<5
Ag	<5	–	<5	<1500	600
S	<10	100	150	<100	200

4. Atomisation

Coarse cobalt powders can easily be produced by breaking a stream of molten metal by a jet or jets of inert gas or water. This inexpensive technique yields a product containing very low levels of impurities unattainable via oxide reduction route. Due to unacceptable cold compactibility and compressibility at temperatures typical to the hot pressing operation, the atomised powders do not lend themselves to the production of diamond impregnated tools. Recent studies showed, however, that both water and gas atomised powders can successfully be used as partial substitutes for the chemically produced material. Mixtures containing from 30 to 50-wt.% of a water atomised material can be processed to nearly full density in the manner typical to conventionally used powders [19].

The flow diagram for the processing of cobalt, and cobalt-base alloy, powders by means of atomisation is shown in Fig 11.

In gas atomisation, the metal melting is normally conducted under air. The atomisation gas (nitrogen or argon) pressures are typically in the range from 1 to 3 MPa but, in some cases, may reach 10 MPa. Thus velocities in the atomisation zone range from about 100 to 500 m/s [20]. The fineness of the powder depends on the amount of kinetic energy transferred from the atomising medium to the melt stream. Therefore, in addition to the liquid metal viscosity, both geometry of the atomising system and gas velocity play equally important role [21].

Median particle sizes are normally in the 40-80 micron range [22]. Therefore the *400mesh* market for diamond tools does not consider any consumption of gas atomised, pure cobalt powder paying more attention to the wear resistant cobalt-base alloys. As shown in Fig 12, a typical gas atomised powder is spherical in shape with adherent fine satellite particles.

In water atomisation, melting procedure is identical to that for gas atomisation. In this method high pressure water jets are used to disintegrate the stream of molten metal. Water has a density 1000 times higher than gas so energy density is high and finer particles can be more easily made. The dependence of particle size on water pressure is given in Table 2.

Particles finer than 38μm (FSSS = 11.7μm [19]) can be made at low cost by high pressure water atomisation and hence pure cobalt powders thereby produced have recently been commercialised with the expectation of imparting free cutting ability to the diamond impregnated tool [23].

Scanning electron image of irregularly shaped, water atomised cobalt powder is shown in Fig 13.

TABLE 2

Effect of water pressure on median particle size [22]

Process	Water pressure MPa	Median particle size μm
High pressure water atomisation	15 30	~ 50 23–30
Ultra high pressure water atomisation	50 100	20–25 ~ 10⁽¹⁾

(1) extrapolated value

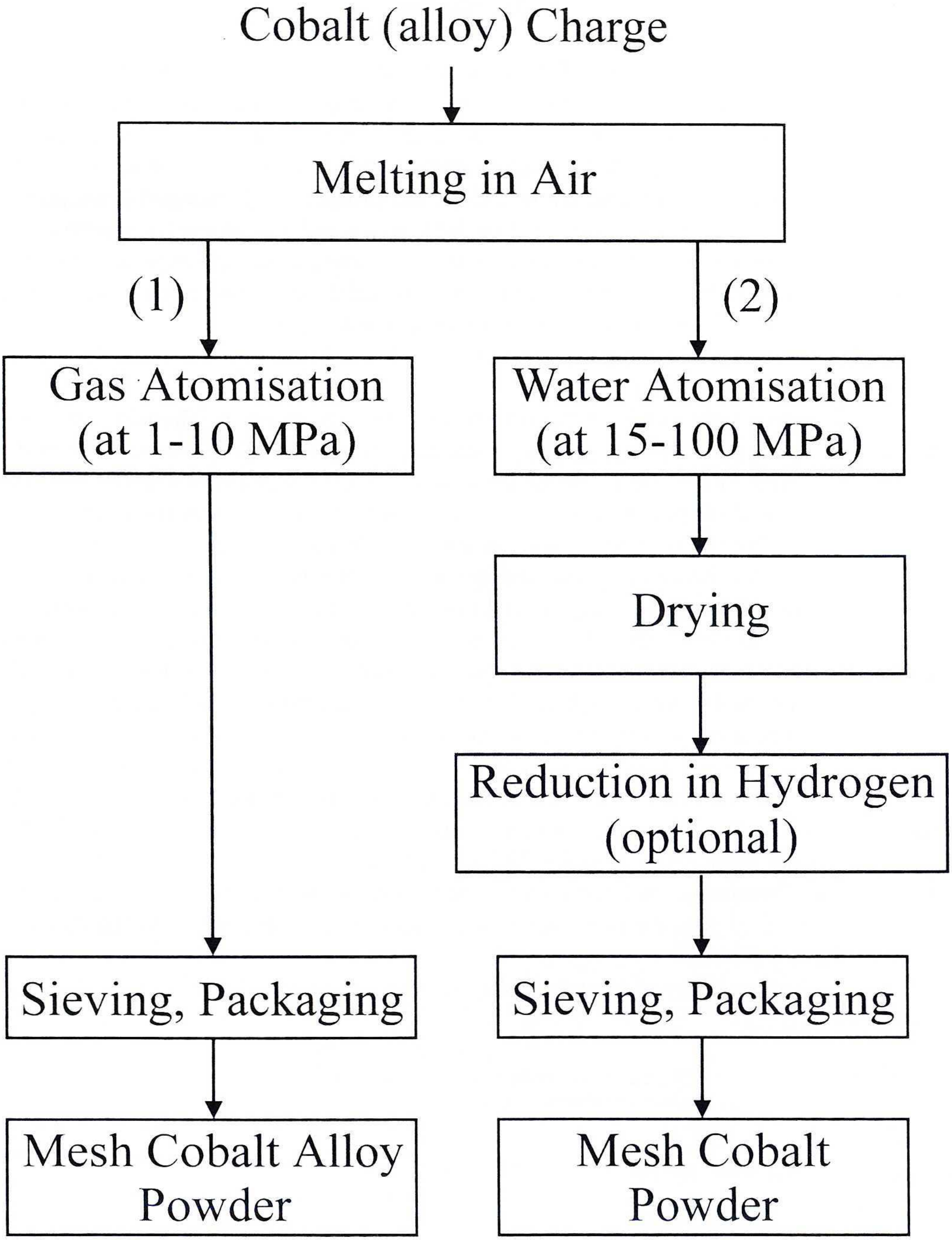

Fig. 11. Cobalt powder production by means of atomisation of molten metal

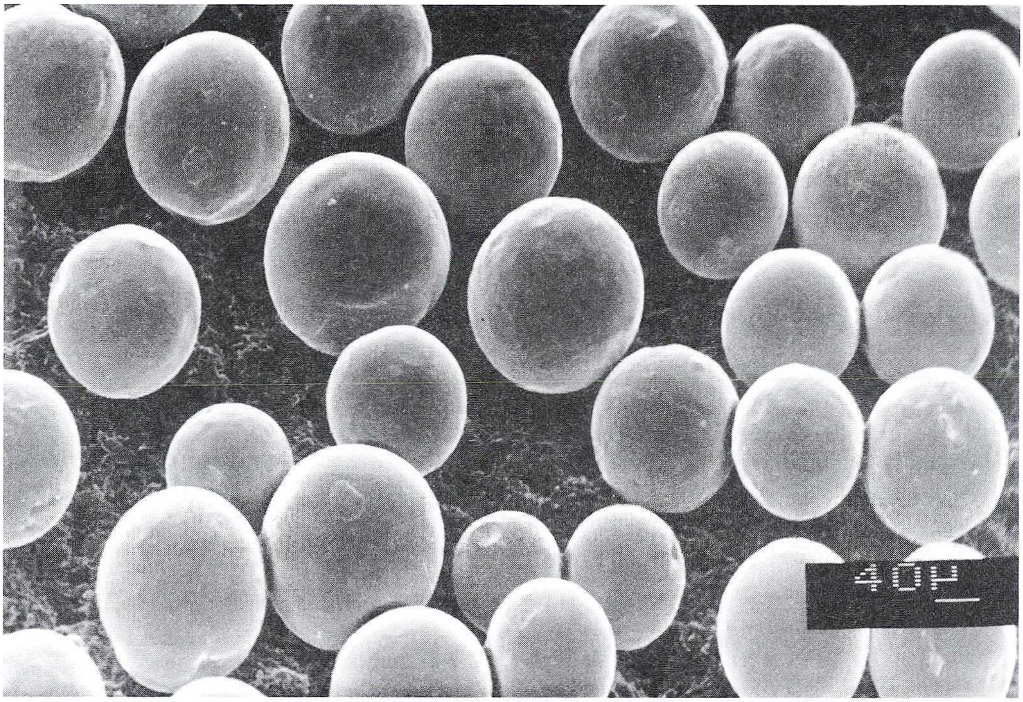

Fig. 12. SEM micrograph of gas atomised cobalt-base alloy (Stellite) powder

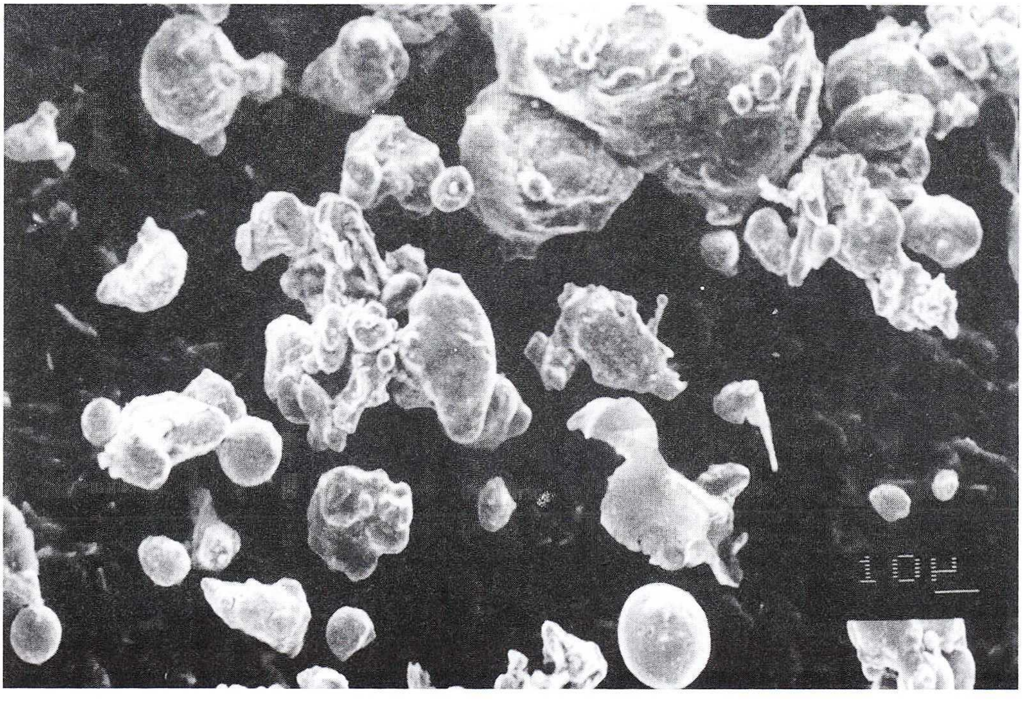

Fig. 13. SEM micrograph of water atomised cobalt powder

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REFERENCES

[1] Determination of average particle size of metal powders using the Fisher Subsieve Sizer, MPIF Standard 32, 1995.

[2] M. H. Tikkanen, A. Taskinen, P. Taskinen, Characteristic properties of cobalt powder suitable for hard metal production, Powder Metallurgy, **18**, 36, 259–282 (1975).

[3] Properties of hydrometallurgically produced cobalt powder, Sherritt Neomet Ltd.

[4] M. Giulietti, M. Danese, R. Guardani, Production of metallic powdered cobalt by precipitation in solution, Proc. Symposium on Industrial Crystallisation, **2**, 5–157–5–161 (1993).

[5] M. A. Rabah, I. F. Hewaidy, F. E. Farghaly, Recovery of molybdenum and cobalt powders from spent hydrogenation catalyst, Powder Metallurgy, **40**, 4, 283–288 (1997).

[6] V. Rosenband, C. Sokolinsky, ReMPTech looks for fine alternative, Metal Powder Report, 16–19, November 1999.

[7] W. Kunda, J. P. Warner, V. N. Mackiw, The hydrometallurgical production of cobalt, The Canadian Mining and Metallurgical Bulletin, January, 1–5, 1962.

[8] M. A. Clegg: Production of nickel, cobalt, and composite powders by hydrometallurgy, Metal Powder Report, 73–80, February 1982.

[9] E. De Bie, P. Doyen, Production and utilization of cobalt powders, Cobalt, 22–32 (1961).

[10] Hydrometallurgically processing fine cobalt, Metal Powder Report, 18–22, December 1996.

[11] G. S. Whiting, G. L. Bolton, B. R. Sutherland, B. H. Rosof, Production of very fine hydrometalurgical powders, Advances in Powder Metallurgy & Particulate Materials, 1, 107–117 (1993).

[12] J. C. Currie, B. R. Sutherland, H. C. Scheie, Production of metallic cobalt powder, Patent International Application No PCT/CA 93/00454, WO 94/10350, 11 May 1994.

[13] Oxygen effects, Union Miniere, Fact sheet, Issue 1, August 1998.

[14] E. Post, Laboratory Report No. 820.025/97, Netzsch Thermische Analyse, Selb, Germany, 11 March 1997. Unpublished.

[15] Hydrometallurgy cobalt, Union Miniere, Fact sheet, Issue 1, August 1998.

[16] Cobalt powders for diamond tools, Union Miniere (technical brochure).

[17] R. S. Young (Ed.), Cobalt. Its Chemistry, Metallurgy, and Uses. Reinhold Publishing Corporation, New York, Chapman & Hall, Ltd., London, 70 (1960).

[18] M. Figlarz, C. Ducamp-Sanguesa, F. Fievet, J-P. Lagier, Preparation and characterization of monodisperse Co, Ni, Cu, and Ag metal particles of uniform shape, Advances in Powder Metallurgy & Particulate Materials – 1992, MPIF, Princeton, NJ, **1**, 179–192.

[19] M. Höhne, Cobalt metal powder and composite sintered articles produced therefrom, US Patent No: 5,482,530, Jan. 9, 1996.

[20] J. J. Dunkley, Atomising Systems Limited, Sheffield, U.K. – private communication.

[21] A. Lawley, An overview of powder atomization processes and fundamentals, The International Journal of Powder Metallurgy & Powder Technology, **13**, 3, 169–188 (1977).

[22] J. Dunkley, Cobalt powder atomisation, Cobalt News, pp. 4–6, January 97.

[23] M. Höhne, Cobalt in diamond tools, Proc. Seminar on PM Diamond Tools, Lausanne, Switzerland, November 2–3, 1995.

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