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材料手册 3

不常用的有色金属

François Cardarelli

Materials Handbook

A Concise Desktop Reference

Second Edition



哈尔滨工业大学出版社
HARBIN INSTITUTE OF TECHNOLOGY PRESS



Engineering and Technology Texts

材料手册 3

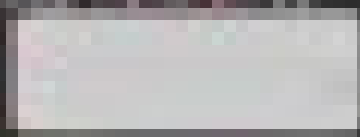
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by François Cardarelli

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4

Less Common Nonferrous Metals

4.1 Alkali Metals

The alkali metals are represented by the six chemical elements of group IA(1) of Mendeleev's periodic chart. These six elements are, in order of increasing atomic number, lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr). The name alkali metals comes from the fact that they form strong alkaline hydroxides (i.e., MOH, with $M = \text{Li, Na, K, etc.}$) when they combine with water (i.e., strong bases capable of neutralizing acids). The only members of the alkali metal family that are relatively abundant in the Earth's crust are sodium and potassium. Among the alkali metals only lithium, sodium, and, to a lesser extent, potassium are widely used in industrial applications. Hence, only these three metals will be reviewed in detail in this chapter. Nevertheless, a short description of the main properties and industrial uses of the last three alkali metals (i.e., Rb, Cs, and Fr) will be presented at the end of the section. Some physical, mechanical, thermal, electrical, and optical properties of the five chief alkali metals (except francium, which is radioactive with a short half-life) are listed in Table 4.1.

Table 4.1. Select physical and chemical properties of five alkali metals

Properties at 298.15K (unless otherwise specified)		Lithium					Sodium (Natrium)					Potassium (Kalium)					Rubidium					Cesium (Cesium)				
Designation		Chemical symbol (IUPAC)	Chemical abstract registry number [CAS RN]	Unified numbering system [UNS]	Earth's crust abundance (mg.kg ⁻¹)	Seawater abundance (mg.kg ⁻¹)	World estimated reserves (R/tonnes)	World annual production of metal in 2004 (P/tonnes)	Price of pure metal in 2004 (C/ \$US.kg ⁻¹) (purity, wt.%)	Atomic number (Z)	Relative atomic mass Ar (¹² C=12.000) ¹	Electronic configuration	Fundamental ground state	Atomic radius (pm)	Covalent radius (pm)	Electron affinity (EA/eV)	First ionization energy (eV)	Second ionization energy (eV)	Third ionization energy (eV)	Electronegativity χ_s (Pauling)	Electronegativity χ_a (Allred and Rochow)	Electron work function (WS/eV)	X-ray absorption coefficient CuK _{α1,2} ((μ/ρ)/cm ² .g ⁻¹)	Thermal neutron cross section (σ ₀ /10 ⁻²⁸ m ²)	Isotopic mass range	Isotopes including natural and isomers
		Li	[7439-93-2]	[L06990]	20	0.18	9 ∞ 10 ⁶	1500 (metal) 87,700 (carbonate)	95,40 (99.8)	3	6.941(2)	[He] 2s ¹	² S _{1/2}	156	123	0.618	5.39172	75.64018	122.4543	0.98	0.97	2.93	0.716	0.045	4-11	8
		Na	[7440-23-5]	[L11001]	23 600	10 770	unlimited	90,000 (metal)	250 (99.95)	11	22.989770(2)	[Ne] 3s ¹	² S _{1/2}	192	157	0.548	5.13908	47.2864	71.6200	0.93	1.01	2.36	30.1	0.53	17-35	21
		K	[7440-09-7]	[L08001]	20,900	399	>10 ¹⁰	200 (metal)	650 (99.95)	19	39.0983(1)	[Ar] 4s ¹	² S _{1/2}	238	203	0.501	4.34066	31.6300	45.8060	0.82	0.91	2.29	143	2.1	32-54	24
		Rb	[7440-17-7]	[L09001]	90	0.12	n.a.	n.a.	20,000 (99.8)	37	85.4678(3)	[Kr] 5s ¹	² S _{1/2}	250	216	0.486	4.17713	27.2850	40.0000	0.82	0.89	2.261	117	0.38	72-102	38
		Cs	[7440-46-2]	[L02001]	3	0.0004	n.a.	20 (metal)	40,800 (99.98)	55	132.90545(2)	[Xe] 6s ¹	² S _{1/2}	272	253	0.472	3.89390	23.15745	-	0.79	0.86	1.95	318	29	112-151	56

Crystal structure at room temperature (phase or β)*Strukturbericht* designation

Space group (Hermann–Mauguin)

Pearson's notation

Lattice parameters (a /pm)Miller's indices of slip plane (hkl)Latent molar enthalpy transition (L /kJ.mol⁻¹)Phase-transition temperature α - β (T /K)Density (293K) (ρ /kg.m⁻³)Young's or elastic modulus (300K) (E /GPa)Coulomb's or shear modulus (G /GPa)Bulk or compression modulus (K /GPa)Compressibility (β /10⁻⁵ MPa⁻¹)

Mohs hardness (HM)

Vickers hardness (HV)

Brinell hardness (HB)

Ultimate tensile strength (σ_{UTS} /MPa)Longitudinal velocity of sound (V_L /m.s⁻¹)Transverse velocity of sound (V_T /m.s⁻¹)Poisson ratio ν (dimensionless)Temperature of fusion (T_m /K) Melting point ($m.p.$ /°C)Temperature of vaporization (T_{vap} /K) Boiling point ($b.p.$ /°C)

Volume expansion on melting (vol.%)

Thermal conductivity (k /W.m⁻¹.K⁻¹)Coefficient of linear thermal expansion (α /10⁻⁶.K⁻¹)Molar heat capacity (C_p /J.mol⁻¹.K⁻¹)Specific heat capacity (c_p /J.kg⁻¹.K⁻¹)Vapor pressure at melting point (p /Pa)Standard molar entropy (S°_{298} /J.mol⁻¹.K⁻¹)Crystallographic properties
[at 293.15K]

Mechanical properties (annealed)

Thermal and
thermodynamic²
properties [293.15K]

Table 4.2. (continued)

Properties at 298.15K (unless otherwise specified)		Lithium	Sodium (Natrium)	Potassium (Kalium)	Rubidium	Cesium (Cesium)
Thermal and thermodynamic properties [293.15K]	Molar enthalpy difference ($H_{298} - H_f^\circ$)/J.mol ⁻¹)	4.622	6.447	7.082	7.490	7.717
	Latent molar enthalpy of fusion (ΔH_{fus})/kJ.mol ⁻¹)	3.00 (432.21)	2.602(113.181)	2.334(61.12)	2.198(25.74)	2.087 (15.703)
	Latent molar enthalpy of vaporization (ΔH_{vap})/kJ.mol ⁻¹)	147.109 (21194)	97.424 (4238)	76.735 (1963)	75.77 (886)	65.90 (496)
	Latent molar enthalpy of sublimation (ΔH_{sub})/kJ.mol ⁻¹)	161.6 (23282)	108.90 (4737)	90.00 (2302)	87.5 (1024)	78.70 (592)
	Molar enthalpy of formation ($\Delta_f H^\circ$)/kJ.mol ⁻¹) (oxide)	-598.73 (-43130)	-417.98 (-9091)	-363.17 (-4645)	-339.0 (-1985)	-345.8 (-1300)
	Electrical resistivity (ρ)/ $\mu\Omega$.cm)	8.55-9.29	4.2	6.15	12.5	18.8
Electrical and electrochemical [293.15K]	Temperature coefficient of resistivity (0-100°C) (/10 ⁻³ K ⁻¹)	4.271-4.350	4.34-5.50	5.70-5.81	4.80	6.00
	Pressure coefficient of electrical resistivity (/TPa ⁻¹)	-21	-383	-697	-629	5
	Hall coefficient at 293.15K (R_H /n Ω .m.T ⁻¹) [0.5 T < B < 2.0 T]	-2.2	-2.3	-4.2	-5.9	-7.8
	Seebeck absolute coefficient (e_s)/ μ V.K ⁻¹)	+14.37	-4.4	-12	-8.26	+0.2
	(Absolute thermoelectric power)					
	Thermoelectric power versus platinum (Q_{sp} /mV vs. Pt) (0-100°C)	+1.82	+0.29	-0.83	+0.46	+1.50
Magnetic and optical properties	Electrochemical equivalence (E_0 /Ah.kg ⁻¹)	3860	1166	685	314	202
	Nernst standard electrode potential (E_0 /V _{sat}) [M ⁺ + e ⁻ = M ⁰]	-3.045	-2.713	-2.924	-2.924	-2.923
	Mass magnetic susceptibility (χ /10 ⁻⁶ kg ⁻¹ .m ³)	+25.6	+8.8	+6.7	+2.49	+2.8
	Wavelength maximum intensity atomic spectra line (Bunsen flame color) (λ /nm)	670.8 (deep red)	589 (bright yellow)	766 (purple-red)	424 (violet)	460 (bluish purple)
	Reflective index under normal incidence (650 nm)	0.913	0.975	0.950	n.a.	n.a.

¹ Standard atomic masses from: Loss, R.D. (2003) Atomic weights of the elements 2001. *Pure Appl. Chem.*, 75(8), 1107-1122.

² Thermodynamic properties from: Chase, M.W. Jr. (1998) NIST-JANAF Thermochemical tables, 4th. ed., Part. I & II.- *J. Phys. Chem. Ref. Data*, Monograph No. 9, Springer, Berlin Heidelberg New York.

4.1.1 Lithium

4.1.1.1 Description and General Properties

Lithium [7439-93-2], chemical symbol Li, atomic number 3, and relative atomic mass (i.e., atomic weight) 6.941(2), is the lightest element of the alkali metals, i.e., group IA(1) of Mendeleev's periodic chart. The word lithium comes from the Greek word *lithos*, meaning stone. Highly pure lithium is a soft, ductile, and malleable metal (like lead) having a Mohs hardness of 0.6; hence it is actually the hardest of the alkali metals. Nevertheless, small amounts of interstitial impurities (e.g., H, C, O, N) or solid inclusions (e.g., Li_2O , Li_3N) strongly modify its mechanical properties. Moreover, it is the lightest of all the metals and solid elements with the lowest density $534 \text{ kg}\cdot\text{m}^{-3}$, which is roughly half that of pure water. The pure metal has two allotropes; the alpha phase corresponds to a very low-temperature crystalline structure (i.e., below -196°C) that is hexagonal close-packed (hcp). Above 25°C , the crystallographic structure changes slowly up to the room-temperature beta phase, which is body-centered cubic (bcc). Lithium thermal properties include the highest specific heat capacity of all the elements ($3569 \text{ J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$), a low vapor pressure of the liquid metal, and a high coefficient of linear thermal expansion ($56 \mu\text{m}/\text{m}\cdot\text{K}$). Recently, a Japanese group observed superconductivity in lithium metal when it was compressed inside a diamond anvil cell to pressures above 30 GPa. Actually, lithium metal becomes superconducting with a critical transition temperature (T_c) of 13 K at 35 GPa or 20 K at 48 GPa. This is the highest superconducting critical temperature ever observed in an elemental superconductor. At these pressures, lithium transforms into a complex allotropic cubic structure with 16 atoms per unit cell and becomes a semiconductor. When freshly cut lithium metal has a silvery lustrous appearance such as sodium and potassium. However, owing to its strong chemical reactivity with oxygen, nitrogen, and water, it tarnishes readily in moist air and becomes yellowish, forming a mixture of several compounds (i.e., LiOH , Li_2CO_3 , and Li_3N). Hence, it should be stored in airtight containers, in an inert gas atmosphere, or, better, totally immersed in benzene, heptane, or a mineral oil such as petrolatum or Nujol®, totally free from traces of oxygen or water.

Lithium metal can be handled safely in dry air with less than 5% relative humidity, such as that found in dry rooms, without tarnishing. Actually, lithium reacts vigorously with water, forming a corrosive cloud of lithium hydroxide, LiOH , particles and evolving hydrogen gas. Nevertheless, this hydrolysis is less vigorous than with sodium or potassium, probably due to the fairly poor solubility and strong adherence of lithium hydroxide LiOH to metal surface in water. Lithium also reacts violently with concentrated inorganic acids and reactive gases such as chlorine. Nevertheless, it does not react with oxygen at room temperature, and lithium oxide, Li_2O , only forms when the metal is heated above 100°C . Lithium ignites spontaneously in air near its melting point (i.e., 180.5°C). Lithium reacts with nitrogen, even at room temperature, to form the reddish-brown nitride Li_3N , especially if traces of moisture are present. Lithium nitride Li_3N [26134-62-3], with a density of $1270 \text{ kg}\cdot\text{m}^{-3}$ and a melting point of 813°C , must not be confused with lithium azide, LiN_3 [19597-69-4], which has a density of $1830 \text{ kg}\cdot\text{m}^{-3}$. Like sodium and potassium, lithium is entirely soluble in liquid ammonia, yielding when dilute a deep blue solution with good electronic conductivity. The saturated solution of metallic lithium in ammonia (10.17 wt.% Li) has a bronze color and a density of $477 \text{ kg}\cdot\text{m}^{-3}$ at 20°C . From an electrochemical point of view, it has the highest negative standard electrode potential ($-3.045 \text{ V}/\text{SHE}$), a high electrochemical equivalence ($3860 \text{ Ah}\cdot\text{kg}^{-1}$), and a good electronic conductivity, which makes it the most attractive anode material available for high-specific-energy and energy-density electrochemical power sources,³ both primary and rechargeable batteries. Moreover, the small ionic radius of lithium (60 pm) explains its cation's ability to pass through its own passivation layer, and this advantage is extensively used in primary cells with liquid cathodes (e.g., SO_2 , SOCl_2).

³ Grady, H.R. (1980) Lithium metal for the battery industry. *J. Power Sources*, 5, 127–135.

Lithium colors the flame of a Bunsen gas burner with a characteristic crimson color (670.8 nm). Moreover, extremely thin foils of lithium are transparent to far-UV radiation. Natural lithium contains the two stable nuclide isotopes ${}^6\text{Li}$ (7.59 at.%) and ${}^7\text{Li}$ (92.41 at.%). However, samples with a modified isotopic composition may be found in commercially available material because it has been subjected to an undisclosed or inadvertent isotopic fractionation. Therefore, substantial deviations in the atomic weight of the element from that given in the literature can occur. For these reasons, in commercially available materials, lithium has an atomic relative mass that range between 6.94 and 6.99; if a more accurate value is required, it must be determined for the specific material by high-resolution mass spectrometry. For instance, the less abundant lithium-6 isotope, owing to its high thermal neutron cross section (940 barns), is an interesting material to serve as breeder blanket for producing tritium gas by following a neutron-capture nuclear reaction: ${}^6\text{Li} (n, \alpha) {}^3\text{H}$. The tritium gas thus produced is suitable for thermonuclear fusion power systems. By contrast, lithium-7, with less than 0.01% at. ${}^6\text{Li}$, is transparent to thermal neutrons and has been proposed as a high-temperature coolant for thermonuclear reactor heat-exchanger loops. Hence many methods have been used to achieve the isotopic fractionation of the two natural lithium isotopes on a small scale, especially in the USA, Russia, and France. Of these, the countercurrent liquid-liquid exchange of lithium isotopes between an aqueous solution of lithium hydroxide (LiOH) and a lithium-mercury amalgam⁴ stream was developed with a separation factor approaching 1.072. Lithium in the molten state is a very corrosive medium, like liquid sodium, and readily attacks metals such as aluminum, copper, lead, platinum, silicon, silver, and zinc. Nevertheless, below 550°C, common ferrous alloys such as pure iron (e.g., Armco® iron), or stainless steels AISI 304L or 316L series,⁵ with a carbon content below 0.12 wt.% C, are satisfactory for handling⁶ and contain the molten metal.⁷ Above 600°C, corrosion-resistant materials for handling and containing liquid lithium with less than 100 ppm wt. free oxygen are, in order of decreasing resistance,⁸ molybdenum, tungsten, rhenium (up to 1650°C), pure tantalum, tantalum-alloy grades such as Ta-10Hf, Ta-8.5W-2.5Hf, T-111 (up to 1000–1200°C),⁹ niobium, and Nb-1Zr alloy (up to 1300°C), titanium, zirconium, and hafnium (up to 820°C), but their corrosion resistance strongly depends on the amount of trace impurities, especially when dissolved oxygen,¹⁰ carbon, and nitrogen in molten lithium.¹¹

Regarding ceramic-containment materials,¹² silica, SiO_2 , and alumina, Al_2O_3 , are strongly attacked and hence readily dissolve in liquid lithium. By contrast, alkaline-earth oxides such as beryllia (BeO), magnesia (MgO), and calcia (CaO) and rare-earth oxides such as ceria (CeO_2), yttria (Y_2O_3), chromite spinel (FeCr_2O_4), and yttrium aluminum garnet ($\text{Y}_3\text{Al}_2\text{O}_{12}$) seem to be noncorroded below 500°C, while aluminum, titanium, and zirconium nitrides or

⁴ Saito, E.; Dirian, G. (1962) Process for the isotopic enrichment of lithium by chemical exchange. *Brit. Pat.* 902,755, Aug. 9.

⁵ Ruedl, E.; Coen, V.; Sasaki, T.; Kolbe, H. (1998) Intergranular lithium penetration of low Ni-Cr-Mn austenitic stainless steels. *J. Nuclear Mater.*, **110**, 28–36.

⁶ Hoffmann, E.E.; Mandly, W.D. (1957) Corrosion resistance of the metal and alloys to sodium and lithium. US Atomic Energy Comm., ORNL-2271, Oak Ridge National Laboratory, p. 11.

⁷ Beskorovainyi, N.M.; Ivanov, V.K. (1967) Mechanism underlying the corrosion of carbon steels in lithium. – in Emeliyanov, V.S.; and Evstyukin, A.I. (eds.) *High Purity Metals and Alloys*. Consultants Bureau, pp. 120–129.

⁸ The maximum working temperatures mentioned correspond to a molten lithium with an extra low level of impurities.

⁹ Klueh, R.L. (1974) Oxygen effects on the corrosion of niobium and tantalum by liquid lithium. *Met. Trans.* **5**, 875–879.

¹⁰ Klueh, R.L. (1973) Effect of Oxygen on the Corrosion of Niobium and Tantalum by Liquid Lithium – U.S. Atomic Energy Comm. Report ORNL-TM-4069, Oak Ridge National Laboratory.

¹¹ Smith, D.L.; Natesan, K. (1974) Influence of Nonmetallic Impurity Elements on the Compatibility of Liquid Lithium with Potential Containment Materials – *Nucl. Technol.* **22**, 392–404.

¹² Singh, R.N. (1976) Compatibility of ceramics with liquid Na and Li. *J. Am. Ceram. Soc.*, **59**, 112–115.

titanium and zirconium carbides seem to be quite inert in this medium below 1000°C. From a safety point of view, fires of solid lithium with water are slightly different than other alkali metals owing to the low density of the metal, which forms a pool of burning liquid metal that floats on any liquid. Lithium fires can only be efficiently stopped with special and efficient extinguishing agents such as copper or graphite powders or by the commercial product under the common trade name Lith-X®, sold by ANSUL. Actually, sand and silicates are forbidden because they react with the molten metal.

4.1.1.2 History

The two lithium-containing minerals petalite and spodumene were discovered in Sweden by Jose de Andrada between 1790 and 1800. Later, in 1817, lithium was first discovered in petalite ore by the Swedish mineralogist Johann Arfvedson. The element was named after the Greek *lithos*, meaning stone, because it was first discovered in a mineral. One year later, in 1818, the pure lithium metal was first isolated independently by the British chemist Sir Humphry Davy and the French chemist Brandé by electrolysis in molten salts containing dissolved lithium oxide.¹³ But it was not until 1925 that lithium metal was first industrially produced by Metallgesellschaft A.G. in Germany and soon after by The Maywood Chemical Company in New Jersey (USA). The Foote Minerals Company began commercial production in the United States at the end of the 1930s. At that time the first industrial uses of lithium chemicals were as fluxing additive in ceramics, as lithium hydride for generating hydrogen in emergency-signaling balloons, and in high-temperature lubricant greases. In 1942, the Lithium Corporation of America, known by the acronym Lithcoa (now part of Food Machinery Corporation or simply FMC), began mining operations of a rich spodumene-bearing pegmatite located at Cherryville near Gastonia in North Carolina and the production of lithium carbonate from the concentrate at Bessemer City in response to a US military demand. After World War II, growth in lithium production was mainly concentrated in both the USA and USSR to provide large quantities of enriched lithium-6 for preparing tritium used in thermonuclear weapons.

Because the isotopic fractionation process produces large quantities of lithium-7 as a by-product, large stocks of depleted lithium in the form of lithium hydroxide but contaminated with traces of mercury became available and were stockpiled until 1995. In the 1960s large amounts of lithium became available for new industrial applications. At the same time, electrochemists started to consider lithium as a potential anode material since it was mentioned in the original patent¹⁴ of the French engineer Hajek, who was the first in 1949 to suggest lithium metal as an anode material in primary batteries. This marks the beginning of lithium metal use in industrial applications. Actually, several years later, the lithium battery concept is claimed in the French patent of Herbert and Ulam.¹⁵ During the 1960s several American laboratories began R&D in this field. At present, as a consequence of these great developments, lithium occupies today an important place in high energy density electrochemical generators, either in primary batteries such as Li/SO_2 , Li/SOCl_2 , and $\text{Li}/\text{SO}_2\text{Cl}_2$ or in secondary (i.e., rechargeable) batteries such as lithium-ion and lithium metal polymer electrolytes. In 1964, Foote Minerals started to recover lithium carbonate directly from its brine operation at Silver Peak in the Nevada desert. Twenty years later the same company began brine operation in 1984 at the Salar de Atacama in Chile from its wholly owned Chilean operations, Sociedad Chilena de Litio (SCL). And in 1984, two new producers of lithium mineral concentrates emerged. In 1980, Greenbushes Tin (now Sons of Gwalia Ltd.) identified in western Australia a spodumene deposit during an extensive drilling program in search of tantalum

¹³ Weeks, M.E. (1956) *Discovery of the Elements*, 6th ed. Journal of Chemical Education Press, Easton, PA, pp. 484–490.

¹⁴ Hajek, J. (1949) French Pat., Oct. 8

¹⁵ Herbert, D.; Ulam, J. (1949) French Pat., Nov. 26