METALLIC COBALT PARTICLES
(WITH OR WITHOUT TUNGSTEN CARBIDE)

1. Exposure Data

1.1 Chemical and physical data

1.1.1 *Nomenclature*

Metallic cobalt

Chem. Abstr. Serv. Reg. No.: 7440-48-4
Deleted CAS Reg. No.: 177256-35-8; 184637-91-0; 195161-79-6
Chem. Abstr. Name: Cobalt
IUPAC Systematic Name: Cobalt
Synonyms: C.I. 77320; Cobalt element; Cobalt-59

Cobalt sulfate heptahydrate

Chem. Abstr. Serv. Reg. No.: 10026-24-1
Chem. Abstr. Name: Sulfuric acid, cobalt(2+) salt (1:1), heptahydrate
IUPAC Systematic Name: Cobaltous sulfate heptahydrate
Synonyms: Cobalt monosulfate heptahydrate; cobalt(II) sulfate heptahydrate; cobalt(II) sulfate (1:1), heptahydrate

Tungsten carbide

Chem. Abstr. Serv. Reg. No.: 12070-12-1
Deleted CAS Reg. No.: 52555-87-0; 182169-08-0; 182169-11-5; 188300-42-7; 188300-43-8; 188300-44-9; 188300-45-0
Chem. Abstr. Name: Tungsten carbide
IUPAC Systematic Name: Tungsten carbide
Synonyms: Tungsten carbide (WC); tungsten monocarbide; tungsten monocarbide (WC)

1.1.2 *Molecular formulae and relative molecular mass*

Co	Relative atomic mass: 58.93
$CoSO_4.7H_2O$	Relative molecular mass: 281.10
WC	Relative molecular mass: 195.85

1.1.3 *Chemical and physical properties of the pure substance* (from Lide, 2003, unless otherwise specified)

Cobalt

(*a*) *Description*: Hexagonal or cubic crystalline grey metal; exists in two allotropic modifications; both forms can exist at room temperature, although the hexagonal form is more stable than the cubic form (O'Neil, 2001)
(*b*) *Boiling-point*: 2927 °C
(*c*) *Melting-point*: 1495 °C
(*d*) *Density*: 8.86 g/cm^3
(*e*) *Solubility*: Soluble in dilute acids; ultrafine metal cobalt powder is soluble in water at 1.1 mg/L (Kyono *et al.*, 1992)

Cobalt sulfate heptahydrate

(*a*) *Description*: Pink to red monoclinic, prismatic crystals (O'Neil, 2001)
(*b*) *Melting-point*: 41 °C, decomposes
(*c*) *Density*: 2.03 g/cm^3
(*d*) *Solubility*: Soluble in water; slightly soluble in ethanol and methanol (O'Neil, 2001)

Tungsten carbide

(*a*) *Description*: Grey hexagonal crystal
(*b*) *Boiling-point*: 6000 °C (Reade Advanced Materials, 1997)
(*c*) *Melting-point*: 2785 °C
(*d*) *Density*: 15.6 g/cm^3
(*e*) *Solubility*: Insoluble in water; soluble in nitric and hydrofluoric acids

1.1.4 *Technical products and impurities*

Cobalt-metal and tungsten carbide powders are produced widely in high purity for use in the hard-metal industry, in the manufacture of superalloys and for other applications. [Superalloys are alloys usually based on group VIIIA elements (iron, cobalt, nickel) developed for elevated temperature use, where relatively severe mechanical stressing is encountered and where high surface stability is frequently required (Cobalt Development Institute, 2003).] Specifications of cobalt-metal powders are closely controlled to meet the requirements of particular applications. Commercial cobalt-metal powders are available in purities ranging from 99% to ≥ 99.999% in many grades, particle size ranges and forms; commercial tungsten carbide powders are available in purities ranging from 93% to 99.9%, also in many grades, particle size ranges and forms. Tables 1 and 2 show the specifications for selected cobalt-metal and tungsten-carbide powder products.

1.1.5 *Analysis*

(*a*) *Biological monitoring*

The presence of cobalt in samples of whole blood, plasma, serum and urine is used as a biological indicator of exposure to cobalt (Ichikawa *et al.*, 1985; Ferioli *et al.*, 1987; Angerer *et al.*, 1989). Soluble cobalt compounds are readily absorbed and excreted in the urine (see Section 4.1) and therefore urinary cobalt is considered a good indicator of exposure to these, but not to insoluble cobalt compounds (Cornelis *et al.*, 1995).

For an accurate determination of cobalt concentration in body fluids, it is necessary to use blood collection devices which do not themselves produce detectable amounts of cobalt. All containers must be washed with high purity acids. Urine samples may be acidified with high purity nitric acid and stored at 4 °C for one week, or at –20 °C for longer periods, prior to analysis (Minoia *et al.*, 1992; Cornelis *et al.*, 1995).

(*b*) *Analytical methods for workplace air and biological monitoring*

Analytical methods used until 1988 for the determination of cobalt in air particulates (for workplace air monitoring) and in biological materials (for biological monitoring) have been reviewed in a previous monograph on cobalt and its compounds (IARC, 1991). These methods are primarily flame and graphite-furnace atomic absorption spectrometry (F-AAS, and GF-AAS, respectively) and inductively coupled plasma atomic emission spectrometry (ICP-AES). Minor applications of electrochemical methods, namely adsorption voltametry, differential pulse anodic stripping voltametry and neutron activation analysis (NAA) for the determination of cobalt in serum have also been mentioned (IARC, 1991; Cornelis *et al.*, 1995).

Inductively coupled plasma mass spectrometry (ICP-MS) has become more widely available since the early 1990s, and is increasingly used for multi-elemental analysis of human blood, serum or urine, including determination of cobalt concentrations in these body fluids (Schmit *et al.*, 1991; Moens & Dams, 1995; Barany *et al.*, 1997; Sariego Muñiz *et al.*, 1999, 2001).

(*c*) *Reference values for occupationally non-exposed populations*

Normal concentrations of cobalt in the body fluids of healthy individuals are uncertain. Cornelis *et al.* (1995) give a range of 0.1–1 μg/L for cobalt concentrations in urine. Results obtained in national surveys of healthy adults yielded a mean cobalt concentration in urine of 0.57 μg/L in a population sample in Italy (Minoia *et al.*, 1990) and of 0.46 μg/L in a population sample in the United Kingdom of Great Britain and Northern

Table 1. Specifications for selected technical cobalt-metal powder products

Minimum % cobalt	Maximum %[a] contaminants permitted	Grade/particle size/crystal structure	Country of production	Reference
99.85	C, 0.02; S, 0.001; P, 0.01; Fe, 0.015	Not stated	India	Jayesh Group (2003)
> 99.95	C, 0.0015–0.002; Cu, < 0.0005; H, < 0.0005; Fe, < 0.001; Pb, < 0.0002; Ni, 0.03–0.05; N, < 0.0001; O, < 0.005; Si, < 0.0003; S, 0.0002–0.035; Zn, 0.0001–0.0002	Electrolytic and S-type/ 25 mm cut squares	Canada	Falconbridge (2002)
99.9	Bi, < 0.00002; C, 0.0025; Cu, 0.0001; H, 0.0002; Fe, 0.0004; Pb, 0.0003; Ni, 0.095; N, 0.0004; O, 0.005; Se, < 0.00002; S, 0.0005; Zn, 0.0008	Electrolytic rounds/button-shaped pieces circa 35 mm in diameter and circa 5 mm thick	Canada	Inco Ltd (2003)
99.999	[mg/kg] Cu, Cd, Pb, Cr, Al, Ag, Na, Sb, W, Li, Mg, Mn, Mo, Si, Ti, Cl, K, Ca and Ni, < 1; Fe, < 2; Zn and As, < 5; S, < 10; C, < 20	Shiny silver-grey cathode plates/hexagonal	Belgium	Umicore Specialty Metals (2002)
99.5	Ni, 0.05; Fe, 0.11; Mn, 0.01; Cu, 0.007; Pb, < 0.001; Zn, 0.003; Si and Ca, 0.04; Mg, 0.02; Na, 0.005; S, 0.01; C, 0.025; O_2, 0.30	Coarse particle/400 or 100 mesh/50% hexagonal, 50% cubic	Belgium	Umicore Specialty Metals (2002)
99.8	Ni, 0.15; Ag, 0.02; Fe, 0.003; Mg, Mn and Cu, < 0.0005; Zn and Na, 0.001; Al, Ca and Si, < 0.001; Pb, < 0.002; S, 0.006; C, 0.07; O_2, 0.5	5M powder/3.3–4.7 µm/ 90% hexagonal, 10% cubic	Belgium	Umicore Specialty Metals (2002)

Table 1 (contd)

Minimum % cobalt	Maximum %[a] contaminants permitted	Grade/particle size/crystal structure	Country of production	Reference
99.88	Ni, 0.05; Fe, 0.005; Mg, Mn, Pb and S, < 0.001; Ca, Cu and Zn, 0.003; Si, < 0.002; Na 0.002; C, 0.015; O_2, 0.35	Extra fine powder/1.2–1.5 µm/70% hexagonal, 30% cubic	Belgium	Umicore Specialty Metals (2002)
99.8	Ni, 0.10; Ag, 0.12; Al, Fe, Na and Pb, < 0.001; Cu, Mg and Mn, < 0.0005; Zn, 0.0011; Ca, 0.0013; Si, < 0.003; S, 0.005; C, 0.22; O_2, 0.8	Half micron powder/ 0.55 µm/80% hexagonal, 20% cubic	Belgium	Umicore Specialty Metals (2002)
99.7	[mg/kg] C, 1000; Ni and Cl, 500; Fe and Ca, 70; Na, 60; Mg, 30; Cu and Zn, 20; Al, Mn, Pb and S, < 10; Si, < 20; O_2, 0.8%	Submicron-size powder/ 0.8 µm/85% hexagonal, 15% cubic	Belgium	Umicore Specialty Metals (2002)
99.8	Ni, 0.15; Ag, 0.12; Fe and Na, 0.001; Al, Cu, Mg and Mn, < 0.0005; Zn, 0.0013; Ca, 0.0015; Pb, < 0.002; Si, < 0.001; S, 0.006; C, 0.18; O_2, 0.7	Ultrafine powder/0.9 µm/ 90% hexagonal, 10% cubic	Belgium	Umicore Specialty Metals (2002)
> 99.8	[mg/kg] Ca, Fe and Si, < 100; Ni, < 400–1000; O_2, < 0.8%	Extrafine powder/1.05–1.45 µm	France	Eurotungstene Metal Powders (2003)
99.80	C and Ni, 0.20; Ag, 0.15; Fe, 0.02; Cu, 0.005; S, 0.01; O, 0.80	Ultrafine powder/0.9–8.0 µm	Luxembourg	Foxmet SA (2003)
99.8	[mg/kg] Ni, 600; C, 300; Fe, 100; Cu and S, 50; O, 0.50%	Extrafine powder/1.40–3.90 µm	Luxembourg	Foxmet SA (2003)

Table 1 (contd)

Minimum % cobalt	Maximum %[a] contaminants permitted	Grade/particle size/crystal structure	Country of production	Reference
99.20	[mg/kg] Ni and Fe, 1000; Ca, 750; C and S, 300; O, 0.50%	Fine powder-400 mesh/4.2–14.0 µm	Luxembourg	Foxmet SA (2003)
99.90	Ni, 0.30; C, 0.10; Fe and S, 0.01; Cu, 0.001; O, 0.60	Fine powder-5M/4.0 µm	Luxembourg	Foxmet SA (2003)
99.80	Ni, 0.05; C, 0.10; Fe, 0.003; S, 0.03; Cu, 0.002	Coarse powder-‘S’ grade/75–600 µm	Luxembourg	Foxmet SA (2003)
99.8	[mg/kg] C, 1000; S, 350; Ni, 200; Fe, 35; Cu and Zn, 15	Coarse powder-‘DGC’ grade/45–600 µm	Luxembourg	Foxmet SA (2003)
Not stated	Not stated	Coarse powder-100 & 400 mesh; battery grade briquette; extrafine powder (standard & high density); submicron (0.8 µm) powder	USA	OM Group (2003)

[a] Unless stated otherwise

Table 2. Specifications for selected technical tungsten-carbide (WC) powder products

Minimum % WC	Maximum %[a] contaminants permitted	Grade/particle size	Country of production	Reference
Not stated	Total C, 6.11–6.16; free C, 0.03; [mg/kg] Al, Cr and Na, 10; Ca and Ni, 20; Co, Cu, K, Mg and Mn, 5; Mo, 50; Si and Fe, 30	100–200 mesh 0.7–20.0 µm	Israel	Metal-Tech Ltd (2003)
93–94	Total C, 6; free C, 0.04	Mesh size, 200	India	Jayesh Group (2003)
99.70–99.90	Total C, 6.08–6.29; free C, 0.05–0.16; Fe, 0.02; Mo, 0.01	Standard grade/0.7–12 µm	Japan	Japan New Metals Co. Ltd (2003)
Not stated	Total C, 6.05–6.25; free C, 0.10; Fe, 0.05; Mo, 0.02; Cr, 1; V, 1	Fine grade/0.45–0.75 µm	Japan	Japan New Metals Co. Ltd (2003)
99.8	Total C, 6.13; free C, 0.10; Fe, 0.05; Mo, 0.02	Standard grade/0.7–7.1 µm	Japan	A.L.M.T. Corp. (2003)
99.8	Total C, 6.13; free C, 0.05; Fe, 0.02; Mo, 0.02	Coarse grade/2.5–16 µm	Japan	A.L.M.T. Corp. (2003)
Not stated	Total C, 6.15–6.20; free C, 0.15–0.25; Fe, 0.02; Mo, 0.02	Ultrafine grade/0.1–0.70 µm	Japan	A.L.M.T. Corp. (2003)
Not stated	Total C, 6.11–6.18; free C, < 0.08; [mg/kg] Al and Ca, < 10; Cr, < 40; Fe, < 200; K, Mg and Na, < 15; Mo, < 50; Ni, < 25; Si, < 40; V, 1400–2000; O_2, < 0.16–0.25%	0.6–1.1 µm (doped with 0.2% VC)	France	Eurotungstene Metal Powders (2003)
Not stated	Combined C, 6.05 min.; free C, 0.08; O_2, 0.025–0.030	2.6–5.5 µm	France	Eurotungstene Metal Powders (2003)

Table 2 (contd)

Minimum % WC	Maximum %[a] contaminants permitted	Grade/particle size	Country of production	Reference
Not stated	Total C, 3.9–4.2; free C, 0.1; Fe, 0.4	Fused powders (eutectic mixture of WC and W_2C)/ < 45–450 µm	France	Eurotungstene Metal Powders (2003)
Not stated	Not stated	DS/0.45–2.5 µm MAS/5.0–50 µm HC/2.5–14 µm DR/3–10 µm MA/4–12 µm	Germany	Starck (2003)
99.7	Total C, 6.13; free C, 0.06; [mg/kg] Fe and Mo, 250; Co, 100; Cr, 75; Ca, Ni and Si, 50; Al, 25; Na, 20; Cu, 15	Fine grade powder/0.9–6.3 µm	Luxembourg	Foxmet SA (2003)
Not stated	Total C, 3.90–4.20 ; free C, 0.10; Fe, 0.40; O, 0.10	Fused powder/0–150 µm	Luxembourg	Foxmet SA (2003)
80–88% WC & 12–20% Co	Not stated	pre-alloyed WC/Co powder/ 0–300 µm	Luxembourg	Foxmet SA (2003)
10–50% WC & 50–90% Co	Not stated	Ready-mixed powder	Luxembourg	Foxmet SA (2003)
Not stated	Total C, 6.08–6.24; free C, 0.05; Fe, 0.03; Mo and Nb, 0.15; Ta, 0.1; Ti, 0.20	Macrocrystalline powder/0–420 µm	USA	Kennametal (2003)

Table 2 (contd)

Minimum % WC	Maximum %[a] contaminants permitted	Grade/particle size	Country of production	Reference
Not stated	Not stated	Conventional carburized powder/0.8–4.8 µm Cast carbide vacuum-fused powder/44–2000 µm Chill cast carbide/37–420 µm) Sintered WC/Co hard metal/44–2000 µm	USA	Kennametal (2003)

[a] Unless stated otherwise

Ireland (White & Sabbioni, 1998). Significant differences between concentrations of cobalt in the urine of men and women (median values of [0.22] and [0.39 µg/L], respectively) were reported by Kristiansen *et al.* (1997).

Concentrations of cobalt in blood and serum are expected to be at the lower end of the 0.1–1 µg/L range (Versieck & Cornelis, 1980); a median cobalt concentration in serum of 0.29 µg/L was determined by Iyengar and Woittiez (1988). In an Italian population, Minoia *et al.* (1990) reported median concentrations of cobalt in blood and serum of 0.39 µg/L and 0.21 µg/L, respectively. Alimonti *et al.* (2000) recently reported cobalt concentrations in the range of 0.20–0.43 µg/L in the serum of newborns from an urban area of Rome, suggesting that there is no age dependence in serum cobalt concentrations.

1.2 Production and use

1.2.1 *Production*

(*a*) *Cobalt*

World production of refined cobalt has increased steadily over the last decade, due partly to new operations and partly to a net increase in production by established producers. World demand for cobalt is strongly influenced by general economic conditions and by demand from industries that consume it in large quantities, such as superalloy melters and manufacturers of rechargeable batteries (Shedd, 2003).

World cobalt resources identified to date are estimated at about 15 million tonnes. The vast majority of these resources are in nickel-bearing laterite deposits or, to a much smaller extent, in nickel–copper sulfide deposits in Australia, Canada and the Russian Federation and in the sedimentary copper deposits of the Democratic Republic of Congo and Zambia. In addition, it is postulated that millions of tonnes of cobalt exist in manganese nodules and crusts on the ocean floor (Shedd, 2003).

Cobalt is extracted from several mineral ores, including arsenide, sulfoarsenide (cobaltite), sulfide (chalcocite, carrollite), arsenic-free cobalt–copper (heterogenite), lateritic and oxide ores. Cobalt is recovered from concentrates and occasionally directly from the ore itself by hydrometallurgical, pyrometallurgical and electrometallurgical processes. Cobalt powder can be produced by a number of methods, but those of industrial importance involve the reduction of oxides, the pyrolysis of carboxylates, and the reduction of cobalt ions in aqueous solution with hydrogen under pressure. Very pure cobalt powder is prepared by the decomposition of cobalt carbonyls. Grey cobalt(II) oxide (CoO) or black cobalt(II)/cobalt(III) oxide (Co_3O_4) is reduced to the metal powder by carbon monoxide or hydrogen. The purity of the powder obtained is 99.5% with a particle size of approximately 4 µm, although the density and particle size of the final product depend on the reduction conditions and on the particle size of the parent oxide. The thermal decomposition of cobalt carboxylates such as formate and oxalate in a controlled reducing or neutral atmosphere produces a high-purity (about 99.9%), light, malleable cobalt powder, with a particle size of approximately 1 µm which is particularly suitable for the manufacture of hard metals (see below). The particle size, form and porosity of the powder grains can be changed by altering the pyrolysis conditions (Hodge, 1993; Donaldson, 2003).

World mine and refinery production figures for cobalt from 1997 to 2001 are presented in Tables 3 and 4, respectively (Shedd, 2001). Available information indicates that cobalt is manufactured by five companies in China, four companies each in India and the United States of America (USA), three companies in Japan, and two companies each in Belgium, Brazil, Canada, the Netherlands, the Russian Federation and the United Kingdom. Argentina, France, Germany, Italy, Mexico, Norway, the Philippines, Poland and Turkey each have one manufacturing company (Chemical Information Services, 2003). Other important cobalt-manufacturing countries include Australia, the Democratic Republic of Congo, Finland, Morocco and Zambia (Shedd, 2001).

Table 3. World cobalt mine production by country (in tonnes of cobalt)[a]

Country[b]	1997	1998	1999	2000	2001
Australia	3 000	3 300	4 100	5 600	6 200
Botswana	334	335	331	308	325
Brazil	400	400	700	900	1 100
Canada	5 709	5 861	5 323	5 298	5 334
China	200	40	250	90	150
Cuba	2 358	2 665	2 537	2 943	3 411
Democratic Republic of the Congo	3 500	5 000	6 000	7 000	4 700
France (New Caledonia)	1 000	1 000	1 100	1 200	1 400
Kazakhstan	300	300	300	300	300
Morocco	714	287	863	1 305	1 300
Russian Federation	3 300	3 200	3 300	3 600	3 800
South Africa	465	435	450	580	550
Zambia	6 037	11 900	5 640	4 600	8 000
Zimbabwe	126	138	121	79	95
Total	27 400	34 900	31 000	33 800	36 700

From Shedd (2001)

[a] Figures represent recoverable cobalt content of ores, concentrates or intermediate products from copper, nickel, platinum or zinc operations.

[b] In addition to the countries listed, Bulgaria, Indonesia, the Philippines and Poland are known to produce ores that contain cobalt, but information is inadequate for reliable estimates of output levels.

(*b*) *Metallic carbides*

Carbon reacts with most elements of the periodic table to form a diverse group of compounds known as carbides, some of which have extremely important technological applications.

Table 4. World cobalt refinery production by country (in tonnes of cobalt)[a]

Country[b]	Product	1997	1998	1999	2000	2001
Australia	Metal (including metal powder), oxide, hydroxide	617	1 395	1 700	2 610	3 470
Belgium	Metal powder, oxide, hydroxide	1 200	1 200	950	1 110	1 090
Brazil	Metal	266	364	651	792	889
Canada	Metal (including metal powder), oxide	3 792	4 415	4 196	4 364	4 378
China	Metal	470	410	300	410	450
Democratic Republic of the Congo	Metal	2 808	4 490	5 180	4 320	4 071
Finland	Metal, powder, salts	5 000	5 250	6 200	7 700	8 100
France	Chloride	159	172	181	204	199
India	Metal, salts	110	120	120	206	250
Japan	Metal	264	329	247	311	350
Morocco	Metal	225	242	472	1 200	1 200
Norway	Metal	3 417	3 851	4 009	3 433	3 314
Russian Federation	Unspecified	4 100	3 500	3 600	4 400	5 000
South Africa	Metal, powder, sulfate	316	296	306	397	371
Uganda	Metal	0	0	77	420	634
Zambia	Metal	4 403	4 837	4 236	3 342	4 657
Total		27 100	30 900	32 400	35 200	38 400

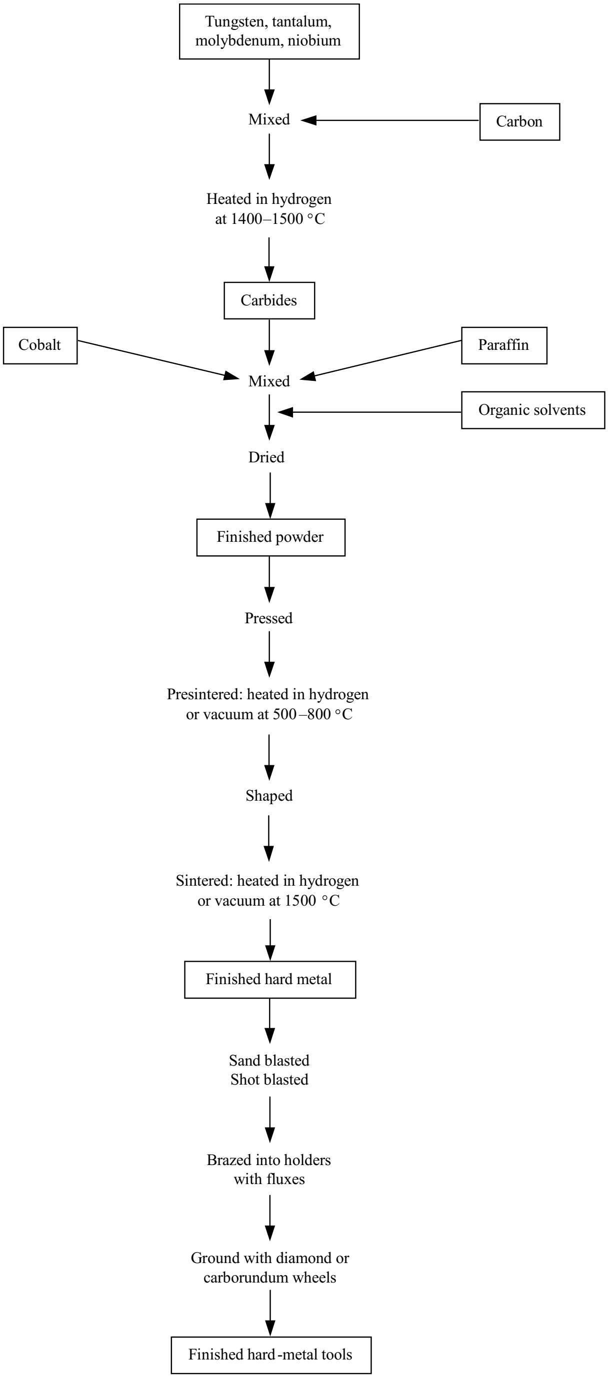
From Shedd (2001)

[a] Figures represent cobalt refined from ores, concentrates or intermediate products and do not include production of downstream products from refined cobalt.

[b] In addition to the countries listed, Germany and Slovakia may produce cobalt, but available information is inadequate to make reliable estimates of production.

Metallic carbides (industrial hard carbides) comprise the carbides of metals of groups IVB–VIB. Metallic carbides combine the physical properties of ceramics with the electronic nature of metals; they are hard and strong, but at the same time good conductors of heat and electricity (Oyama & Kieffer, 1992). Tungsten carbide, titanium carbide and tantalum carbide are used as structural materials in extremely high temperatures or in corrosive atmospheres. Carbides are generally stable at high temperatures and metallic carbides are prepared by the direct reaction between carbon and metals at high temperatures. For example, fine tungsten powders blended with carbon and heated in a hydrogen atmosphere at 1400–1500 °C produce tungsten carbide (WC) particles varying in size from 0.5 to 30 µm. Each particle is composed of numerous tungsten carbide crystals. Small amounts of vanadium, chromium or tantalum are sometimes added to tungsten and carbon powders before carburization to produce very fine (< 1 µm) tungsten carbide powders (Stoll & Santhanam, 1992) (Figure 1).

Figure 1. Steps in the manufacture of hard-metal tools



From Kusaka *et al.* (1986)

Available information indicates that tungsten carbide is manufactured by five companies in the USA, four companies in Japan, three companies in Germany and two companies each in Brazil and France. Argentina, Austria, Canada, India, Israel, Portugal and the Republic of Korea each have one manufacturing company (Chemical Information Services, 2003).

(*c*) *Hard metals*

Hard metals are materials in which metallic carbides are bound together or cemented by a soft and ductile metal binder, usually cobalt or nickel. Although the term 'cemented carbide' is widely used in the USA, these materials are better known internationally as 'hard metals' (Santhanam, 1992). Hard metals are manufactured by a powder metallurgy process consisting of a sequence of carefully-controlled steps designed to obtain a final product with specific properties, microstructure and performance (Santhanam, 1992).

Figure 1 illustrates the steps involved in the preparation of hard metals and the manufacture of hard-metal tools. The carbides or carbide solid solution powders are prepared, blended, compacted, presintered and shaped, and subjected to sintering and postsintering operations. The sintered product (finished hard metal) may be either put to use directly, or ground, polished and coated (Santhanam, 1992). [Sintering is the agglomeration of metal powders at temperatures below their melting-point, as in powder metallurgy; while heat and pressure are essential, decrease in surface area is the critical factor; sintering increases strength, conductivity and density (Lewis, 2001).]

The binder metal (cobalt or nickel) is obtained as a very fine powder and is blended with carbide powders in ball mills, vibratory mills or attritors [grinding machines] using carbide balls. The mills are lined with carbide, low-carbon steel or stainless-steel sleeves. Intensive milling is necessary to break up the initial carbide crystallites and disperse the cobalt among the carbide particles to enhance wetting by cobalt during sintering. Milling is performed under an organic liquid such as alcohol, hexane, heptane or acetone; in the process, a solid lubricant such as paraffin wax or poly(ethylene glycol) is added to the powder blend to strengthen the pressed or consolidated powder mix. After milling, the organic liquid is removed by drying. In a spray-drying process, commonly used in the hard-metal industry, a hot inert gas such as nitrogen impinges on a stream of carbide particles to produce free-flowing spherical powder aggregates (Santhanam, 1992).

The milled and dried grade powders are pressed to desired shapes in hydraulic or mechanical presses. Special shapes may require a presintering operation followed by machining or grinding to the final form. Cold isostatic pressing, followed by green forming [forming the powder into the desired shape], is also common in the manufacture of wear-resistant components and metal-forming tools. Rods and wires are formed by an extrusion process (Santhanam, 1992).

For sintering, the pressed compacts are set on graphite trays and are heated initially to approximately 500 °C in an atmosphere of hydrogen or in a vacuum to remove the lubricant. Subsequently, the compacts are heated under vacuum to a final sintering temperature ranging from 1350 to 1550 °C, depending on the amount of metal binder and the microstructure desired. During final sintering, the binder melts and draws the carbide particles together, shrinking the compact by 17–25% (on a linear scale) and yielding a virtually pore-free, fully dense product (Santhanam, 1992).

In the 1970s, the hard-metal industry adapted hot isostatic pressing (HIP) technology to remove any residual internal porosity, pits or flaws from the sintered product. The HIP process involves reheating vacuum-sintered material to a temperature 25–50 °C less than the sintering temperature under a gaseous (argon) pressure of 100–150 MPa (14 500–21 750 psi). An alternative method developed in the early 1980s, the sinter-HIP process, uses low-pressure HIP, up to 7 MPa (1015 psi), combined with vacuum sintering. The pressure is applied at the sintering temperature when the metallic binder is still molten, resulting in void-free products.

After sintering, hard-metal products that require shaping to meet surface finish, tolerance or geometric requirements undergo grinding with metal-bonded diamond wheels or lapping with diamond-containing slurries (Santhanam, 1992).

Recycling of hard-metal scrap is of growing importance and several methods are available. In one method, the scrap is heated to 1700–1800 °C in a vacuum furnace to vaporize some of the cobalt and embrittle the material. After removal from the furnace, the material is crushed and screened. [Screening is the separation of an aggregate mixture into two or more portions according to particle size, by passing the mixture through one or more standard screens.] In chemical recycling, the cobalt is removed by leaching, leaving carbide particles intact. In the zinc reclaim process, commercialized in the late 1970s, the cleaned scrap is heated with molten zinc in an electric furnace at approximately 800 °C under an inert gas. The zinc reacts with the cobalt binder and the carbide pieces swell to more than twice their original volume. The zinc is distilled off under vacuum and reclaimed. The carbide pieces are pulverized and screened to produce a fine powder. The cobalt is still present in the particles and there is no change in grain size from the original sintered scrap. The coldstream reclaim method uses a high velocity airstream to accelerate hard-metal particles with sufficient energy to cause them to fracture against a target surface. This process, so called because the air cools as it expands from the nozzles, is used in combination with the zinc reclaim process (Santhanam, 1992).

(*d*) *Cobalt alloys*

Multimetallic complexes, which include cobalt alloys, are the components in tool steels and Stellite-type alloys that are responsible for hardness, wear resistance and excellent cutting performance (Oyama & Kieffer, 1992). [Stellite is an alloy containing cobalt and chromium, and sometimes other metals.]

1.2.2 *Use*

Cobalt compounds have been used as blue colouring agents in ceramic and glass for thousands of years, although most of the blue colour of ancient glasses and glazes has been found to be due to copper. Cobalt has been found in Egyptian pottery dating from about 2600 BC, in Persian glass beads dating from 2250 BC, in Greek vases and in pottery from Persia and Syria from the early Christian era, in Chinese pottery from the Tang (600–900 AD) and Ming (1350–1650 AD) dynasties and in Venetian glass from the early fifteenth century. Leonardo Da Vinci was one of the first artists to use cobalt as a brilliant blue pigment in oil paints. The pigment was probably produced by fusing an ore containing cobalt oxide with potash and silica to produce a glass-like material (a smalt), which was then reduced to the powdered pigment. In the sixteenth century, a blue pigment called zaffre was produced from silver–cobalt–bismuth–nickel–arsenate ores in Saxony (IARC, 1991; Donaldson, 2003).

It was not until the twentieth century, however, that cobalt was used for industrial purposes. In 1907, a scientist in the USA, E. Haynes, patented Stellite-type alloys that were very resistant to corrosion and wear at high temperatures (Kirk, 1985). Cobalt was first added to tungsten carbide in 1923 to produce hard metals (Anon., 1989) and permanent magnetic alloys known as Alnicos (cobalt added to alloys of aluminum, nickel and iron) were first described in 1933 (Johnston, 1988; IARC, 1991).

Cobalt is an important metal with many diverse industrial and military applications. Its largest use is in superalloys, which are used primarily to make parts for aircraft gas turbine engines. Cobalt is also an important component of steel when high strength is required, as it increases the tempering resistance of steel; high-strength steels (maraging steels) are used in the aerospace, machine tool and marine equipment industry. Cobalt is also used to make magnets, corrosion- and wear-resistant alloys, high-speed steels, hard-metal and cobalt–diamond tools, cobalt discs and other cutting and grinding tools, catalysts for the petroleum and chemical industries, drying agents for paints, varnishes and inks, ground coats for porcelain enamels, pigments, battery electrodes, steel-belted radial tyres, airbags in automobiles and magnetic recording media (IARC, 1991; Shedd, 2001; Donaldson, 2003).

The major uses of cobalt worldwide in 2003 included: superalloys, 20%; other alloys, 10%; hard metals, 13%; wear-resistant materials, 6%; magnets, 7%; recording materials, 5%; ceramics/enamels/pigments, 12%; batteries, 8%; tyres, paint driers, soaps, 9%; and catalysts, 10% (Hawkins, 2004). According to data from 2002, in the USA, approximately 51% of cobalt was used in superalloys; 8% in cemented carbides (hard metals); 19% in various other metallic uses; and the remaining 22% in a variety of chemical applications (Shedd, 2003).

Cobalt-metal powder (100 mesh or chemical grade) is a common raw material for metal carboxylate production and catalyst manufacture. Fine cobalt powders (400 mesh) are used in hard metals, diamond tools, batteries, magnets, cobalt-containing powdered metal alloys and specialty chemicals. High-purity (99.8%) cobalt briquettes [small lumps or blocks of compressed granular material] are used as raw materials for the production of inorganic cobalt salts and cobalt alloys. Battery-grade cobalt briquettes are used to prepare mixed nitrate solutions for the production of sintered-type nickel hydroxide electrodes. These electrodes are used in nickel–cadmium and nickel–metal hydride batteries. Battery-grade cobalt powders, oxidized as is or after being dissolved in an acid solution, are used as raw materials to produce cobalt oxide precursors for lithium ion and polymer batteries (OM Group, 2003).

The four most important carbides for the production of hard metals are tungsten carbide (WC), titanium carbide (TiC), tantalum carbide (TaC) and niobium carbide (NbC). Traditionally, cemented carbide (hard-metal) inserts and tools for metal-cutting and metal-working have accounted for the largest percentage of carbide industry sales. However, hard-metal tool consumption in non-metal-working fields, notably in the construction and transportation industries, has grown rapidly. In contrast, the demand for primary materials has been somewhat reduced by the use of recycled hard-metal scrap (Santhanam, 1992; Stoll & Santhanam, 1992).

Cobalt sulfate is the usual source of water-soluble cobalt since it is the most economical salt and shows less tendency to deliquesce or dehydrate than the chloride or nitrate salts. It is used in storage batteries, in cobalt electroplating baths, as a drier for lithographic inks and varnishes, in ceramics, enamels and glazes to prevent discolouring and in cobalt pigments for decorating porcelain (O'Neil, 2001).

Uses of other cobalt compounds are described in detail by IARC (1991).

1.3 Occurrence and exposure

1.3.1 *Natural occurrence*

Cobalt occurs in nature in a widespread but dispersed form in many rocks and soils. The cobalt concentration in the earth's crust is about 20 mg/kg. The largest concentrations of cobalt are found in mafic (igneous rocks rich in magnesium and iron and comparatively low in silica) and ultramafic rocks; the average cobalt content in ultramafic rocks is 270 mg/kg, with a nickel:cobalt ratio of 7. Sedimentary rocks contain varying amounts of cobalt, averaging 4 mg/kg in sandstone, 6 mg/kg in carbonate rocks and 40 mg/kg in clays and shales. Concentrations of cobalt in metamorphic rock depend on the amount of the element in the original igneous or sedimentary source. Cobalt has also been found in meteorites (Donaldson *et al.*, 1986; O'Neil, 2001; Donaldson, 2003).

Cobalt salts occur in nature as a small percentage of other metal deposits, particularly copper; cobalt sulfides, oxides and arsenides are the largest mineral sources of cobalt (Schrauzer, 1989; IARC, 1991; Donaldson, 2003).

1.3.2 *Occupational exposure*

Occupational exposure to aerosols containing cobalt metal or solubilized cobalt compounds may occur during the refining of cobalt, the production of alloys, at various stages in the manufacture of hard metals, the maintenance and resharpening of hard-metal tools and blades and during the manufacture and use of diamond tools containing cobalt (see below). However, only about 15% of cobalt produced is used in cemented carbides (hard metals) and diamond tooling and there are many other potential sources of occupational exposure to cobalt (see Section 4, Table 15).

Several studies have reported occupational exposure to cobalt by measuring concentrations in ambient air in industrial sites where hard-metal and diamond grinding wheels were produced. In addition, analytical methods have been recently standardized for the determination of cobalt concentrations in urine and blood (Kristiansen *et al.*, 1997; White, 1999). It should be noted that many workers inhaling different chemical species of cobalt may also be exposed to nickel, tungsten, chromium, arsenic, molybdenum, beryllium, silica and silicates, asbestos, nitrosamines, diamond powders and iron. Exposure to other substances co-occurring with cobalt have also been reported.

(*a*) *Hard-metal production and use*

Exposure to hard-metal dust takes place at all stages of the production of hard metals, but the highest levels of exposure to cobalt have been reported to occur during the weighing, grinding and finishing phases (Reber & Burckhardt, 1970; McDermott, 1971; National Institute for Occupational Safety and Health, 1981; Sprince *et al.*, 1984; Hartung, 1986; Kusaka *et al.*, 1986; Balmes, 1987; Meyer-Bisch *et al.*, 1989; Auchincloss *et al.*, 1992; Stebbins *et al.*, 1992). For example, in two factories in the USA producing hard metals, peak cobalt concentrations in air taken during weighing, mixing and milling exceeded 500 µg/m^3 in more than half of all samples (Sprince *et al.*, 1984), and in powder rooms with poorly-regulated control of cobalt dusts, concentrations of cobalt in air ranged between 10 µg/m^3 and 160 µg/m^3 (Auchincloss *et al.*, 1992).

Table 5 shows the cobalt concentrations in air determined for all stages in the manufacturing process in a study of exposure to hard metals among hard-metal workers in Japan (Kusaka *et al.*, 1986; Kumagai *et al.*, 1996). The concentrations of cobalt and nickel in air were shown to be distributed lognormally (Kusaka *et al.*, 1992; Kumagai *et al.*, 1997). The workers were further studied with respect to prevalence of asthma in association with exposure to cobalt (Kusaka *et al.*, 1996a,b).

Table 6 summarizes data on cobalt concentrations in workplace air and urine of workers in hard-metal production up to 1986 (presented in the previous monograph on cobalt; IARC, 1991), together with more recent studies.

In a factory producing hard metal in Italy, the mean concentration of cobalt in workplace air on Thursday afternoons was 31.7 ± 33.4 µg/m^3, thus exceeding the current ACGIH threshold limit value (TLV) for occupational exposure of 20 µg/m^3 (Scansetti *et al.*, 1998; ACGIH Worldwide®, 2003a). Among hard-metal workers in several small factories in northern Italy, cobalt concentrations in the urine of six operators on machines without aspirators were up to 13 times higher than those in the reference population (Cereda *et al.*, 1994).

A British study reported median concentrations of cobalt in urine of 19 nmol/mmol creatinine in workers in the hard-metal industry and 93 nmol/mmol creatinine in workers manufacturing and handling cobalt powders, salts and pigments in the chemical industry (White & Dyne, 1994).

Table 5. Cobalt concentrations in air in different workshops in the hard-metal industry

Workshop	No. of workers	No. of samples of workplace air	Cobalt concentration ($\mu g/m^3$)					
			AM[a]	GM[b]	Min.	Max.	GSD_W[c]	GSD_B[d]
Powder preparation								
Rotation	15	60	459	211	7	6390	NA	NA
Full-time	2	12	147	107	26	378	1.88	2.27[e]
Press								
Rubber	8	26	339	233	48	2910	2.77	1.00
Steel	23	34	47	31	6	248	2.43	NA
Shaping	67	179	97	57	4	1160	2.56	1.79
Sintering	37	82	24	13	1	145	1.99	1.99
Blasting	3	7	2	2	1	4	1.88	1.00[e]
Electron discharging	10	18	3	2	1	12	2.69	1.00
Wet grinding	191	517	45	21	1	482	2.30	2.31
Dry grinding without ventilation	1	2	1292	NA	1113	1471	NA	NA

From Kusaka *et al.* (1986); Kumagai *et al.* (1996)
NA, not applicable or not available
[a] AM, arithmetic mean
[b] GM, geometric mean
[c] GSD_W, geometric standard deviation within-worker variation
[d] GSD_B, geometric standard deviation between-worker variation
[e] Because number of workers in this job group was small, the GSD_B value is not reliable.

Concentrations of different tungsten species (W, WC, WO, WO_4^{2-}), cobalt and nickel were studied in air and in urine samples from workers in different areas in a hard-metal factory in Germany. The results are summarized in Tables 7–9 (Kraus *et al.*, 2001).

In addition, the process of depositing carbide coatings, by flame or plasma guns, on to softer substrates to harden their surfaces, may also expose workers to hard metals (Rochat *et al.*, 1987; Figueroa *et al.*, 1992).

Hard metals have applications in tools for machining metals, drawing wires, rods and tubes, rolling or pressing, cutting various materials, drilling rocks, cement, brick, road surfaces and glass, and many other uses in which resistance to wear and corrosion are needed, such as high-speed dental drills, ballpoint pens and tyre studs. During the use of hard-metal tools (e.g. in drilling, cutting, sawing), the levels of exposure to cobalt or hard-metal dust are much lower than those found during their manufacture. However, the grinding of stone and wood with hard-metal tools and the maintenance and sharpening of these tools may release cobalt into the air at concentrations of several hundred micrograms per cubic metre (Mosconi *et al.*, 1994; Sala *et al.*, 1994; Sesana *et al.*, 1994).

Table 6. Biomonitoring of occupational exposure to cobalt in the hard-metal industry

Industry/activity	No. of samples	Sex	Concentration of cobalt in ambient air (mg/m^3)[a]	Concentration of cobalt in blood and urine	Comments	Reference
Hard-metal production (two subgroups)	10	M	a. Mean, 0.09 b. Mean, 0.01 (personal samples)	Blood: a. Mean, 10.5 µg/L b. Mean, 0.7 µg/L Urine: a. Mean, [106] µg/L b. Mean, [~3] µg/L Sampling on Friday pm	Significant correlations: air:urine, *r* = 0.79; air:blood, *r* = 0.87; blood:urine, *r* = 0.82	Alexandersson & Lidums (1979); Alexandersson (1988)
Hard-metal production	7	–	Range, 0.180–0.193	Urine: sampling on Sunday (24 h), mean: 11.7 µg/L	Time of sampling: Monday am for basic exposure level; Friday evening for cumulative exposure level	Pellet *et al.* (1984)
Hard-metal grinding (seven subgroups)	153	–	Up to 61 µg/m^3 (stationary samples)	Median values for all subgroups: serum, 2.1 µg/L; urine, 18 µg/L	Significant correlation: serum (x)/urine (y) y = 2.69x + 14.68	Hartung & Schaller (1985)

Hard-metal tool production (11 subgroups)	170
	5
		M
		F
			Mean, 28–367 µg/m^3 (personal samples)	Mean: blood, 3.3–18.7 µg/L; urine, 10–235 µg/L
				Sampling on Wednesday or Thursday at end of shift
					Significant correlations (based on mean values):
					air (x)/urine (y):
					y = 0.67x + 0.9;
					air (x)/blood (y):
					y = 0.004x + 0.23;
					urine (x)/blood (y):
					y = 0.0065x + 0.23
						Ichikawa *et al.* (1985)

Table 6 (contd)

Industry/activity	No. of samples	Sex	Concentration of cobalt in ambient air (mg/m^3)[a]	Concentration of cobalt in blood and urine	Comments	Reference
Hard-metal production (six subgroups)	27	–	Breathable dust: range, 0.3–15 with 4–17% cobalt	Mean: serum, 2.0–18.3 µg/L; urine, 6.4–64.3 µg/g creatinine	Significant correlation: serum:urine, $r = 0.93$	Posma & Dijstelberger (1985)
Hard-metal production	26	M	Range, approx. 0.002–0.1; median, approx. 0.01 (personal samples)	Urine: (a) Monday at end of shift, up to 36 µg/L; (b) Friday at end of shift, up to 63 µg/L	Significant correlations: air (x)/urine (y): (a) $y = 0.29x + 0.83$; (b) $y = 0.70x + 0.80$	Scansetti *et al.* (1985)
Machines with aspirators	6–8	–	Mean ± SD: SS: 3.47 ± 2.15 PS: 4.43 ± 2.70	Urine: GM ± GSD[b], 2.66 ± 1.69 µg/L	SS: stationary sample PS: personal sample	Cereda *et al.* (1994)
Machines without aspirators	6–16	–	Mean ± SD: SS: 6.68 ± 2.27 PS: 47.75 ± 3.53	Urine: GM ± GSD[b], 28.50 ± 3.97 µg/L	SS: stationary sample PS: personal sample	Cereda *et al.* (1994)
Hard-metal workers	6	M + F	Mean ± SD (range): Mon: 21.16 ± 17.18 (11–56) Thu: 31.66 ± 33.37 (7–92)	Urine: mean ± SD (range), 13.23 ± 9.92 (2.58–29.8) 30.87 ± 21.94 (8.17–62.6)	Mon: Monday morning Thu: Thursday afternoon	Scansetti *et al.* (1998)

Updated from Angerer & Heinrich (1988); IARC (1991)
–, not stated
[a] Unless stated otherwise
[b] GM, geometric mean; GSD, geometric standard deviation

Table 7. Concentration of cobalt, nickel and tungsten in air in different workshops in the hard-metal industry

Workshop	Sampling method[a]	No. of samples	Concentration in air (μg/m^3)		
			Cobalt	Tungsten	Nickel
Forming	P	5	0.61–2.82	7.8–97.4	0.23–0.76
	S	1	1.32	6.2	0.30
Pressing	P	3	0.87–116.0	5.3–211.0	0.32–3.0
Powder processing	P	4	7.9–64.3	177.0–254.0	0.76–1.65
Production of tungsten carbide	P	1	0.39	19.1	0.40
Sintering	P	1	343.0	12.1	29.6
	S	1	1.3	5.9	0.07
Grinding (wet)	P	1	0.20	3.3	0.13
Grinding (dry)	P	1	0.48	81.3	0.31
Heavy alloy production	P	2	0.85–1.84	125.0–417.0	0.48–2.17
	S	3	0.63–8.50	50.0–163.0	0.72–1.70

From Kraus *et al.* (2001)

[a] P, personal sampling; S, stationary sampling

Coolants are used in the hard-metal industry during the process of grinding of hard-metal tools after sintering and in their maintenance and resharpening. During such operations, the continuous recycling of coolants has been shown to result in increased concentrations of dissolved cobalt in the metal-working liquid and, hence, a greater potential for exposure to (ionic) cobalt in aerosols released from these fluids (Einarsson *et al.*, 1979; Sjögren *et al.*, 1980; Hahtola *et al.*, 2000; Tan *et al.*, 2000). It has been shown that approximately 60% of cobalt trapped in the coolant was in the dissolved form, the remainder being in the form of suspended carbide particles (Stebbins *et al.*, 1992; Linnainmaa *et al.*, 1996). Mists of the coolants in the wet process of grinding hard-metal tools were found to disturb local ventilation systems (Lichtenstein *et al.*, 1975) and, as a result, cobalt concentrations in the air were higher than those from the dry grinding process (Imbrogno & Alborghetti, 1994). Used coolants may contain nitrosamines (Hartung & Spiegelhalder, 1982).

(*b*) *Cobalt-containing diamond tooling*

Diamond tools are used increasingly to cut stone, marble, glass, wood and other materials and to grind or polish various materials, including diamonds. Although these tools are not composed of hard metal, as they do not contain tungsten carbide, they are often considered in the same category. They are also produced by powder metallurgy, whereby microdiamonds are impregnated in a matrix of compacted, extrafine cobalt powder. Consequently, the proportion of cobalt in bonded diamond tools is higher (up to 90%) than in hard metal.

Table 8. Concentration of cobalt, nickel and tungsten in urine of workers in different workshops in the hard-metal industry

Workshop	No. of workers	Metal[a]	Concentration in urine		
			Mean (95% CI) µg/g creatinine	Median µg/g creatinine	Range µg/g creatinine
Forming	23	Co	13.5 (3.7–23.3)	4.2	0.75–106.4
		W	10.7 (6.7–14.6)	9.5	0.33–33.1
		Ni	0.40 (0.19–0.62)	0.3	< DL[b]–2.2
Pressing	30	Co	5.5 (2.9–8.1)	2.8	0.36–35.9
		W	8.6 (4.1–13.1)	6.5	1.5–71.0
		Ni	0.42 (0.28–0.56)	0.4	< DL–1.6
Heavy alloy production	3	Co	1.6 (0.15–3.0)	1.4	1.1–2.2
		W	24.9 (–34.9–84.8)	21.6	2.6–50.5
		Ni	2.9 (–4.8–10.6)	2.2	0.21–6.3
Powder processing	14	Co	28.5 (–5.6–62.7)	11.2	0.75–227.8
		W	12.2 (8.0–16.5)	11.6	2.6–25.1
		Ni	0.53 (0.04–1.0)	0.1	< DL–3.1
Production of tungsten carbide	4	Co	2.1 (–1.9–6.0)	1.1	0.31–5.7
		W	42.1 (4.3–79.9)	48.9	10.0–60.6
		Ni	0.91 (0.13–1.7)	0.8	0.51–1.5
Sintering	6	Co	4.1 (0.12–6.0)	2.6	0.31–9.6
		W	12.5 (–5.7–30.7)	5.5	2.1–46.8
		Ni	0.47 (0.11–0.84)	0.4	< DL–1.0
Grinding	5	Co	2.2 (–0.57–5.0)	1.4	0.19–6.0
		W	94.4 (11.2–177.5)	70.9	10.6–168.6
		Ni	0.25 (0.02–0.48)	0.2	< DL–0.5
Maintenance	2	Co	3.0 (–18.9–24.9)	3.0	1.3–4.7
		W	3.4 (–21.1–27.8)	3.4	1.5–5.3
		Ni	0.63 (–3.5–4.7)	0.6	0.31–1.0

From Kraus *et al*. (2001)

[a] Co, cobalt; W, tungsten; Ni, nickel

[b] DL, detection limit

Exposures to cobalt have been described during the manufacture and use of cobalt–diamond tools. Diamond polishers have been reported to inhale metallic cobalt, iron and silica from so-called cobalt discs during the polishing of diamond jewels (Demedts *et al*., 1984; Gheysens *et al*., 1985; Van Cutsem *et al*., 1987; Van den Eeckhout *et al*., 1988; Nemery *et al*., 1990; Van den Oever *et al*., 1990; Nemery *et al*., 1992).

Table 9. Monitoring of workplace air and workers' urine for different tungsten species in the hard-metal industry

Workshop	No. of samples[a]	Tungsten species[b]	Air concentration ($\mu g/m^3$) mean (range)	Urine concentration ($\mu g/g$ creatinine) mean (range)
Powder processing	4	W	203.5 (177.0–254.0)	13.8 (2.6–21.1)
Forming, pressing, sintering	8	WC	53.5 (5.3–211.0)	9.5 (2.2–33.1)
Production of tungsten carbide	1	WC, WO, W	19.1	59.6
Grinding (wet)	1	WO_4^{3-}	3.3	70.9
Grinding (dry)	1	WO, WC	81.3	10.6

From Kraus *et al.* (2001)

[a] Same number of samples for air and for urine

[b] W, tungsten metal; WC, tungsten carbide; WO, tungsten oxide; WO_4^{3-}, tungstenate

Concentrations of cobalt in the workplace air in one study were below 50 $\mu g/m^3$ (range, 0.1–45 $\mu g/m^3$) (Van den Oever *et al.*, 1990). In an Italian factory using diamond wheels to cut wood and stone, mean cobalt concentrations in air were found to be 690 $\mu g/m^3$ and dropped to 115 $\mu g/m^3$ after proper ventilation systems were installed (Ferdenzi *et al.*, 1994). Elevated concentrations of cobalt were also reported in the urine of these workers (Van den Oever *et al.*, 1990; Suardi *et al.*, 1994).

(*c*) *Alloys containing cobalt*

Production and use of cobalt alloys gives rise to occupational exposure to cobalt during the welding, grinding and sharpening processes; the welding process with Stellite alloy (cobalt–chromium) was found to generate average concentrations of cobalt in air of 160 $\mu g/m^3$ (Ferri *et al.*, 1994). A factory producing Stellite tools was reported to have concentrations of cobalt in the air of several hundred micrograms per cubic metre (Simcox *et al.*, 2000), whereas concentrations averaging 9 $\mu g/m^3$ were noted in another Stellite-producing factory (Kennedy *et al.*, 1995).

(*d*) *Cobalt pigments*

Porcelain plate painters in Denmark have been exposed for many decades to cobalt (insoluble cobalt–aluminate spinel or soluble cobalt–zinc silicate) at concentrations which exceeded the hygiene standard by 1.3–172-fold (Tüchsen *et al.*, 1996). During the period 1982–92, the Danish surveillance programme showed a reduction in exposure to cobalt both in terms of concentrations in air and urine; the concentration of cobalt in air decreased from 1356 $nmol/m^3$ [80 $\mu g/m^3$] to 454 $nmol/m^3$ [26 $\mu g/m^3$], and that in urine of workers from 100-fold to 10-fold above the median concentration of unexposed control subjects (Christensen & Poulsen, 1994; Christensen, 1995; Poulsen *et al.*, 1995).

A group of workers producing cloisonné [enamel ware] in Japan and exposed to lead, chromium, cadmium, manganese, antimony, copper and cobalt compounds showed peak cobalt concentrations in blood that were twofold higher compared with the referent group, although cobalt concentrations in urine were similar (Arai *et al.*, 1994).

(*e*) *Production of cobalt metal and cobalt salts*

In a factory in Belgium engaged in hydrometallurgical purification, workers were exposed to cobalt metal, cobalt oxide and cobalt salts without being exposed to tungsten, titanium, iron or silica, or their carbides, or to diamond. The mean concentration of cobalt in the workplace air was 127.5 $\mu g/m^3$ (median, 84.5 $\mu g/m^3$; range, 2–7700 $\mu g/m^3$). Cobalt concentrations in urine samples from workers taken after the workshift on Fridays averaged 69.8 μg/g creatinine (median, 72.4 μg/g; range, 1.6–2038 μg/g creatinine) (Swennen *et al.*, 1993). Cobalt concentrations in urine at the end of the workshift correlated well with workers' exposure on an individual basis to cobalt metal and cobalt salts, but not with exposure to cobalt oxide. Cobalt concentrations of 20 and 50 $\mu g/m^3$ in air would be expected to lead to cobalt concentrations in urine of 18.2 and 32.4 μg/g creatinine, respectively (Lison *et al.*, 1994).

Recycling of batteries for the purpose of recovering cobalt, nickel, chromium and cadmium was found to result in cobalt concentrations in workplace air of up to 10 $\mu g/m^3$ (Hengstler *et al.*, 2003).

Workers in a factory in the Russian Federation producing cobalt acetate, chloride, nitrate and sulfates were reported to be exposed to cobalt in dust at concentrations of 0.05–50 mg/m^3 (Talakin *et al.*, 1991). In a nickel refinery also in the Russian Federation, exposures to airborne cobalt of up to 4 mg/m^3 were reported; nickel and cobalt concentrations were strongly correlated, although inhaled concentrations of nickel were far greater than those of cobalt (Thomassen *et al.*, 1999).

In a cobalt plant in Kokkola, Finland, workers were potentially exposed to metallic cobalt and cobalt sulfates, carbonates, oxides and hydroxides (Linna *et al.*, 2003). The highest concentration of cobalt in urine was recorded in a worker in the reduction department (16 000 nmol/L [943 μg/L]). Among workers in the solution, purification and chemical departments, cobalt concentrations in urine ranging from 300 to 2000 nmol/L [18 to 118 μg/L] were reported, while mean concentrations of cobalt in the air of all work areas were below 100 $\mu g/m^3$.

In a plant in South Africa converting cobalt metal to cobalt oxide, the highest concentrations of cobalt in ambient air and in urine samples of workers were 9.9 mg/m^3 and 712 μg/g creatinine, respectively (Coombs, 1996).

High concentrations of cobalt, as well as antimony, arsenic, cadmium, chromium, lanthanum, lead and selenium, were reported in the lungs of a group of smelter workers in Sweden (Gerhardsson & Nordberg, 1993). Workers from a smelter, a petroleum refinery and a chemical plant in the USA were found to have significantly lower concentrations of cobalt in the seminal plasma, while concentrations of zinc, copper and nickel were high compared with a referent group of hospital workers (Dawson *et al.*, 2000).

(*f*) *Other exposures*

In the United Kingdom, workers in metal thermal spraying were found to inhale cobalt, chromium and nickel. Monitoring of the workplace air and the urine of workers showed concentrations of cobalt in air of 20–30 μg/m^3 and in urine of 10–20 μmol/mol creatinine, a range 10- to 20-fold higher than in unexposed controls (Chadwick *et al.*, 1997).

Non-occupational exposure to cobalt arises from surgical implants and dental prostheses, and from contact with metallic objects, e.g. jewellery. A slight increase in mean cobalt concentrations was reported in the urine of patients with cobalt-alloy knee and hip prostheses (Sunderman *et al.*, 1989).

1.3.3 *Environmental exposure*

(*a*) *Air*

Cobalt is released into the air from volcanoes and burning fuels (coal, oil). Bertine and Goldberg (1971) estimated a concentration of cobalt of 5 mg/kg in coal and 0.2 mg/kg in oil. The active volcano Mt. Erebus in Antarctica releases considerable amounts of trace elements into the environment, including cobalt (Kyle & Meeker, 1990; Hamilton, 1994). In Mumbai, India, Sadasivan and Negi (1990) found mean concentrations of cobalt in atmospheric aerosols of 1.1 ± 1.5 ng/m^3 (range, 0.3–2.3 ng/m^3), originating from iron debris in the soil. Between 1962 and 1974, average cobalt concentrations in the air in the United Kingdom declined significantly in all but one of seven sampling sites (Hamilton, 1994). Atmospheric concentrations of cobalt in rural areas of developed countries are usually below 1 ng/m^3 (Hamilton, 1994).

(*b*) *Water and sediments*

Cobalt concentrations in sea water range from 0.01–4 μg/L and in fresh and ground waters from 0.1–10 μg/L (Nilsson *et al.*, 1985). Of 720 river water samples examined in the USA, 37% contained traces of cobalt, in the range of 1–5 μg/L, 5 μg/L being the limit of solubility. Because cobalt is present only in low concentrations, no maximal level has been set for drinking-water (Calabrese *et al.*, 1985).

Cobalt concentrations in sediments may vary from < 6 ppm (low) to > 125 ppm (very high) (Hamilton, 1994).

(*c*) *Soils and plants*

Cobalt is omnipresent in soil, but is far from being distributed evenly. Apparently there exists a correlation between the content of cobalt in soil and in the parent rock; as a consequence, soils that are geochemically rich or poor in cobalt can be recognized. Cobalt concentrations in most soils range from 0.1–50 ppm and the amount of cobalt taken up by plants from 0.1 to 2 ppm (Nilsson *et al.*, 1985; Hamilton, 1994). However, industrial pollution may lead to much higher concentrations; close to a hard-metal (tool grinding) factory in the USA, soil was contaminated with cobalt at concentrations up to 12 700 mg/kg (Abraham & Hunt, 1995).

Lack of cobalt in soils results in vitamin B_{12} deficiency in ruminants (Domingo, 1989; Hamilton, 1994).

(*d*) *Foods and beverages*

Individual intake of cobalt from food is somewhat variable, but typically in the range 10–100 μg/day. Higher intake may result from taking some vitamin preparations (IARC, 1991).

1.4 Regulations and guidelines

Regulations and guidelines for occupational exposure to cobalt in some countries are presented in Table 10. ACGIH Worldwide® (2003b) recommends a semi-quantitative biological exposure index (BEI) of 15 μg/L in urine and 1 μg/L in blood, and recommends monitoring cobalt in urine or blood of individuals at the end of their last shift of the working week as an indicator of recent exposure.