# COBALT AND COBALT ALLOYS

Cobalt [7440-48-4], a transition series metallic element having atomic number 27, is similar to silver in appearance. Cobalt was used as a coloring agent by Egyptian artisans as early as 2000 BC and cobalt-colored lapis or lapis lazuli was used as an item of trade between the Assyrians and Egyptians. In the Greco-Roman period cobalt compounds were used as ground coat frit and coloring agents for glasses. The common use of cobalt compounds in coloring glass and pottery led to their import to China during the Ming Dynasty under the name of Mohammedan blue.

The ancient techniques for mining cobalt and the use of cobalt compounds were lost during the Dark Ages. However, in the sixteenth century mining techniques became widely known through the works of Georgius Agricola, the German mineralogist. At that time cobalt was supplied as smalt or zaffre, the latter being a cobalt arsenide of sulfide ore that was roasted to yield a cobalt oxide. When fused with potassium carbonate to form a type of glass, zaffre became smalt. In the sixteenth century the ability of cobalt to color glass (qv) blue was rediscovered. Metallic cobalt, isolated in 1735 by a Swedish scientist, was established as an element in 1780.

Cobalt and cobalt compounds (qv) have expanded from use as colorants in glasses and ground coat frits for pottery (see Colorants for CERAMICS) to drying agents in paints and lacquers (see DRYING), animal and human nutrients (see MINERAL NUTRIENTS), electroplating (qv) materials, high temperature alloys (qv), hardfacing alloys, high speed tools (see TOOL MATERIALS), magnetic alloys (see MAGNETIC MATERIALS, BULK; MAGNETIC MATERIALS THIN-FILM), alloys used for prosthetics (see PROSTHETIC AND BIOMEDICAL DEVICES), and uses in radiology (see RADIOACTIVE TRACERS). Cobalt is also used as a catalyst for hydrocarbon refining from crude oil for the synthesis of heating fuels (1,2) (see Fuels, synthetic; Petroleum).

# 1. Occurrence

Cobalt is the thirtieth most abundant element on earth and comprises approximately 0.0025% of the earth's crust (3). It occurs in mineral form as arsenides, sulfides, and oxides; trace amounts are also found in other minerals of nickel and iron as substitute ions (4). Cobalt minerals are commonly associated with ores of nickel, iron, silver, bismuth, copper, manganese, antimony, and zinc. Table 1 lists the principal cobalt minerals and some corresponding properties. A complete listing of cobalt minerals is given in Reference 4.

The cobalt resources of the United States are estimated to be about 1.3 million tons. Most of these resources are in Minnesota, but other important occurrences are in Alaska, California Missouri, Montana, and Idaho. Although large, most U.S. resources are in subeconomic concentrations. The identified world cobalt resources are about 11 milion tons. The vast majority of these resources are in nickel-bearing laterite deposits, with most of the rest occurring in nickel-copper deposits hosted in mafic and ultramafic rocks in Australia, Canada, and Russia, and in the sedimentary copper deposits of Congo (Kihshasa) and Zambia, In addition million of tons of hypothetical and speculative cobalt resources exist in manganese nodules on the ocean floor (5).

**1.1. Future Sources.** Lateritic ores (8) are becoming increasingly important as a source of nickel, and cobalt is a by-product. In the United States, laterites are found in Minnesota, California, Oregon, and Washington. Deposits also occur in Cuba, Indonesia, New Caledonia, the Philippines, Venezuela, Guatemala, Australia, Canada, and Russia (see NICKEL AND NICKEL ALLOYS).

The laterites can be divided into three general classifications: (1) iron nickeliferrous limonite which contains approximately 0.8-1.5 wt% nickel. The nickel to cobalt ratios for these ores are typically 10:1; (2) high silicon serpentinous ores that contain more than 1.5 wt% nickel; and (3) a transition ore between type 1 and type 2 containing about 0.7-0.2 wt% nickel and a nickel to cobalt ratio of approximately 50:1. Laterites found in the United States (9) contain 0.5-1.2 wt% nickel and the nickel occurs as the mineral goethite. Cobalt occurs in the lateritic ore with manganese oxide at an estimated wt% of 0.06 to 0.25 (10).

# 2. Properties

The electronic structure of cobalt is [Ar]  $3d^74s^2$ . At room temperature the crystalline structure of the  $\alpha$  (or  $\varepsilon$ ) form, is close-packed hexagonal (cph) and lattice parameters are a = 0.2501 nm and c = 0.4066 nm. Above approximately  $417^{\circ}$ C, a face-centered cubic (fcc) allotrope, the  $\gamma$  (or  $\beta$ ) form, having a lattice parameter a = 0.3544 nm, becomes the stable crystalline form. The mechanism of the allotropic transformation has been well described (6,11–13). Cobalt is magnetic up to 1123°C and at room temperature the magnetic moment is parallel to the *c*-direction. Physical properties are listed in Table 2.

	CAS			Approximate	D ''		
Mineral	Registry number	Chemical formula	Crystalline form	hardness, Mohs'	Density, kg/m <sup>3</sup>	Cobalt, wt%	Location
			Arsenides				
smaltite	[12044-42-1]	$CoAs_2$	cubic	6.0	6.5	23.2	United States, Canada Morocco
safflorite	[12044 - 43 - 8]	$CoAs_2$	orthogonal	5.0	7.2	28.2	Morocco, Canada
skutterudite	[12196-91-7]	$\text{CoAs}_3^{\tilde{b} \cdot c}$	cubic	6.0	6.5	20.8	Ontario, Morocco
			Sulfides				
carrollite	[12285-42-6]	$egin{array}{c} { m CuCo_2S_4, CuS} & \cdot \ { m Co_2S_3, Co_3S_4} \end{array}$	cubic	5.5	4.85	38.7	Congo, Zambia
linnaeite	[1308-08-3]	$\mathrm{Co}_3\mathrm{S}_4$	cubic	5	4.5	48.7	Congo
siegenite	[12174-56-0]	$(Co, Ni)_3S_4$				26.0	United States
cattierite	[12017-06-0]	$\operatorname{CoS}_2^b$					Congo
			Arsenide-sulfide				
cobaltite	[1303-15-7]	CoAsS	cubic	6	6.5	35.5	United States, Canada Australia
			Oxide				
asbolite	[12413-71-7]	$CoO \cdot 2MnO_2 \cdot 4H_2O$	ore	1 - 2	1.1		Congo, Zambia
erythrite	[149-32-6]	$3$ CoO $\cdot$ As <sub>2</sub> O <sub>5</sub> $\cdot$ 8H <sub>2</sub> O	ore	2	3	29.5	
heterogenite	[12332-83-0]	$\mathrm{CuO} \cdot \mathrm{2Co_2O_3} \cdot \mathrm{6H_2O},\ \mathrm{Co_2O_3} \cdot \mathrm{H_2O}^d$	ore	4	3.5	57	Congo
sphaerocobaltite	[14476 - 13 - 2]	CoCO <sub>3</sub>	ore			49.6	Congo, Zambia

# Table 1. Important Cobalt Minerals and Corresponding Properties<sup>a</sup>

<sup>a</sup> Refs. 6 and 7.

<sup>b</sup>May also include some nickel. <sup>c</sup>May also include some nickel and some iron. <sup>d</sup>CuO·2Co<sub>2</sub>O<sub>3</sub>·6H<sub>2</sub>O and CoO·3Co<sub>2</sub>O<sub>3</sub>·CuO·7H<sub>2</sub>O are also present.

Property		Value	
at wt	58.93		
transformation temperature, °C	417		
heat of transformation, $J/g^a$	251		
mp, °C	1493		
latent heat of fusion, $\Delta H_{\rm fus}$ , J/g <sup>a</sup>	259.4		
bp, °C	3100		
latent heat of vaporization, $\Delta H_{\rm vap}$ , J/g <sup>a</sup>	6276		
specific heat, $J/(g \cdot {}^{\circ}C)^{\alpha}$			
15–100°C	0.442		
molten metal	0.560		
coefficient of thermal expansion, $^{\circ}\mathrm{C}^{-1}$			
cph at RT	12.5		
fcc at 417°C	14.2		
thermal conductivity at RT, W/(m · K)	69.16		
thermal neutron absorption, Bohr atom	34.8		
resistivity, at $20^{\circ}$ C <sup>b</sup> , $10^{-8} \Omega \cdot m$	6.24		
Curie temperature, °C	1121		
saturation induction, $4\pi I_S$ , T <sup>c</sup>	1.870		
permeability, µ			
initial	68		
max	245		
residual induction, $T^c$	0.490		
coercive force, A/m	708		
Young's modulus, GPa <sup>d</sup>	211		
Poisson's ratio	0.32		
hardness, <sup><i>f</i></sup> , diamond pyramid, of % Co	99.9	$99.98^{e}$	
at 20°C	225	253	
at $300^{\circ}$ C	141	145	
at $600^{\circ}$ C	62	43	
at 900°C	$\frac{1}{22}$	17	
strength of 99.9% cobalt, MPa <sup>g</sup>	as cast	annealed	sintered
tensile	237	588	679
tensile yield	138	193	302
compressive	841	808	
compressive yield	291	387	

Table 2. Properties of Cobalt

<sup>a</sup> To convert J to cal, divide by 4.184.

 $^{b}$  Conductivity = 27.6% of International Annealed Copper Standard.

<sup>c</sup> To convert T to gauss, multiply by 10<sup>4</sup>.

<sup>d</sup> To convert GPa to psi, multiply by 145,000.

<sup>e</sup> Zone refined.

<sup>f</sup>Vickers.

<sup>g</sup> To convert MPa to psi, multiply by 145.

Many different values for room temperature mechanical properties can be found in the literature. The lack of agreement depends, no doubt, on the different mixtures of  $\alpha$  and  $\gamma$  phases of cobalt present in the material. This, on the other hand, depends on the impurities present, the method of production of the cobalt, and the treatment.

The hardness on the basal plane of the cobalt depends on the orientation and extends between 70 and 250 HK. Cobalt is used in high temperature alloys of the superalloy type because of its resistance to loss of properties when heated to fairly high temperatures. Cobalt also has good work-hardening characteristics, which contribute to the interest in its use in wear alloys.

Whereas finely divided cobalt is pyrophoric, the metal in massive form is not readily attacked by air or water or temperatures below approximately  $300^{\circ}$ C. Above  $300^{\circ}$ C, cobalt is oxidized by air. Cobalt combines readily with the halogens to form halides and with most of the other nonmetals when heated or in the molten state. Although it does not combine directly with nitrogen, cobalt decomposes ammonia at elevated temperatures to form a nitride, and reacts with carbon monoxide above  $225^{\circ}$ C to form the carbide Co<sub>2</sub>C. Cobalt forms intermetallic compounds with many metals, such as Al, Cr, Mo, Sn, V, W, and Zn.

Metallic cobalt dissolves readily in dilute  $H_2SO_4$ , HCl, or HNO<sub>3</sub> to form cobaltous salts (see also COBALT COMPOUNDS). Like iron, cobalt is passivated by strong oxidizing agents, such as dichromates and HNO<sub>3</sub>, and cobalt is slowly attacked by  $NH_4OH$  and NaOH.

Cobalt cannot be classified as an oxidation-resistant metal. Scaling and oxidation rates of unalloyed cobalt in air are 25 times those of nickel. The oxidation resistance of Co has been compared with that of Zr, Ti, Fe, and Be. Cobalt in the hexagonal form (cold-worked specimens) oxidizes more rapidly than in the cubic form (annealed specimens) (3).

The scale formed on unalloyed cobalt during exposure to air or oxygen at high temperature is double-layered. In the range of 300 to 900°C, the scale consists of a thin layer of the mixed cobalt oxide [1308-06-1],  $Co_3O_4$ , on the outside and a cobalt(II) oxide [1307-96-6], CoO, layer next to the metal. Cobalt(III) oxide [1308-04-9],  $Co_2O_3$ , may be formed at temperatures below 300°C. Above 900°C,  $Co_3O_4$  decomposes and both layers, although of different appearance, are composed of CoO only. Scales formed below 600°C and above 750°C appear to be stable to cracking on cooling, whereas those produced at 600–750°C crack and flake off the surface.

## 3. Source and Supplies

World production and reserves are listed in Table 3 (5).

The United States is the world's largest consumer of cobalt. With the exception of negligible amounts of by-product cobalt produced as intermediate products from mining operations, the United States did not mine or refine cobalt in 2000 (5).

Projects in Australia and Uganda will increase production. Cobalt supply is expected to increase 3-6%. Demand for cobalt depends on world economic conditions. Supply is expected to increase faster than demand.

The United States government maintained significant quantities of cobalt metal in the National Defense Stockpile (NDS) for military, industrial, and essential civilian use. Since 1993, sales of excess cobalt for NDS has contributed to U.S. and world supplies. U.S. government has set a disposal limit for cobalt of 2720 tons during fiscal 2001 (5).

In 1999, two Internet web sites were established for selling cobalt. A cobalt producer established one site and the other was established by a brokerage firm (14). In 2000, OMG also opened a cobalt web site.

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	Mine p	$roduction^b$		
	1999	$2000^c$	$\operatorname{Reserves}^b$	Reserve base
United States				860,000
Australia	4,100	5,700	880,000	1,300,000
Canada	5,300	5,000	45,000	260,000
Congo (Kinshasa) <sup>d</sup>	7,000	7,000	2,000,000	2,500,000
Cuba	2,200	2,300	1,000,000	1,800,000
New Caledonia <sup>e</sup>	1,000	230,000	860,000	
Philippines	na	na	na	400,000
Russia	3,300	4,000	140,000	230,000
Zambia	4,700	4,000	360,000	540,000
other countries	2,300	3,200	90,000	1,200,000
World total (rounded)	29,900	32,300	4,700,000	9,900,000

<sup>*a*</sup> Data in metric tons.

 $^{b}$  na = not available.

<sup>c</sup>Estimated.

<sup>d</sup>Formerly Zaire.

<sup>e</sup> Overseas territory of France.

#### 4. Processing

**4.1. Sulfide Ores.** In the ores from the Congo, cobalt sulfide as carrollite is mixed with chalcopyrite and chalcocite [21112-20-9]. For processing, the ore is finely ground and the sulfides are separated by flotation (qv) using frothers. The resulting products are leached with dilute sulfuric acid to give a copper–cobalt concentrate that is then used as a charge in an electrolytic cell to remove the copper. Because the electrolyte becomes enriched with cobalt, solution from the copper circuit is added to maintain a desirable copper concentration level. After several more steps to remove copper, iron, and aluminum, the solution is treated with milk of lime to precipitate the cobalt as the hydroxide.

Zambian copper sulfide ores are leaner in cobalt and are, therefore, concentrated twice. In the first stage, the bulk of the copper ore is floated off in a high lime circuit. The carrollite is not carried by the lime, but is recovered in a second pass using different flotation methods. The second concentration, which contains 25% Cu, 17% Fe, and 3.5–4% Co, undergoes a sulfatizing roasting to convert the cobalt to water-soluble cobalt sulfate. The iron and copper in the concentrate form insoluble oxides and sulfates. After roasting, the matte is leached with water and filtered. After removing the last of the copper, milk of lime is added to precipitate the cobalt hydroxide which is filtered and dissolved in sulfuric acid. The resulting solution is then used as an electrolyte from which cobalt is electrodeposited. The cobalt thus produced is marketed either in a granulated form or still attached to the cathode (see METALLURGY, EXTRACTIVE).

**4.2.** Arsenic-Free Cobalt-Copper Ores. The arsenic-free cobalt ores of the Congo are treated by smelting. Ores such as heterogenite which have high cobalt content can be sent directly to an electric furnace in lump form.

The fines must be sintered before being charged. Smelting the cobalt-copper feed along with lime and coke produces a slag and two alloys.

**4.3. Arsenic Sulfide Ores.** The high grade ores of Morocco are magnetically separated to give arsenides and oxides (see SEPARATION, MAGNETIC). Ores that are most concentrated in the arsenides are subjected to an oxidizing roast to remove the arsenic. The concentrates are used as feed in a blast furnace, resulting in speiss, matte, and perhaps boullion. The cobalt-containing speiss is then crushed and roasted and the roasted speiss is treated with sulfuric acid and the solids removed and roasted. After the iron compounds are precipitated with sodium chlorate and lime, the cobalt-nickel solution is treated with sodium hypochlorite to precipitate a cobalt hydrate.

Pressure-acid leaching was used to extract cobalt from Blackbird mine ores before its closing in 1974. The result was a very fine cobalt powder which was subjected to a seeding process to produce cobalt granules. Leaching methods are also used in the refinement of lateritic ores.

**4.4. Lateritic Ores.** The process used at the Nicaro plant in Cuba requires that the dried ore be roasted in a reducing atmosphere of carbon monoxide at 760°C for 90 minutes. The reduced ore is cooled and discharged into an ammoniacal leaching solution. Nickel and cobalt are held in solution until the solids are precipitated. The solution is then thickened, filtered, and steam heated to eliminate the ammonia. Nickel and cobalt are precipitated from solution as carbonates and sulfates. This method (9) has several disadvantages: (1) a relatively high reduction temperature and a long reaction time; (2) formation of nickel oxides; (3) a low recovery of nickel and the contamination of nickel with cobalt; and (4) low cobalt recovery. Modifications to this process have been proposed but all include the undesirable high 760°C reduction temperature (10).

A similar process has been devised by the U.S. Bureau of Mines (9) for extraction of nickel and cobalt from United States laterites. The reduction temperature is lowered to  $525^{\circ}$ C and the holding time for the reaction is 15 minutes. An ammoniacal leach is also employed, but oxidation is controlled, resulting in high extraction of nickel and cobalt into solution. Mixers and settlers are added to separate and concentrate the metals in solution. Organic strippers are used to selectively remove the metals from the solution. The metals are then removed from the strippers. In the case of cobalt, spent cobalt electrolyte is used to separate the metal-containing solution and the stripper. Metallic cobalt is then recovered by electrolysis from the solution. Using this method, 92.7 wt% nickel and 91.4 wt% cobalt have been economically extracted from domestic laterites containing 0.73 wt% nickel and 0.2 wt% cobalt (9).

**4.5. Deep Sea Nodules.** Metal prices influence the type of extraction process used for sea nodules. Whereas there are those typically rich in manganese, most of the mining and refining expenses must be met by the price of commodity metals such as copper and cobalt rather than by an abundant metal like manganese. It has been suggested that a method be used that would selectively remove cobalt, nickel, and copper, leaving manganese stored in the tailings for future use (14,15). This method involves smelting of the reduced new nodules to produce a manganiferrous slag and an alloy containing the metals. The alloy is converted into a matte by oxidation and sulfidation. An oxidative pressure leach is used to produce a purified solution from which the metal is obtained

(14). Research is continuing in the areas of pyrometallurgy, hydrometallurgy, and electrometallurgy to find more efficient extraction techniques (16-19) (see OCEAN RAW MATERIALS).

# 5. Economic Aspects

In 2000, approximately 45% of U.S. cobalt use was in superalloys, which are used primarily in aircraft gas turbine engines, 9% was in cemented carbides for cutting and wear-resistant applications, 9% was in magnetic alloys, and the remaining 37% in various chemical uses. The total estimated value of cobalt consumed in 2000 was  $$300 \times 10^6$  (5).

Table 4 gives U.S. consumption of cobalt between 1998 and 2000 by form. Table 5 gives consumption according to products.

Table 4. U.S. Consumption of Cobalt, t <sup>a</sup>						
Form	1998	1999	$2000^b$			
$rac{metal}{scrap}$ chemical compounds $^c$	4,240 3,080 1,860	$3,780 \\ 2,720 \\ 1,910$	$3,170 \\ 2,460 \\ 1,700$			
Total	9,180	8,420	7,320			

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<sup>a</sup> Ref. 5.

<sup>b</sup> Jan.-Nov. 2000.

<sup>c</sup> Includes oxide.

Table 5.	U.S.	Reported	Consumption	of Cobalt by
End Use	a,b			

Use	1998	1999	$2000^{c}$
steel	134	154	129
superalloys	410	3,830	3,280
magnetic alloys	771	794	690
magnetic alloys other $alloys^d$	421	291	W
cemented carbides $^{e}$	844	755	705
chemical and ceramic uses <sup>f</sup>		2,530	2,250
Miscellaneous and unspecified	2,900	64	266
Total	9,810	8,420	7,320

<sup>a</sup> Refs. 5,14.

<sup>b</sup> W Withheld to avoid disclosing company proprietary data; included with "Miscellaneous and unspecified," Data are rounded to no more than three significant digits; may not add to totals shown.

<sup>c</sup> May include revisions to prior months, Jan.–Nov. 2000.

<sup>d</sup> Includes diamond bit matrices, cemented and sintered carbides, and cast carbide dies or parts.

 $^e$  Includes diamond bit matrices, cemented and sintered carbides, and cast carbide dies or parts.

 $^{f}$  Includes catalysts, driers in paints or related usage, feed or nutritive additive, glass decolorizer, ground coat frit, pigments, and other uses.

During much of its history, the price of cobalt metal was set primarily by the producers. In the 1990s, the African producers lost much of their influence on cobalt prices (20). This was the result of reduced production in Zambia and Zaire (now the Democratic Republic of the Congo). Free market prices can change rapidly. Free market can originate from producers, government stockpile releases, or consumers with excess metal. Prices reflect overall supply and demand, but can change if there is a perception of short term availability. Sudden changes are not always evident.

A crisis in the 1970s led to an increase in prices (ie, cessation of sales from stockpiles, invasion of mines in Zaire). In the 1980s to mid-1990, Zaire and Zambia were successful in returning stability to cobalt prices. Free market prices ended during the second half of 1990. Prices from 1990 on reflect changes in supply/demand, political unrest in leading producer countries, selling from stockpiles, delayed purchases, etc. (21).

During the first ten months of 2000, average spot price of electrolytic cobalt varied between 6.12-7.94/kg (13.50 to 17.50/lb) (5).

# 6. Analytical Methods

There have been numerous analytical procedures developed for the identification and determination of cobalt metal in a variety of matrices. Some of the most popular instrumental and wet chemical techniques are briefly summarized in this section. The complete methods are documented in Analytical Chemistry reference texts or have been published as ASTM procedures.

**6.1. Wet Chemical Methods.** For qualitative spot test the 1-nitroso-2naphthol method and the ammonium thiocyanate method are used (22). The compleximetric titration-EDTA (27) method was developed for the determination of cobalt in cobalt paint drivers (23). A gravimetric method is based on a cobalt complex with  $\alpha$ -nitroso naphthol (24). Electrogravimetry can also be used (25).

**6.2.** Instrumental Methods. Atomic absorption spectrophotometry (30) (aas) method was developed to determine low concentration of cobalt in metal mixtures. Both aqueous and organic solutions can be analyzed, however analyses in aqueous solutions are less problematic and more common (26). The inductively coupled plasma spectrophotometry technique is somewhat comparable to aas. Its advantage is a broad linear range, long term stability and a greater sensitivity. A factor of 10 improvement is achieved for the detection limit of cobalt (27). The technique is susceptible to emission interferences. A photometric method was developed for the determination of cobalt in stainless steel in the range of 0.01 to 0.3% (28). The optical emission spectrophotometry – point to plane technique was developed for cast metal which can be machined to be compatible with the instrument (29). In the ion-exchange–Potentiometric titration method, cobalt is separated from interfering elements by selective elution from an anion-exchange column using hydrochloric acid. The potentiometric titration is performed using a platinum and saturated calomel electrode (30). The x-ray emission spectrophotometry method was developed for the analysis of stainless steel. The concentrations of the elements are determined by relating the measured radiation

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of unknown samples to analytical curves prepared from standard reference materials (31).

## 7. Environmental Concerns

Cobalt is ubiquitous in the environment and occurs naturally in many different chemical forms. The most important natural sources of cobalt to the environment are soil and dust, seawater, volcanic eruptions, and forest fires (32). The most important synthetic sources of cobalt are the byprocesses of burning coal and oil; exhaust from cars and other vehicles; industrial processes that use cobalt and compounds; and sewage sludge from cities (32).

Relatively small amounts of cobalt are released to the environment from manufacturing operations. Cobalt is not currently mined in the United States, and users of cobalt and cobalt compounds obtain the material through import and by recycling scrap metal. Because of cobalt's intrinsic value, the overwhelming majority of cobalt wastes are recycled. Based on recent Toxics Release Inventory (TRI) information collected by the U.S. Environmental Protection Agency (EPA), more than 93% of all cobalt wastes generated by reporting industries during 1996, the most recent reporting year, were recycled. Much of the remainder was treated. Less than 1% of cobalt waste was released to the environment (33).

General population exposure to cobalt is very low. Cobalt has been detected in the ambient air at levels ranging from 0.4 to 1.0 ng/m<sup>3</sup>, although higher transient concentrations have been detected in some industrial areas. Elemental cobalt is insoluble. Cobalt compounds vary in their solubility, however, and cobalt has been detected in surface waters. The median concentration of cobalt in U.S. surface waters has been found to average 2  $\mu$ g/L. Wastewaters from refining and other industrial activities may contain higher concentrations (34). Bioaccumulation factors for cobalt range from 100 to 4000 in marine fish and 4 to 1000 in freshwater fish (34).

Cobalt and compounds are subject to the toxic chemical release reporting requirements of the Emergency Planning and Community Right-to-Know Act (EPCRA) (35). Under EPCRA, owners and operators of certain facilities that manufacture, process, or otherwise use cobalt or cobalt compounds must report their releases to all environmental media. Cobalt compounds also are hazardous substances subject to the comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund) (36). Cobalt and its compounds additionally are regulated by the Clean Water Effluent Guidelines for a number of industrial point sources, including the following: nonferrous metals manufacturing (37) inorganic chemicals manufacturing (38) and battery manufacturing (39).

# 8. Health and Study Factors

Cobalt is essential for human health. Low levels of cobalt, as part of the vitamin  $B_{12}$  complex, are necessary to maintain good health, and the Food and Drug Administration has recognized a number of cobalt compounds as safe for use

in materials that come in contact with food (40). Cobalt also stimulates the production of red blood cells and, accordingly, has been widely used as a treatment for anemia, particularly in pregnant women. For these reasons, cobalt is unlikely to produce adverse health effects in the general population at levels typically found in the environment.

General population exposure to cobalt is very low. Workers in certain occupations are exposed to higher concentrations. The main route of absorption of cobalt during occupational exposure is via the respiratory tract, due to inhalation of dusts, fumes, or mists containing cobalt or cobalt compounds. Occupational exposures occur principally through the production of cobalt powder, or in hard metal production, processing, and use (41). Workers in the hard metal industry, in particular, have been found to be exposed to concentrations of cobalt in the workplace ranging from 1 to 300  $\mu$ g/m<sup>3</sup> (42).

The principal occupational health problem associated with exposure to cobalt is pulmonary effects, particularly in the hard metal industry where cobalt-containing dust is generated. Because the dust in such industries always contains agents in combination with cobalt (tungsten carbide and other substances such as tungsten, titanium carbide, tantalum carbide, and vanadium carbide), it is unclear whether cobalt is solely responsible for the observed health effects. EPA has concluded that long-term exposure to cobalt by inhalation causes respiratory effects, such as irritation, wheezing, and fibrosis (43). Nevertheless, the respiratory effects of exposure to cobalt and its compounds depend to a large extent on the form of cobalt involved, and bronchial obstruction and interstitial lung fibrosis have been principally found in workers exposed to very fine dust.

To address the potential inhalation toxicity of cobalt and cobalt compounds, the Occupational Health and Safety Administration (OSHA) has established a permissible exposure limit (PEL) in the workplace of 0.1 mg/m<sup>3</sup> for cobalt metal, dust, and fume as an 8-h time weighted average (44). This OSHA standard is based on concerns for cobalt's potential pulmonary toxicity. Similarly, the American Conference of Governmental Industrial Hygienists (ACGIH) recently established a threshold limit value (TLV) of 0.02 mg/m<sup>3</sup> for elemental cobalt and inorganic cobalt compounds to protect against potential pulmonary toxicity and sensitivity reactions (45). The National Institute of Occupational Safety and Health (NIOSH) has established a risk level of 0.5 mg/m<sup>3</sup> for exposure to cobalt and cobalt compounds. In the United Kingdom, the Advisory Committee on Toxic Substances of the Health and Safety Commission also has established a maximum exposure limit of 0.05 mg/m<sup>3</sup> following an examination of cobalt-related health effects information.

The carcinogenic toxicity potential of cobalt and cobalt compounds is well characterized. IARC, for example, published in 1991 a monograph on the carcinogenic risks to humans from cobalt and cobalt compounds (46). Following a comprehensive review of animal and human studies, IARC concluded that there is inadequate evidence for the carcinogenicity of cobalt and cobalt compounds in humans, but that there is sufficient evidence for the carcinogenicity of cobalt metal powder and cobalt oxides in experimental animals. Based on this evidence, IARC identified cobalt and its compounds as Class 2B potential human carcinogens (47). ACGIH also has concluded that cobalt and cobalt compounds are carcinogenic in animals. ACGIH assigned cobalt and its compounds an A3 classification (48). Likewise, the German Commission has identified cobalt in the form of respirable dust/aerosols to be a potential human carcinogen (49). Similarly, the Registry of Toxic Effects of Chemical Substances (RTECs) published by NIOSH identifies cobalt as a Group 2B potential carcinogen based on the IARC Monograph (50).

The National Toxicology Program (NTP) released a draft report on the carcinogenicity of one highly soluble cobalt compound, cobalt sulfate heptahydrate (51). The NTP draft report indicates an increased incidence of certain neoplasms in the respiratory tracts of rats and mice exposed to high concentrations of the compound by inhalation. It is unclear, however, whether the findings represent cobalt's potential carcinogenicity, or nonspecific responses to the physical acidic sulfate salt solution. It is also unclear whether the result observed following exposure to a highly soluble cobalt compound would be observed in animals exposed to elemental cobalt, or other far less soluble cobalt compounds.

#### 9. Uses

**9.1. As Metal.** The largest consumption of cobalt is in metallic form in magnetic alloys, cutting and wear-resistant alloys, and superalloys. Alloys in this last group are used for components requiring high strength as well as corrosion and oxidation resistance, usually at high temperatures.

During World War II German scientists developed a method of hydrogenating solid fuels to remove the sulfur by using a cobalt catalyst (see COAL CONVER-SION PROCESSES). Subsequently, various American oil refining companies used the process in the hydrocracking of crude fuels (see CATALYSIS; SULFUR REMOVAL AND RECOVERY). Cobalt catalysts are also used in the Fisher-Tropsch method of synthesizing liquid fuels (52–54) (see FUELS, SYNTHETIC).

Cobalt-molybdenum alloys are used for the desulfurization of high sulfur bituminous coal, and cobalt-iron alloys in the hydrocracking of crude oil shale (qv) and in coal liquefaction (7).

**9.2. As Salts.** The second largest use of cobalt is in the form of salts (see COBALT COMPOUNDS), which have the largest application as raw material for electroplating (qv) baths and as highly effective driers for lacquers, enamels, and varnishes. Addition of cobalt salts to paint greatly increases the rate at which paint (qv) hardens. Cobalt oxide colors glass pink or blue depending on the environment of the CoO<sub>x</sub> molecule within the glass. The pink colors are formed in boric oxide or alkali-borate glasses. The cobalt concentration determines the intensity of the color obtained, eg, glass used in making foundryman's goggles requires 4.5 kg of cobalt for every ton of glass. By contrast, the glass used in making decorative bottles requires only about 280 g/t. Cobalt is also used to decolorize soda–lime–silica glass. Pottery enamels react very similarly because the fusible enamels are forms of fusible glasses (see ENAMELS, PORCELAIN OR VITREOUS). Colors varying from blue to black can be obtained, depending on the oxides added to the frit to improve the adherence of porcelain enamel to steel sheet metal.

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Combinations of cobalt compounds are also used as ceramic pigments (qv) ranging in colors of violet, blue, green, and pink (54–56).

Radioactive cobalt, <sup>60</sup>Co, produced by bombarding stable <sup>59</sup>Co with low energy neutrons, has application in radiochemistry, radiography, and food sterilization (57–59) (see FOOD PROCESSING; RADIOISOTOPES; STERILIZATION TECHNIQUES).

<sup>60</sup>Co has many applications as a strong  $\gamma$  source. Cancer therapy machines, using <sup>60</sup>Co as their source, treat more than one million people around the world each year (60). <sup>60</sup>Co is also used in  $\gamma$ -imaging medical diagnostic cameras. Its industrial applications include thickness gauges, liquid flow measurement, and level control.

One of its most widespread uses is in sterilization facilities. Most medical products and supplies, including sutures, masks, gloves, dressings, scalpel blades, catheters, and syringes, are prepackaged and then sterilized by <sup>60</sup>Co irradition. It is also used for blood products and pharmaceuticals that cannot tolerate sterilization by heat or chemical processes.

Food irradiation is an application of <sup>60</sup>Co with great potential, but growth in this area is slow because of the public perception of radiation. Nevertheless, food irradiation has been approved for use in 40 countries, and is endorsed by the UN World Health Organization, the American Medical Association, the Institute of Food technologists, the Science Council of Canada, Health and Welfare Canada, and the U.S. Food and Drug Administration (FDA). It has several advantages over conventional food preservation techniques (1) it does not leave additives in the product, as some chemical preservatives do; (2) fruits and vegetables retain their taste, texture, and nutritional value, unlike the results of conventional heating, freezing, additives, drying, or powdering; and (3) it is proven effective in neutralizing common foodborne pathogens such as Campylobacter (for which it is the only known control in poultry meat), Cryptosporidium *Escherichia coli* (for which it is the most effective control in ground beef), Listeria, Salmonella, and Toxoplasma. Approval of food irradiation proceeds on an individual-case basis, so it is slow. In January 1998, the FDA approved the irradiation of red meat (61).

Many of the uses of <sup>60</sup>Co can also be provided by <sup>137</sup>Cs (half-life 30 years,  $\gamma$ -ray energy 662 keV), a reactor fission product, but <sup>60</sup>Co is by far the most widely used of the two.

Cobalt is an essential ingredient in animal nutrition. It has been shown that animals deprived of cobalt show signs of retarded growth, anemia, loss of appetite, and decreased lactation. Dressing the top soil of pastures with cobalt increases the cobalt content of the vegetation. Cobalt is known to be necessary to the synthesis of vitamin  $B_{12}$  [68-19-9] (see VITAMINS), a lack of which has been linked to pernicious anemia in humans. Cobalt is also used as the target material in electrical x-ray generators (see X-RAY TECHNOLOGY).

## 10. Cobalt Alloys

Pure metallic cobalt has a solid-state transition from cph (lower temperatures) to fcc (higher temperatures) at approximately 417°C. However, when certain elements such as Ni, Mn, or Ti are added, the fcc phase is stabilized. On the

other hand, adding Cr, Mo, Si, or W stabilizes the cph phase. Upon fcc-phase stabilization, the energy of crystallographic stacking faults, ie, single-unit cph inclusions that impede mechanical slip within the fcc matrix, is high. Stabilizing the cph phase, however, produces a low stacking fault energy. In the case of high stacking fault energy, fcc stabilization, only a few stacking faults occur, and the ductility of the alloy is high. When foreign elements are dissolved throughout the matrix lattice, the mechanical slip is generally impeded. This results in increased hardness and strength, a metallurgical phenomenon known as solidsolution hardening.

Mechanical properties depend on the alloying elements. Addition of carbon to the cobalt base metal is the most effective. The carbon forms various carbide phases with the cobalt and the other alloying elements (see CARBIDES). The presence of carbide particles is controlled in part by such alloying elements such as chromium, nickel, titanium, manganese, tungsten, and molybdenum that are added during melting. The distribution of the carbide particles is controlled by heat treatment of the solidified alloy.

Cobalt alloys are strengthened by solid-solution hardening and by the solidstate precipitation of various carbides and other intermetallic compounds. Minor phase compounds, when precipitated at grain boundaries, tend to prevent slippage at those boundaries thereby increasing creep strength at high temperatures. Aging and service under stress at elevated temperature induce some of the carbides to precipitate at slip planes and at stacking faults thereby providing barriers to slip. If carbides are allowed to precipitate to the point of becoming continuous along the grain boundaries, they often initiate fracture (see FRACTURE MECHANICS). A thorough discussion of the mechanical properties of cobalt alloys is given in References 62 and 63 (see also REFRACTORIES).

**10.1. Cobalt-Base Alloys.** As a group, the cobalt-base alloys may generally be described as wear-resistant, corrosion-resistant, and heat-resistant, i.e., strong even at high temperatures. Table 6 lists typical compositions of cobalt-base alloys in these application areas. Many of the alloy properties arise from the crystallographic nature of cobalt, in particular its response to stress; the solid-solution-strengthening effects of chromium, tungsten, and molybdenum; the formation of metal carbides; and the corrosion resistance imparted by chromium. Generally, the softer and tougher compositions are used for high temperature applications such as gas-turbine vanes and buckets. The harder grades are used for resistance to wear.

Historically, many of the commercial cobalt-base alloys are derived from the cobalt-chromium-tungsten and cobalt-chromium-molybdenum ternaries first investigated at the turn of the twentieth century. The high strength and stainless nature of the binary cobalt-chromium alloy, and powerful strengthening agents, tungsten and molybdenum, were identified early on. These alloys were named Stellite alloys after the Latin *stella* for star because of their starlike luster. Stellite alloys were first used as cutting tools and wear-resistant materials.

Following the success of cobalt-base tool materials during World War I, these alloys were used from about 1922 in weld overlay form to protect surfaces from wear. These early cobalt-base hardfacing alloys were used on plowshares, oil well drilling bits, dredging cutters, hot trimming dies, and internal combustion engine valves and valve seats. In 1982, approximately 1500 metric tons of

Alloy trade name	$\mathbf{Cr}$	W	Mo	С	$\mathrm{Fe}^b$	Ni	Si	Mn	
Cobalt-base wear-resistant alloys <sup>c</sup>									
Stellite 1	31	12.5	$1^b$	2.4	3	$3^b$	$2^b$	$1^b$	
Stellite 6	28	4.5	$1^b$	1.2	3	$3^b$	$2^b$	$1^b$	
Stellite 12	30	8.3	$1^b$	1.4	3	$3^b$	$2^b$	$1^b$	
Stellite 21	28		5.5	0.25	2	2.5	$2^b$	$1^b$	
Haynes alloy 6B	30	4	1	1.1	3	2.5	0.7	1.5	
Tribaloy T-800	17.5		29	$0.08^b$					
Stellite F	25	12.3	$1^b$	1.75	3	22	$2^b$	$1^b$	
Stellite 4	30	14.0	$1^b$	0.57	3	$3^b$	$2^b$	$1^b$	
Stellite 190	26	14.5	$1^b$	3.3	3	$3^b$	$2^b$	$1^b$	
Stellite 306 <sup>e</sup>	25	2.0		0.4		5			
Stellite 6K	31	4.5	$1.5^b$	1.6	3	$3^b$	$2^b$	$2^b$	
Cobe	alt-base	high te	mperatu	re alloys	$d \cdot f$				
Haynes alloy 25 (L605)	20	15	0.10	v	3	10	$1^b$	1.5	
Haynes alloy 188	22	14		0.10	3	22	0.35	1.25	
MAR-M alloy 509 <sup>g</sup>	22.5	7		0.60	1.5	10	$0.4^b$	$0.1^b$	
Coba	ılt-base d	corrosic	on-resist	ant alloy	$s^h$				
MP35N, multiphase alloy	20		10	-0		35			
Ultimet <sup>i</sup>	25.5	<b>2</b>	5	$0.08^b$	$3^{j}$	9			

Table 6. Compositions of Cobalt-Base Wear-Resistant Alloys, wt  $\%^a$ 

<sup>*a*</sup> Where the balance of the alloy consists of cobalt.

<sup>b</sup>Value given is maximum value.

<sup>c</sup> Stellite and Tribaloy are registered trademarks of Stoody Deloro Stellite.

<sup>d</sup> Haynes is a registered trademark of Haynes International, Inc.

<sup>e</sup>Also contains 6 wt% niobium.

<sup>*f*</sup>MAR-M-Alloy is a registered trademark of Martin-Marietta.

<sup>g</sup>Also contains 3.5 wt% tantalum, 0.2 wt% titanium, and 0.5 wt% zirconium.

<sup>h</sup> MP35N is a registered trademark of Standard Pressed Steel Co.

<sup>*i*</sup>Also contains 0.1 wt% nitrogen.

<sup>j</sup>Value given is not necessarily maximum.

cobalt-base alloys were sold for the purpose of hardfacing, one-third of this quantity being used to protect valve seating surfaces for both fluid control and engine valves.

In the 1930s and early 1940s, cobalt-base alloys for corrosion and high temperature applications were developed (64). Of the corrosion-resistant alloys, a cobalt-chromium-molybdenum alloy having a moderately low carbon content was developed to satisfy the need for a suitable investment cast dental material (see DENTAL MATERIALS). This biocompatible material, which has the tradename Vitallium, is used for surgical implants. In the 1940s this same alloy underwent investment casting trials for World War II aircraft turbocharger blades, and, with modifications to enhance structural stability, was used successfully for many years in this and other elevated-temperature applications. This early high temperature material, Stellite alloy 21, is in use in the 1990s predominantly as an alloy for wear resistance.

**10.2.** Cobalt-Base Wear-Resistant Alloys. The main differences in the Stellite alloy grades of the 1990s versus those of the 1930s are carbon and tungsten contents, and hence the amount and type of carbide formation in the

microstructure during solidification. Carbon content influences hardness, ductility, and resistance to abrasive wear. Tungsten also plays an important role in these properties.

**10.3.** Types of Wear. There are several distinct types of wear that can be divided into three main categories: abrasive wear, sliding wear, and erosive wear. The type of wear encountered in a particular application is an important factor influencing the selection of a wear-resistant material.

Abrasive wear is encountered when hard particles, or hard projections on a counter-face, are forced against and moved relative to a surface. In alloys such as the cobalt-base wear alloys which contain a hard phase, the abrasion resistance generally increases as the volume fraction of the hard phase increases. Abrasion resistance is, however, strongly influenced by the size and shape of the hard-phase precipitates within the microstructure, and the size and shape of the abrading species (see ABRASIVES).

Sliding wear is perhaps the most complex in the way different materials respond to sliding conditions. The metallic materials that perform best under sliding conditions are cobalt-based either by virtue of oxidation behavior or ability to resist deformation and fracture. Little is known of the influence of metal-tometal bond strength during cold welding. For materials such as the cobalt-base wear alloys having a hard phase dispersed throughout a softer matrix, the sliding-wear properties are controlled predominantly by the matrix. Indeed, within the cobalt alloy family, resistance to galling is generally independent of hard particle volume fraction and overall hardness.

Four distinct forms of erosive wear have been identified: solid-particle erosion, liquid-droplet erosion, cavitation erosion, and slurry erosion.

The abrasion resistance of cobalt-base alloys generally depends on the hardness of the carbide phases and/or the metal matrix. For the complex mechanisms of solid-particle and slurry erosion, however, generalizations cannot be made, although for the solid-particle erosion, ductility may be a factor. For liquiddroplet or cavitation erosion the performance of a material is largely dependent on ability to absorb the shock (stress) waves without microscopic fracture occurring. In cobalt-base wear alloys, it has been found that carbide volume fraction, hence, bulk hardness, has little effect on resistance to liquid-droplet and cavitation erosion (65). Much more important are the properties of the matrix.

**10.4.** Alloy Compositions and Product Forms. The nominal compositions of various cobalt-base wear-resistant alloys are listed in Table 6. The six most popular cobalt-base wear alloys are listed first. Stellite alloys 1, 6, and 12, derivatives of the original cobalt-chromium-tungsten alloys, are characterized by their carbon and tungsten contents. Stellite alloy 1 is the hardest, most abrasion resistant, and least ductile.

Stellite alloy 21 differs from the first three alloys in that molybdenum rather than tungsten is used to strengthen the solid solution. Stellite alloy 21 also contains considerable less carbon. Each of the first four alloys is generally used in the form of castings and weld overlays. Haynes alloy 6B differs in that it is a wrought product available in plate, sheet, and bar form. Subtle compositional differences between alloy 6B and Stellite alloy 6, eg, such as silicon control, facilitate processing. The advantages of wrought processing include greatly enhanced ductility, chemical homogeneity, and resistance to abrasion. The Tribaloy alloy T-800, is from an alloy family developed by DuPont in the early 1970s, in the search for resistance to abrasion and corrosion. Excessive amounts of molybdenum and silicon were alloyed to induce the formation during solidification of hard and corrosion-resistant intermetallic compounds, known as Laves phase. The Laves precipitates confer outstanding resistance to abrasion, but limit ductility. As a result of this limited ductility the alloy is not generally used in the form of plasma-sprayed coatings.

The physical and mechanical properties of the six commonly used cobalt wear alloys are presented in Table 7. In the case of the Stellite and Tribaloy alloys this information pertains to sand castings. Notable are the moderately high yield strengths and hardnesses of the alloys, the inverse relationship between carbon content and ductility in the case of the Stellite alloys, and the enhanced ductility imparted to alloy 6B by wrought processing. Typical applications of the cobalt wear-resistant alloys are given in Table 8. Generally, the alloys are used in moderately corrosive and/or elevated-temperature environments.

**10.5. Cobalt-Base High Temperature Alloys.** For many years, the predominant user of high temperature alloys was the gas-turbine industry. In the case of aircraft gas-turbine power plants, the chief material requirements were elevated-temperature strength, resistance to thermal fatigue, and oxidation resistance. For land-base gas turbines, which typically burn lower-grade fuels and operate at lower temperatures, sulfidation resistance was the primary concern. The use of high temperature alloys (qv) in the 1990s is more diversified, as more efficiency is sought from the burning of fossil fuels and waste, and as new chemical processing techniques are developed.

	Alloy <sup>a</sup>						
Property	1	6	12	21	6B	T-800	
hardness, Rockwell	55	40	48	32	$37^b$	58	
yield strength, MPa <sup>c</sup>		541	649	494	$619^b$		
ultimate tensile strength, MPa <sup>c</sup>	618	896	834	694	$998^b$		
elongation, %	<1	1	< 1	9	11		
thermal expansion coeff,							
$\mu m/(m \cdot C)$							
$20-100^{\circ}\mathrm{C}$	10.5	11.4	11.5	11.0	$13.9^{d}$		
$20-500^{\circ}\mathrm{C}$	12.5	14.2	13.3	13.1	$15.0^d$	12.6	
$20 - 1000^{\circ}$ C	14.8		15.6		$17.4^d$	15.1	
thermal conductivity, $W/(m \cdot K)$					14.8	14.3	
specific gravity	8.69	8.46	8.56	8.34	8.39	8.64	
electrical resistivity, $\mu \Omega \cdot \mathbf{m}$	0.94	0.84	0.88		0.91		
melting range, °C							
solidus	1255	1285	1280	1186	1265	1288	
liquidus	1290	1395	1315	1383	1354	1352	

#### Table 7. Mechanical and Physical Properties of Cobalt-Base Wear-Resistant Alloys

<sup>a</sup> See Table 6.

 $^{b}$  3.2 mm (1/8 in.) thick sheet.

<sup>c</sup> To convert MPa to psi, multiply by 145.

<sup>d</sup> Starting temperature of 0°C.

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Applications	${ m Stellite} \ { m alloys}^a$	Forms	Mode of degradation
		Automotive indust	ry
diesel engine valve seating surface	6, F	weld overlay	solid particle erosion, hot corrosion
control valve seating surfaces	6, 21	<i>Power industry</i> weld overlay	sliding wear, cavitation erosion
steam turbine erosion shields	6B	wrought sheet	liquid droplet erosion
rudder bearings	306	<i>Marine industry</i> weld overlay	sliding wear
hot shear edges bar mill guide rolls	6 12	<i>Steel industry</i> weld overlay weld overlay	sliding wear, impact, abrasion sliding wear, impact, abrasion
control valve seating surfaces	Chen 6	nical processing in weld overlay	<i>dustry</i> sliding wear, cavitation erosion
plastic extrusion screw flights	1, 6, 12	weld overlay	sliding wear, abrasion
pump seal rings dry battery molds	$\begin{array}{c} 6,12 \\ 4 \end{array}$	weld overlay casting	sliding wear abrasion
chainsaw noses	6В, 6	<i>ulp and paper indu</i> wrought sheet weld overlay	<i>stry</i> sliding wear, abrasion
carpet knives wool spinning	6K, 12	<i>Textile industry</i> wrought sheet weld overlay	abrasion
rotary drill bearings	190	Oil and gas indust weld overlay	ry abrasion, sliding wear
helicopter rotor blade erosion shields	6B	Aircraft industry sheet	abrasion

Table 8. Applications of Cobalt-Base Wear-Resistant Alloys

<sup>*a*</sup> See Table 6.

Cobalt-base alloys are not as widely used as nickel and nickel-iron alloys in high temperature applications. Nevertheless, cobalt-base high temperature alloys play an important role because of excellent resistance to sulfidation and strength at temperatures exceeding those at which the  $\gamma'$ - and  $\gamma''$ -precipitates in the nickel and nickel-iron alloys dissolve. Cobalt is also used as an alloying element in many nickel-base high temperature alloys. The various types of ironbase, nickel-base, and cobalt-base alloys for high temperature application are discussed in Reference 66. Nickel-base and cobalt-base castings for high temperature service are also covered.

**10.6.** Alloy Compositions and Product Forms. Stellite 21, an early type of cobalt-base high temperature alloy, is used primarily for wear resistance.

The use of tungsten rather than molybdenum, moderate nickel contents, lower carbon contents, and rare-earth additions typify cobalt-base high temperature alloys of the 1990s as can be seen from Table 5.

Haynes alloys 25, also known as L605 and 188, are wrought alloys available in the form of sheets, plates, bars, pipes, and tubes together with a range of matching welding products for joining purposes. MAR-M alloy 509 is an alloy designed for vacuum investment casting. Selected mechanical properties of these three alloys are given in Table 9.

**10.7. Cobalt-Base Corrosion-Resistant Alloys.** Although the cobaltbase wear-resistant alloys possess some resistance to aqueous corrosion, they

		$Alloy^{a}$	
Property	25	188	MAR-M509
yield strength, MPa <sup>b</sup>			
at 21°C	$445^c$	$464^d$	$585^e$
at $540^\circ\mathrm{C}$		$305^{f}$	$400^d$
tensile strength, MPa <sup>b</sup>			
at 21°C	$970^{c}$	$945^d$	$780^e$
at $540^{\circ}\mathrm{C}$	$800^g$	$740^{f}$	$570^e$
1000-h rupture			
${ m strength}, { m MPa}^b$			
at 870°C	75	70	140
at $980^{\circ}\mathrm{C}$	30	30	90
elongation, %	62	$53^c$	$3.5^e$
thermal expansion coeff,			
$\mu m/(m \cdot K)$			
from 21–93°C	12.3	11.9	
from $21{-}540^{\circ}\mathrm{C}$	14.4	14.8	
from $21{-}1090^{\circ}C$	17.7	18.5	
thermal conductivity, W/			
$(\mathbf{m} \cdot \mathbf{K})$			
$ m at20^{\circ}C$	$9.8^{h}$	10.8	
at $500^\circ \mathrm{C}$	$18.5^{i}$	19.9	
$ m at900^{\circ}C$	$26.5^{j}$	25.1	
specific gravity	9.13	8.98	8.86
electrical resistivity,	0.89	1.01	
$\mu \Omega \cdot \mathbf{m}$			
melting range, °C			
solidus	1329	1302	1290
liquidus	1410	1330	1400

 Table 9. Properties of Cobalt-Base High Temperature Alloys

<sup>*a*</sup> See Table 6.

<sup>b</sup> To convert MPa to psi, multiply by 145.

<sup>c</sup> 3.2 mm (1/8 in.) thick.

 $^{d}$  Sheet 0.75–1.3 mm (0.03–0.05 in.) thick.

<sup>e</sup> As cast.

 $^f {\rm Sheet},$  heat treated at 1175°C for 1 h with rapid air cool.

 $^g$  Sheet, heat treated at 1230°C for 1 h with rapid air cool.

 $^h$  At 38°C.

 $^i$  At 540°C.

<sup>*j*</sup> At 815°C.

are limited by grain boundary carbide precipitation, the lack of vital alloying elements in the matrix after formation of the carbides or Laves precipitates, and, for the case and weld overlay materials, by chemical segregation in the microstructure. By virtue of homogeneous microstructures and lower carbon contents, the wrought cobalt-base high temperature alloys, which typically contain tungsten rather than molybdenum, are even more resistant to aqueous corrosion, but still fall well short of the nickel-chromium-molybdenum alloys in corrosion performance. To satisfy the industrial need for alloys which exhibit resistance to aqueous corrosion yet share the attributes of cobalt as an alloy base, ie, resistance to various forms of wear and high strength over a wide range of temperatures, several low carbon, wrought cobalt-nickel-chromium-molybdenum alloys are produced. The compositions of two of these are presented in Table 5. In addition, the cobalt-chromium-molybdenum alloy Vitallium is widely used for prosthetic devices and implants owing to excellent compatibility with body fluids and tissues.

The two corrosion-resistant alloys presented in Table 5 rely on chromium and molybdenum for their corrosion resistance. The corrosion properties of Ultimet are also enhanced by tungsten. Both alloys are available in a variety of wrought product forms: plates, sheets, bars, tubes, etc. They are also available in the form of welding (qv) consumables for joining purposes.

**10.8. Mechanical Properties.** An advantage of the two corrosion-resistant alloys is that they may be strengthened considerably by cold working. MP35N alloy is intended for use in the work-hardened or work-hardened and aged condition, and the manufacturers have supplied considerable data concerning the mechanical properties of the alloy at different levels of cold work. Some of these data are given in Table 8.

**10.9. Uses.** Applications of both these alloys include pump and valve components and spray nozzles. MP35N alloy is also popular for fasteners, cables, and marine hardware.

**10.10. Economic Aspects.** With cobalt historically being approximately twice the cost of nickel, cobalt-base alloys for both high temperature and corrosion service tend to be much more expensive than competitive alloys. In some cases of severe service their performance increase is, however, commensurate with the cost increase and they are a cost-effective choice. For hardfacing or wear applications, cobalt alloys typically compete with iron-base alloys and are at a significant cost disadvantage.

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