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Authors : Dr. Luis TERCERO (Fraunhofer)

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CRITICAL RAW MATERIAL SUBSTITUTION PROFILES

AUTHOR(S):

LUIS TERCERO ESPINOZA & HENNING STOTZ (FRAUNHOFER ISI)

OTMAR DEUBZER (FRAUNHOFER IZM)

ROCÍO BARROS GARCÍA & GLORIA RODRÍGUEZ LEPE (ICCRAM)

KATARZYNA BILEWSKA, MAŁGORZATA OSADNIK, JACEK MAZUR (IMN)

LENA SUNDQVIST ÖKVIST, JOHAN ERIKSSON & XIANFENG HU (MEFOS)

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INTRODUCTION

Substitution in the context of raw material criticality generally refers to the ability to achieve essentially the same function in a product or service by means other than the usual raw material. In simple terms, the availability of suitable substitutes can be seen as a reasonable way to avoid a "no-build" situation, in which particular products (and services requiring these products) cannot be delivered because of a bottleneck in raw material supply. This is illustrated in Figure 1, where products requiring a particular function based a material/technology requiring a set of raw materials "A" can continue to be produced thanks to the availability of a material/technology based on an alternative set of raw materials "B" can provide an equivalent function.

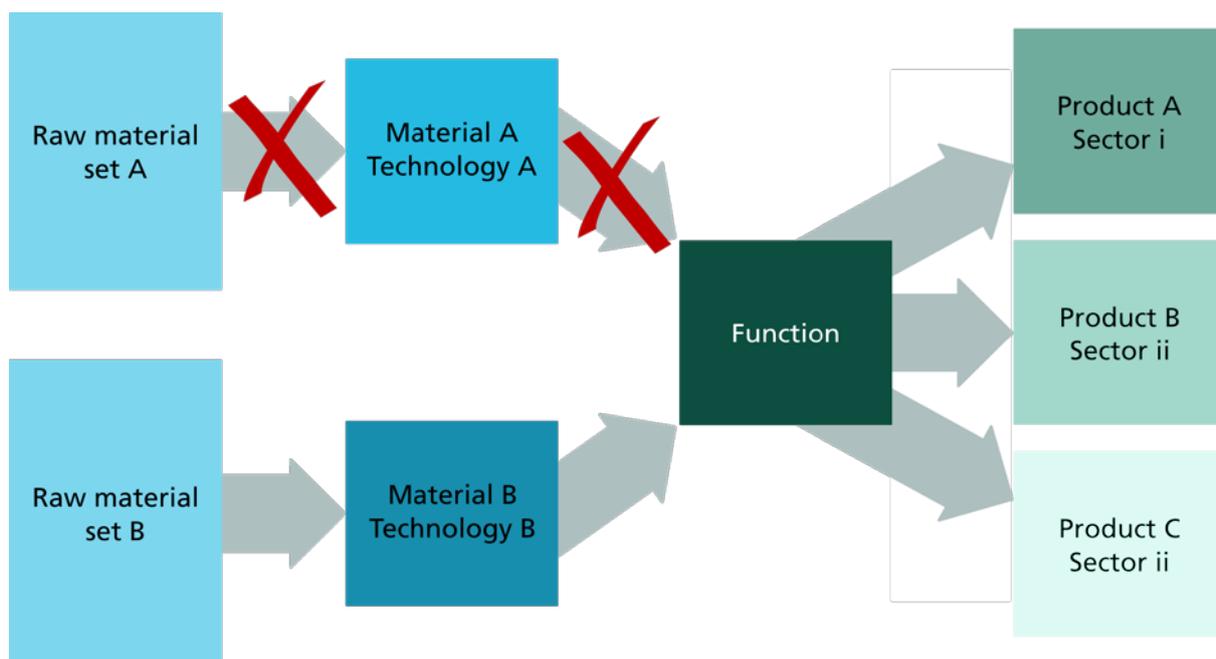


Figure 1: Concept of substitutability as a way of avoiding a "no-build" situation. Modified from Tercero Espinoza (2015).

Although often discussed regarding the best way to assess it, the importance of substitution in the criticality debate appears unquestioned. For example, in the seminal criticality assessment by the NRC (2008), the availability of substitutes is considered to be the "key concept" in determining the importance of a raw material for a particular application, and the Communication launching the Raw Materials Initiative (RMI), the European Commission mentions the lack of viable substitutes as a defining characteristic of criticality (EU 2008).

In line with its importance in the criticality discussion, an assessment of substitutability is a key part of any criticality assessment. Table 1 gives an overview of selected criticality studies at the national/supranational level and how substitutability assessments have been used as indicators. Since assessments of substitutability are generally based on expert opinion, it appears natural that different studies come to different conclusions, if only because the prevailing uses in one country/region/company might differ from those in a different country/region/company. Figure 2 and Figure 3 provide graphical summaries of major substitutability assessments carried out in the past decade.

The work presented in this report follows the logic of European Commission (2010, 2014b) and CRM_InnoNet (2013, 2015). For historical reasons to the project, the scope is the list of critical raw materials for the EU from This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730227

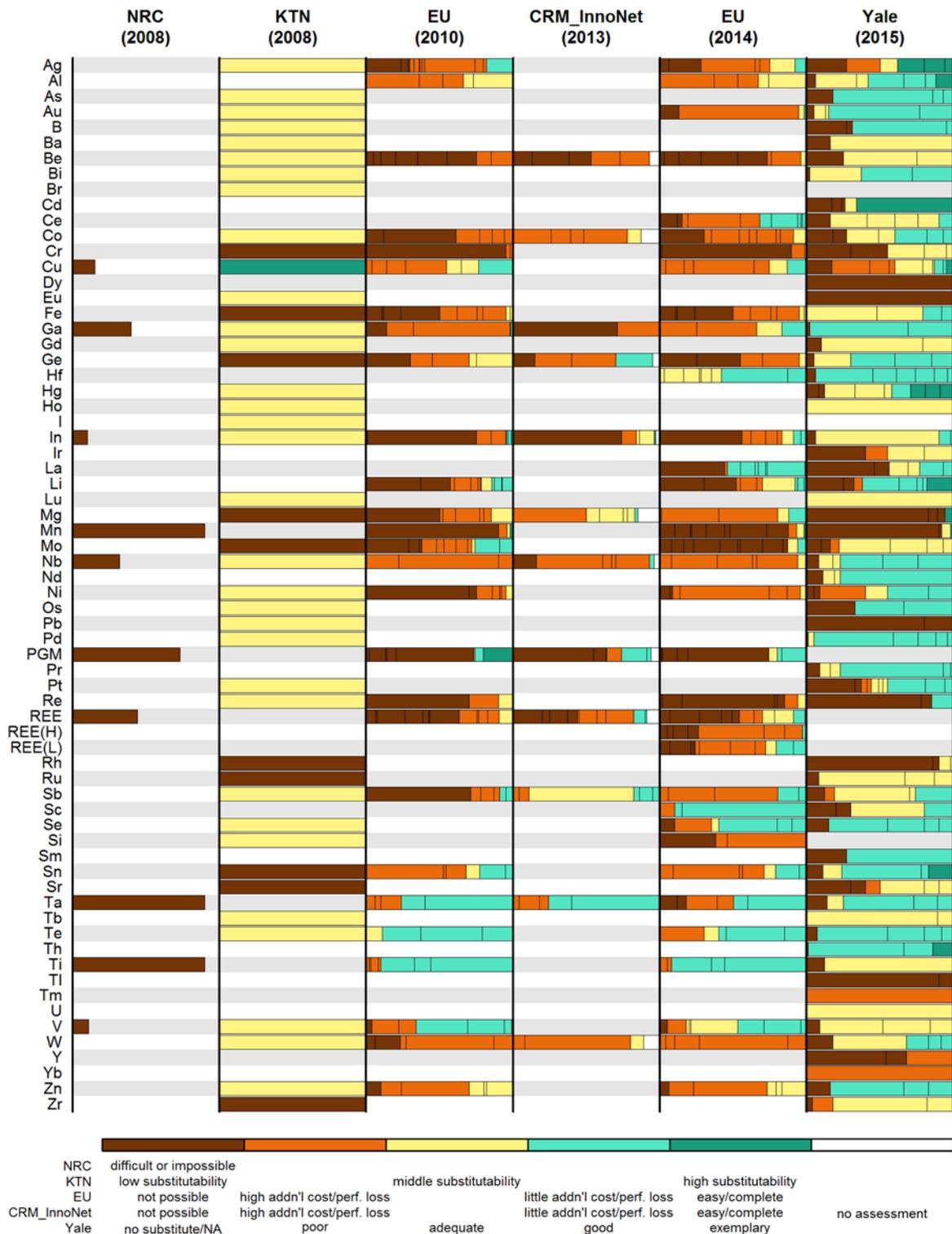


Figure 3: Summary of substitutability estimates for metals and/or elements in major criticality studies (European Commission 2010, 2014b; Graedel et al. 2015; NRC 2008; RE KTN 2008) and in the EU project CRM_InnoNet (2013, 2015) which was focused on substitution.

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ASSESSMENT OF THE SUBSTITUTABILITY OF RAW MATERIALS

ANTIMONY

INTRODUCTION

Antimony is a metal known since antiquity (Enghag 2004). It is silvery-white, shiny, very brittle and semiconducting. Due to its poor mechanical properties, pure antimony is only used in very small quantities; larger amounts are used for alloys and in antimony compounds (Grund et al. 2011; Sitzmann 2004a). Currently, the main use of antimony worldwide is in flame retardants for plastics used mainly in electrical and electronic equipment (European Commission 2014c).

Antimony has been classified as a Critical Raw Material for the EU since 2010 (European Commission 2010, 2014b, 2017b). The substitutability of antimony was assessed by Graedel et al. (2015) and in the CRM_InnoNet project (Tercero Espinoza et al. 2015).

USES AND SUBSTITUTABILITY

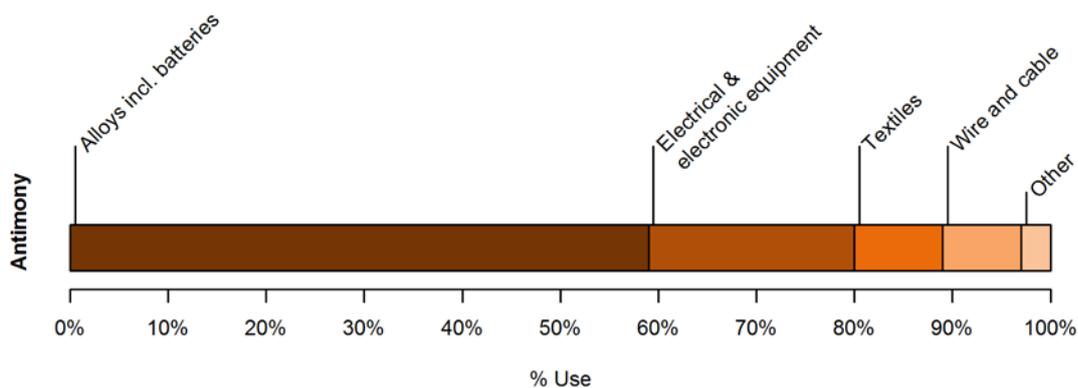


Figure 4: Distribution of recent antimony demand for manufacturing in the EU (data from Bio by Deloitte 2015).

ALLOYS

The largest application for antimony in the EU and second largest application worldwide is in alloys, mostly with lead. The final use of the alloy is determined by both the percentage of antimony in the alloy as well as the other compounds present (Tercero Espinoza et al. 2015).

Antimony increases tensile strength and electrochemical stability of lead alloys when added in the range 1-15%. Uses of these alloys are (Grund et al. 2011; Tercero Espinoza et al. 2015):

- [1.5-3%] grid plates, straps, and terminals of lead-acid batteries. In this case, the addition of antimony also improves fluidity, making the casting of battery grids easier
- [1-9% Sb] cable sheathing and lead pipes
- [7-12%] storage batteries
- [12-15%] small-arms ammunition.

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Antimony-lead alloys containing 2.5–25 % antimony are used in the printing industry (Type metals). The antimony is added in order to lower the casting temperature, increase the hardness and minimize shrinkage during freezing. Antimony also increases hardness in Britannia metal and Pewter (7–20% antimony), allowing highly polished surfaces for vases, lamps, candlesticks, tea and coffee services, and other decorative applications (Grund et al. 2011; Tercero Espinoza et al. 2015).

Antimony is also used in ternary tin-antimony-copper alloys and quaternary tin-antimony-copper-lead alloys (Babitt metal, 4.5–14% antimony) for low load bearings with good anti-seizure properties and corrosion resistance, but low fatigue strength. Lead-based Babitt alloys (antimony, tin, lead, arsenic) contain 8–15% antimony and have better fatigue resistance, allowing their use in heavy duty bearings (Grund et al. 2011; Tercero Espinoza et al. 2015).

Antimony can be substituted by combinations of cadmium, calcium, copper, selenium, strontium, sulfur and tin in most lead alloys (BGS 2016). In particular, the performance of calcium as a substitute in lead alloys for lead-acid batteries is considered good (Graedel et al. 2015).

ELECTRICAL & ELECTRONIC EQUIPMENT

The use of antimony in electrical and electronic equipment is chiefly as antimony trioxide, a component in flame-retardants for plastics. Flame retardant plastics are used in cable coatings and housings for domestic electrical appliances (e.g. TVs, computers). In addition to imparting flame retardant properties, antimony trioxide also reduced the amount of pigment required for coloring the plastics (Grund et al. 2011). Antimony trioxide can be substituted with selected organic compounds, hydrated aluminum oxide or mixtures of zinc oxide and boric oxide, but antimony is seen to offer superior performance (Graedel et al. 2015; Tercero Espinoza et al. 2015).

A further use of antimony in electronics is as a dopant in semiconductors (*n*-type and III/V intermetallic materials) for infrared detectors, Hall-effect devices and diodes (Grund et al. 2011).

TEXTILES

Antimony trioxide is used both as a flame retardant in textiles (nylon, polyester) as well as a catalyst in the synthesis of polyester fibers (Grund et al. 2011). Substitution options are as above for the flame-retardant properties. Titanium-based catalysts are a potential substitute in polymer synthesis, but their performance is not yet adequate (Graedel et al. 2015; Tercero Espinoza et al. 2015).

WIRE & CABLE

The use of antimony in wire and cable includes both cable sheathing (see alloys, above) and plastic coatings (see electrical & electronic equipment) for use e.g. in buildings (cf. Grund et al. 2011). Substitution options are as described above.

SUMMARY

Antimony is used mainly in alloys (mostly lead-based alloys) and as antimony trioxide (mainly, but not only, as a flame retardant). Substitution in the important demand segment "lead-acid batteries" is possible (calcium) with good performance. There are also different options for flame-retardants, but antimony trioxide is still seen as having superior performance. Antimony trioxide is clearly advantageous as a catalyst for polymer synthesis compared to the titanium based options, which are still not market-ready.

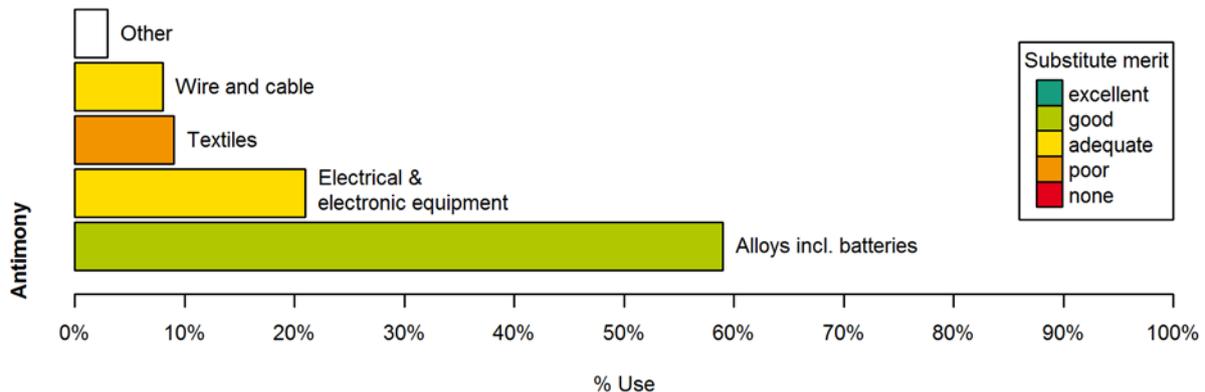


Figure 5: Summary substitutability assessment for antimony.

BERYLLIUM

INTRODUCTION

Beryllium is a silvery-grey, brittle light and non-magnetic metal with low density. With a high modulus of elasticity and the highest heat capacity of all metals (Dunn 2016), beryllium shows superior stiffness at reduced weight and dimensional stability over a wide range of low and high temperatures (Enghag 2004). Beryllium is mostly but not exclusively used in alloyed form together with copper (CuBe), but also with aluminium (AlBe), nickel (NiBe) and other elements (Svilar et al. 2011). As beryllium is one-third lighter than aluminium (BeST 2016a) but about six times stiffer than steel, it is an ideal structural material for aircraft, space, and defence applications. Besides that it is also used in form of electric and electronic connectors for high reliability and safety applications (Enghag 2004; European Commission 2014c; Gunn 2014; Pavel & Tzimas 2016; Svilar et al. 2011). Further industry branches of application comprise the telecommunications and electronics sector, the automobile industry, and industry components.

The European Commission expects a modest demand growth rate for beryllium of <3% per year till 2020 (European Commission 2014b). Beryllium has been classified as critical raw material for the EU since the criticality assessment in 2010, and is also important for defence applications (Pavel & Tzimas 2016). The substitutability of beryllium was assessed by the European Commission (European Commission 2017a), the US Geological Survey (USGS 2017b), the Critical Metals Handbook (Gunn 2014), the Beryllium Science and Technology Association (BeST 2016a) and in the CRM_InnoNet project (CRM_InnoNet 2015).

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USES AND SUBSTITUTABILITY

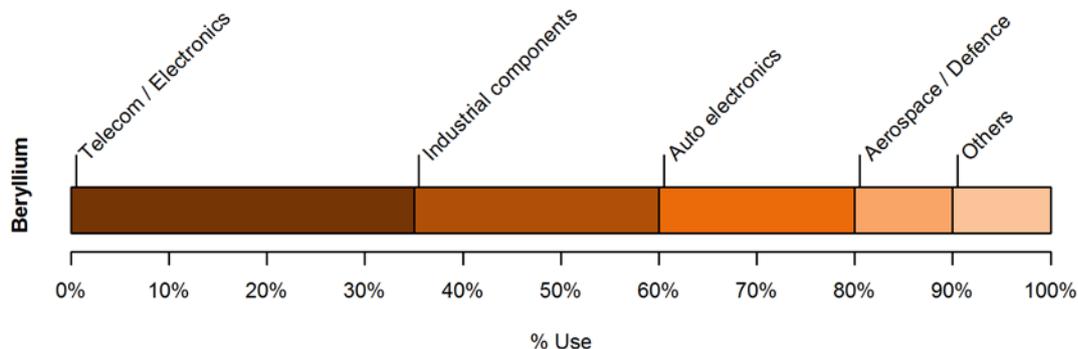


Figure 6: Distribution of recent beryllium demand for manufacturing in the EU (data from Bio by Deloitte 2015).

TELECOM / ELECTRONICS

The largest application for beryllium in the EU is in consumer electronics and telecommunication equipment (Bio by Deloitte 2015). CuBe alloys are used to improve mechanical properties while maintaining good electric conductivity of electronic and electric components, especially connectors, contacts, springs and switches (USGS 2012). Due to the "spring memory" effect, CuBe alloys possess fatigue-free properties which are useful for constant use electrical connections, connector terminals, opening and closings used e.g. in operations under vibrations or in cases where an accidental drop can occur, ensuring continuous operation (BeST 2016d; Svilar et al. 2011). Other uses comprise electrical spring and battery contacts or relays. Applications where those parts are applied also comprise high-definition television, cell phones and computers (Bell 2016a). Undersea optic fibre cable pressure housings are made of CuBe due to its strong corrosion resistance and durability (BeST 2016d; Yamaguchi et al. 2010).

Beryllium oxide (BeO) ceramics (beryllia) show excellent heat conductivity and electric insulating properties and are thus used as heat sinks (heat spreader) for computer chips, semiconductor compounds, high-frequency circuits, and thermostats (Avalon 2018; BeST 2016d; CRM_InnoNet 2015). Other uses of beryllia are as dopant in gallium-arsenide (GaAs), aluminium-gallium-arsenide (AlGaAs) and indium-gallium-arsenide (InGaAs) semiconductors (Bell 2016a).

Beryllium can be substituted in some electronic applications but not without loss of performance or efficiency. For thermal management applications of electronic packaging, heat sinks/spreaders made of beryllium oxide ceramics can be substituted by aluminium metal matrix composites of silicon carbide/boron nitride (BeST 2016a). Other substitute materials for CuBe and NiBe (Be <2%) could include alloys of copper nickel silicon, copper iron, phosphor bronze or copper titanium, however, with a loss in weight reduction, miniaturization, energy savings or performance in terms of equivalent individual properties i.e. strength and ductility, reliability and fatigue resistance, or electrical/thermal conductivity.

INDUSTRIAL COMPONENTS

Component parts made of Be ceramics are used to produce molds for the production of formed rubbers, plastics, and glass objects and for the production of paramagnetic tooling (European Commission 2014c, 2017a). Metallic beryllium is used to produce any kind of bars, plates, rods, tubes and customized forms

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(European Commission 2017a). CuBe alloys are used in valve systems to seal leaking oil wells due to beryllium's extraordinary strength and stress resistance and non-sparking properties (Bell 2016a; BeST 2016b; European Commission 2017a).

AUTOMOBILE ELECTRONICS

The use of beryllium in automobile electronics is in alloyed form (CuBe, AlBe) for lightweight connectors of high reliability, to increase fuel efficiency but also for life safety applications (BeST 2016e). In particular, beryllium is used in the electrical system of cars and trucks. Electrical CuBe connectors are found in air-bag crash sensors (European Commission 2017a), navigation and entertainment system (CRM_InnoNet 2015) and in electrically assisted steering systems substituting older heavier electromechanical or hydraulic systems (Materion Corporation 2018). Component parts made of CuBe are also applied in fuel-injection systems, anti-lock braking, transmissions, electric motors, traction control (BeST 2016e; Materion Corporation 2018), ignition switches, engine control electronic system (Bell 2016a), and for airbags (European Commission 2017a). Light metal components containing trace amount of beryllium (<10ppm) are used for vehicle body panels, car steering components, wheels and seat frames (European Commission 2017a). Substitution options are as described above but in the case for life safety applications, substitution is not an option where significant performance losses are present (CRM_InnoNet 2015).

AEROSPACE / DEFENCE

Due to beryllium's superior mechanical properties as a lightweight metal it is ideally suited for aerospace and military applications where low weight and high rigidity are essential. Uses in defence applications comprise mainly AlBe and CuBe alloys and beryllium in oxide form. Beryllium alloys are used for hull, turret and tank floor of battle tanks, infantry vehicles and artillery and in the airframe body of military aircrafts (Pavel et al. 2016b). AlBe alloys are employed in electronic systems for communication and identification purposes in infantry vehicles, fighter, transport and maritime patrol aircrafts and as electronic connectors for all integrated wire networks in combat helicopters and aforementioned aircrafts (European Commission 2014c; Pavel et al. 2016b). CuBe alloys are used in landing gear bodies and phased array radars for infantry vehicles, fighter and transport aircrafts in the on-board electronics of the inertial navigation system for towed artillery and infantry vehicles, and in GPS/SAL guidance systems of ammunitions (European Commission 2014c; Pavel et al. 2016b). Beryllium in oxide form is used in sensors and electro-optical systems of combat helicopters, for mirrors in combat identification/surveillance and IR equipment and inertial navigation systems of infantry fighter vehicles and artillery, and in transmitters of communication systems (Bell 2016a; Pavel et al. 2016b). Other uses of beryllium are in gyroscopes, gimbals and inner joining elements of missiles and their systems, rocket nozzles, skin panels for rocket boosters, and explosive weapon disposal systems (Bell 2016a; Pavel et al. 2016b). The trigger mechanism for nuclear weapons is based on beryllium (USGS 2012).

Beryllium's use in military applications oftentimes overlaps with those in aerospace applications (Bell 2016a). Metallic beryllium for aerospace applications is used for launching systems into space, sensors in optical systems of satellites, low friction applications in aircraft landing gear bearings and brakes (Bell 2016a; European Commission 2017a). CuBe alloys are used in commutators of DC motors in modern spacecraft (Dunn 2016). As black anodized beryllium shows an increased emissivity it is used in heat shields for the descent of spacecraft, thereby reducing temperature excursions of the heat shield (CRM_InnoNet 2015; Dunn 2016). Beryllium is also used in diaphragms for pressure sensing in aircraft altimeters (Svilar et al. 2011). CuBe alloys are also used as electronic and electric connectors in female connector terminals in aircrafts (CRM_InnoNet 2015).

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Substitute alloys with the same combination of properties are currently not available without loss of performance or reliability for safety related applications making beryllium irreplaceable.

OTHER

Further beryllium applications are found amongst others in the medical, nuclear energy and research related sectors. Beryllium iron and beryllium nickel alloys are used in surgical instruments for springs and membranes (Bell 2016a). Beryllium foils are incorporated in CT scanners and mammography instruments for high-resolution medical radiography due to beryllium's unique properties to be highly transparent to x-rays, its heat resistance and capability to maintain vacuum needed inside of the x-ray tube generator (BeST 2016d; European Commission 2017c). Beryllium foils in new generation mammography instruments enable lower radiation doses per scan while at the same time significantly increasing the resolution for tumor detection (BeST 2016d). Beryllium oxide ceramic materials combine properties of electrical insulation with an extremely high thermal conductivity, a combination which is used to manufacture medical excimer lasers for improving or restoring eyesight, medical lasers for DNA analysis (BeST 2016c) or laser scalpels (Bell 2016a). CuBe connectors are used for precise transmission of electrical signals to delicate non-invasive surgical instruments and monitoring devices (BeST 2016c). Beryllium is used in components of the blood analysis test equipment for detecting HIV and other diseases (BeST 2016c) in magnet resonance imaging (MRI) machines and in pacemakers (Bell 2016a).

Medical isotopes for cancer treatment are produced due to beryllium's capabilities to reflect neutron beams (BeST 2016c). For similar reasons and due to its neutron moderating properties and high temperature resistance, beryllium and BeO are used in research fusion reactors to control the fission reaction (BeST 2016d; USGS 2012). Next generation nuclear fuels may use BeO as additive in uranium oxide pellets, as BeO can cool the fuel pellets more efficiently, thereby enabling lower operating temperatures which can lead to an extended fuel pellet lifespan (Bell 2016a). NiBe alloys are used in overhead fire sprinkler heads to maintain a reliable leak-tight sealing over years of inactivity (BeST 2016d). Other beryllium alloy components are employed in lightweight breathing systems to enable reliable pressure control for air delivery used by firefighters (BeST 2016d). To shield electromagnetic radiation from microwave devices, wireless or RF devices, CuBe meshes are applied (Svilar et al. 2011).

Substitutability of beryllium by other materials in the abovementioned applications is critical, especially when a loss in reliability or performance is expected in critical applications. This is particularly valid in the case of the medical or nuclear energy sector. Thus, there are currently no realistic substitute options available for beryllium in the medical or nuclear energy sector.

SUMMARY

Due to its high price, beryllium is typically only used in applications when it is absolutely necessary i.e. its combined properties are needed, absolute reliability is required or safe operation is of importance. Beryllium is mostly used in alloyed form as copper-beryllium for electrical conducting applications, but also in pure form, as oxide ceramic beryllia or as alloying additive together with other elements (Al, Ni) for lightweight structural mechanical applications. Substitution of beryllium metal or AlBe alloys with >50% Be is only possible for less demanding applications when reliability is not an issue and performance losses are acceptable. In those cases alloys of titanium, magnesium, aluminium, or carbon fibre composites may be applied instead (BeST 2016a). For applications when beryllium's thermal properties are relevant, aluminium metal matrix composites together with silicon carbide / boron nitride can be used instead (BeST 2016a). CuBe and NiBe alloys with Be

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content <2% can only be replaced when safety reduction or performance losses are acknowledged (BeST 2016a). In this case alternate materials include copper nickel silicon, copper iron, phosphorus bronze or copper titanium alloys (BeST 2016a; USGS 2012). In some applications when beryllium is used for structures, optics, or electronic thermal management applications it may be substituted by hybrid composite materials such as polymers or metal matrix composite materials (US Government 2003; USGS 2012).

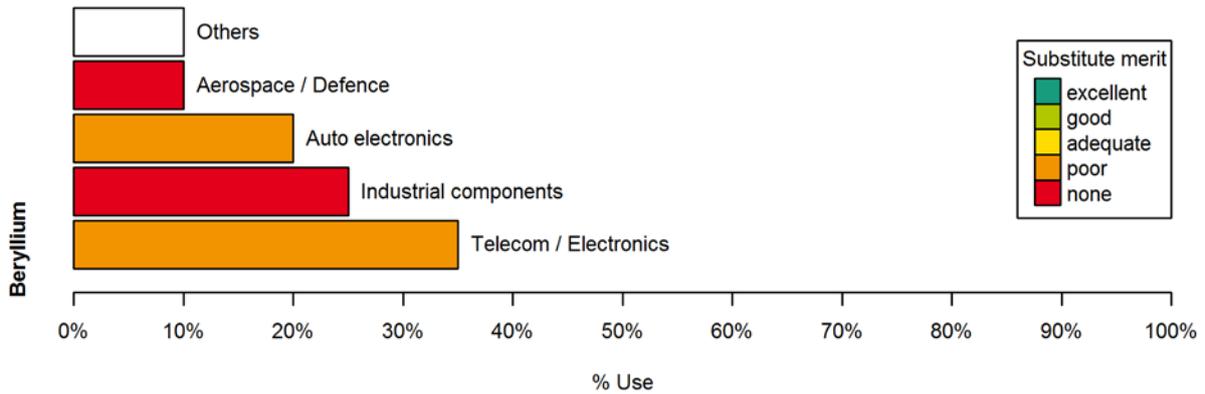


Figure 7: Summary substitutability assessment for beryllium.

BORATES

INTRODUCTION

The chemical element boron nearly always occurs in the earth’s crust and hydrosphere bonded only to oxygen in the form of borate minerals and dissolved boric acid. A very common element, boron is found in all soils and natural waters, but is rarely used in its pure form (Schubert 2015). Borax (an important borate mineral) has been known for at least two thousand years: as fluxes for welding gold before Babylonian times, in glazes by the 11th century in China, and by the end of the 13th century in Europe (used for soldering and enamelling; Enghag 2004; Schubert 2015).

Borates were classified as a critical raw material by the EU in 2017 and 2014 (European Commission 2014b, 2017b). The substitutability of borates has been examined by Graedel et al. (2015), USGS (2017b) and European Commission (European Commission 2014b; 2017a).

USES AND SUBSTITUTABILITY

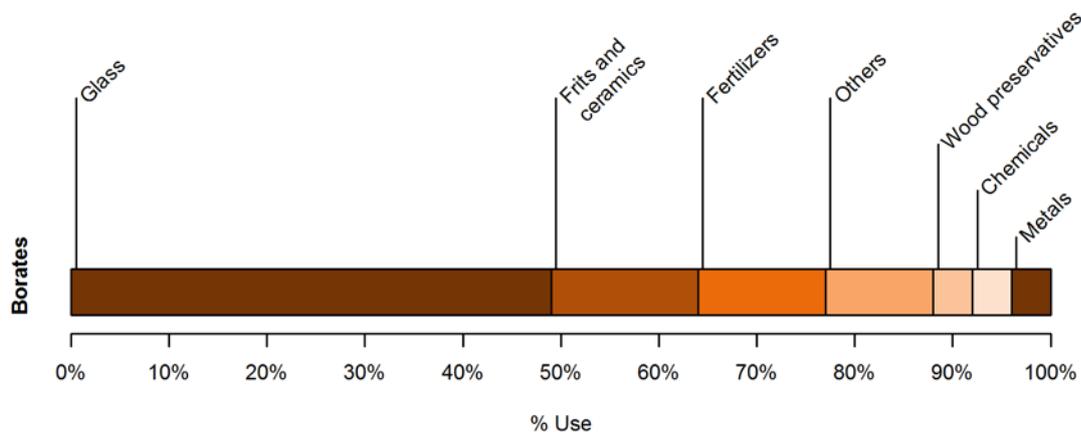


Figure 8: Distribution of recent borates demand in the EU (data from European Commission 2017a).

GLASS

The main use of borates both in the EU and worldwide is for glass, including fiberglass and glass in the more common sense of the word (Bio by Deloitte 2015; European Commission 2017a). Generally, adding borates to glass delivers properties that are difficult to achieve with other additives (Schubert 2015).

Fiberglass is the single largest use of borates worldwide and includes both "glass wool" used in insulation as well as "textile fiberglass" used in reinforced polymer composites (IMA-Europe 2011). Adding borates to the glass melt reduces the melting and fiberizing temperature to a practical range and inhibits devitrification of the glass during manufacturing.

Insulation fiberglass is used in construction (both commercial and residential), vehicles, appliances and machinery for both thermal and acoustic insulation (Schubert 2015). In addition to facilitating production, addition of boron improves shape-resilience of the glass wool during transport and durability during use, as well as thermal insulation performance through the absorption of infrared radiation. Finally, it makes the fibers safer, improving their solubility in lung fluids should fibers be accidentally inhaled during installation. Glass wool currently competes with other insulating materials, most notably rock wool (House-Energy 2013; InsulationShop.co 2018; Knauf Insulation; The house designers 2017).

The main advantages of fiberglass in reinforced plastics is the combination of high strength and low cost, making them the most widely used form of synthetic composite reinforcement (Ehrenstein & Kabelka 2012). Uses of these composite materials include electronic circuit boards, appliances, tools, vehicles, boat and aircraft. Fiberglass composites used for electrical applications (E-glass) must have a low electrical conductivity. E-glass used in printed circuit boards and aerospace applications must contain 5-10% boric oxide, other E-glass 0-10% boric oxide. The use of boron has been reduced or eliminated by some manufacturers where the electrical properties are not important (Schubert 2015). Furthermore, boron oxides evaporate in small quantities from the glass melt (1-10%, De Jong, Bernard H. W. S. et al. 2015), requiring costly emission abatement measures. This led to the development of a boron-free E-glass, recently introduced into the market by a major manufacturer (Thomas et al. 2016).

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Borosilicate glass has the lowest coefficient of thermal expansion of all glasses produced in bulk (De Jong, Bernard H. W. S. et al. 2011). Coupled to high mechanical strength and resistance towards chemicals, borosilicate glass is widely used in various applications such as kitchenware, laboratory equipment, lighting products, tubing, pharmaceutical vials, etc. (Enghag 2004; IMA-Europe 2011). While fused silica and 96% silica glass exhibit even better thermal properties (De Jong, Bernard H. W. S. et al. 2011), a substitution of borosilicate glass appears unpractical at a large scale. Boron is also added glass for display applications, including flat screen TVs, computer monitors, mobile phones, tablets, etc. While there are compositions without boron for the cover glasses of touchscreens, the thin-film transistor glass needed for the displays proper contains about 10% boric oxide (Schubert 2015).

FRITS AND CERAMICS

Borates are used extensively in the manufacture of glazes and enamels, the largest share of which is used to produce wall and floor tiles. Other uses are table ware, roof tiles, and durable ceramics, but also metal (sheet steel, cast iron, aluminum, copper) articles such as stove tops, oven interiors, cookware, tableware, bathtubs and jewelry. Used in the form of borosilicate frits with up to 11% boric oxide, addition of boron reduces melting temperatures and enhances the appearance and durability of the vitrious coatings on ceramics and metals (Schubert 2015). While some enamels can use different glass-producing substances such as phosphates (USGS 2017b), applications requiring thermal cycling need the low thermal expansion coefficient of borosilicate glass.

FERTILIZERS

Boron is a necessary micronutrient for all plants, and is especially needed in periods of rapid growth, fertilization and seed and fruit production. Though this kind of fertilizer is only needed in boron-deficient soils, there is no substitute for it (Enghag 2004; Schubert 2015).

WOOD PRESERVATIVES

Products containing boron are used to preserve wood, both solid lumber and wood composites. Zinc borate protects wood composites (such as oriented strand board) used both in commercial and residential construction against decay and wood-destroying insects including termites. For solid lumber, borates also protect against wood-boring beetles and carpenter ants (Schubert 2015). Borate compounds compete with copper-based compounds and all-organic compounds in this market.

CHEMICALS

Boron-containing chemicals are used in cleaning and personal care products and as flame retardant. In peronal care and cleaning products, borates are used to provide various functions such as buffering, inhibit the reposition of soil or stain particles, water softening, control viscosity, etc. In flame retardants, borates reduce the flammability of cellulosic materials and act as a synergist for compounded synthetic polymers (Schubert 2015). Alternatives are available for soaps and detergents (potassium salts, sodium percarbonate; USGS 2017b).

METALS

The uses of borates in metallurgy are manifold. They are used in the refining of gold and silver to remove impurities in a furnace. They are also used in base metal (lead, zinc, copper, brass, bronze) refining, where they act as fluxes and remove impurities to a slag that can be decanted. In addition, borates are used in steel and stainless steel wire- and tube-drawing operations, where they provide buffering and lubrication, and inhibit corrosion besides acting as a flux. Finally, boron is a part of different alloys, including high-strength aluminum, copper and steel alloys, as well as amorphous metals and magnetic alloys (notably, in neodymium-iron-boron magnets). Finally, in the process of boriding (or boronizing), a thin continuous surface layer of metal boride (very hard and refractory) is created, providing substantial protection against wear and corrosion.

OTHERS

Other uses of borates include nuclear technology (), gypsum wallboard for interior construction (), pulp and paper (), water treatment (corrosion inhibition e.g. in recirculating water systems), industrial fluids (antifreeze, brake fluid, greases, hydraulic fluids) and adhesives (Schubert 2015).

SUMMARY

The uses of borates are very diverse, even within the categories defined above. For glasses--the largest use of borates--substitution alternatives depend on the application: borates may be replaced in fiberglass (boron-free E-glass) or fiberglass insulation itself may be replaced by alternatives such as rock wool. However, the sheer extent of its use appears to be a limitation in itself. No practical substitutes are available for glass that has to resist temperature shocks. A similar mixed picture emerges for the category frits and ceramics: most goes into tiles and floors where other compounds may be used, but replacing borates in applications implying thermal shocks is either not possible or will affect performance. While various substitutes exist for individual chemicals (incl. wood preservatives), no substitution is possible in fertilizers due to the biological function of boron and appears impractical in metallurgy (as a whole) with the myriad uses.

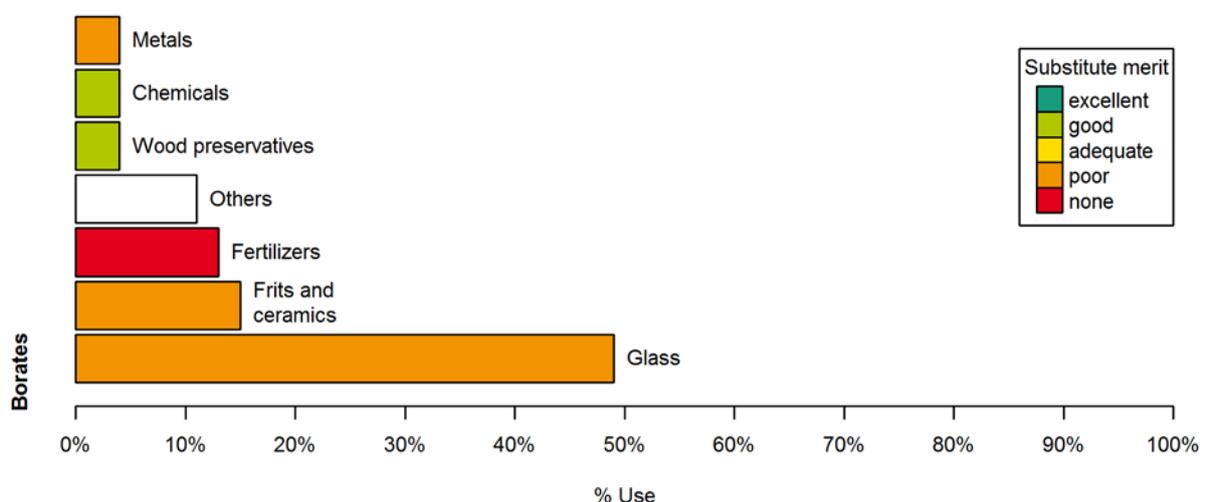


Figure 9: Summary substitutability assessment for borates.

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COBALT

INTRODUCTION

Cobalt is shiny, silver-coloured, brittle metal that is used to produce strong, corrosion and heat resistant alloys, permanent magnets and hard metals (European Commission 2014c). It has a high melting (1493 °C) and boiling (3100 °C) points. It is one of the three magnetic metals (together with nickel and iron) and retains this ferromagnetic property up to 1100 °C, being the highest Curie Point of all metals. Cobalt also has valuable catalytic properties. The first use of cobalt, dating back to Ancient Egypt, was as a pigment in conjunction with silica providing blue pigments for glassware and ceramics. However, cobalt is a very versatile metal and over the 20th century it started to be employed for a large variety of applications such as metallurgical uses (e.g. superalloys), electronics, magnets, rechargeable batteries, inks and pigments, catalysts, alloys, healthcare, etc. (Cobalt Institute 2017).

Cobalt has been classified as a Critical Raw Material for the EU since the original criticality assessments in 2010 (European Commission 2010, 2014b, 2017b). The substitutability of cobalt was assessed by Graedel et al. (2015) and in the CRM_InnoNet project (Tercero Espinoza et al. 2015).

USES AND SUBSTITUTABILITY

The European industry manufactures various finished products containing around 11 kt of cobalt and consisting mainly in superalloys and hard metals:

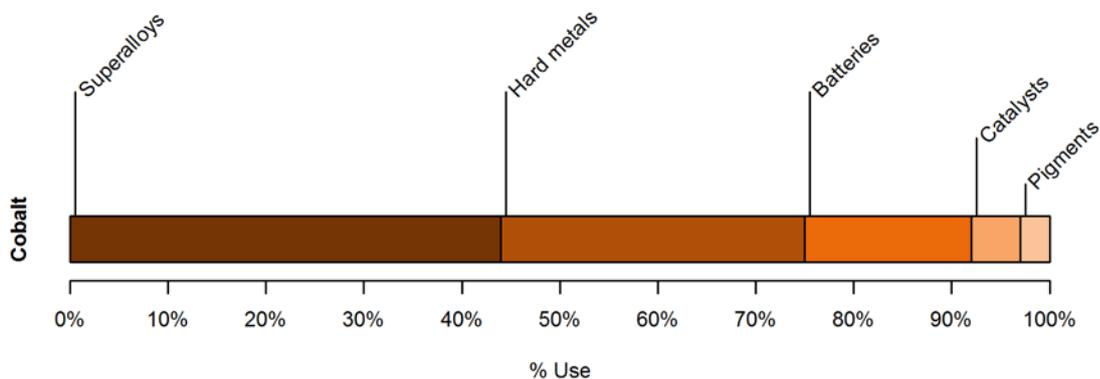


Figure 10: Distribution of recent cobalt shares of finished products manufactured in the EU (data from Bio by Deloitte 2015).

SUPERALLOYS

Historically, the major end-use of cobalt is in superalloys. They are defined as "alloys developed for elevated temperature service where severe mechanical stressing is encountered and high surface stability is frequently required". There are three classes of alloys that meet this definition: cobalt-based, nickel-based and iron-based. The most common cobalt alloy is with nickel but also with iron to provide superior thermal performance, corrosion, weldability and wear resistance in a wide range of alloys used in applications such as jet aircraft engines, turbine blades for gas turbines, space vehicles or chemical equipment. A key sector for cobalt-

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containing superalloys for example is aerospace, where these properties are vital for reliable and efficient turbines (Cobalt Institute 2017).

Fiber-reinforced metal matrix composites (MMC), ceramic-ceramic and carbon-carbon composites, titanium aluminides, nickel-based single crystal alloys or iron-based super-alloys may substitute cobalt-based ones to some extent. Loss of performance at high temperatures (due to the unique physical properties of Co) can, however, be expected in some cases. Therefore, substitution for cobalt in jet engine castings will probably not occur and cannot be considered as a meaningful solution to the cobalt supply problem (Tercero Espinoza et al. 2015).

HARD METALS

Cemented carbides are a range of composite materials consisting of hard carbide particles bonded together by a metallic binder. One of the key uses of cobalt metal is as a binder for tungsten carbide (WC) and sometimes for titanium-carbo-nitrides or tantalum-carbides. The addition of cobalt to the carbide increases resistance to wear, hardness and toughness, essential qualities for cutting tools, metal rollers and engine components. Cemented carbides are used in many different industries, including automotive, aerospace, energy, mining and general engineering (Cobalt Institute 2017).

Researchers have investigated using other elements as binders, including nickel and iron. No other metal fulfils the characteristics mentioned above. Despite most of the competing matrix materials having a lower cost, there is a certain loss of performance. Therefore, cobalt is practically irreplaceable in cemented carbides and in the hard metal industry.

BATTERIES

Cobalt is important for maintaining the life of rechargeable batteries. Early versions of lithium ion batteries that did not utilise cobalt often overheated and failed. These problems arise due to dendrite formations piercing the membrane between the cathode and the anode. By including cobalt in the cathode, the lithium ions are prevented from forming dendrites by bonding to the cobalt. Preventing the formation of dendrites ultimately leads to the longer-life of the battery, along with the capability of quick charging and low stand-by energy losses. Cobalt also prolongs the life in service of cylindrical alkaline batteries. During storage, the inner surface of the battery becomes lightly oxidised over time. Due to the battery case being the current conductor, the higher surface resistance caused by the oxidation leads to higher heat generation and less power. Eventually, the battery will then need to be replaced for the application to be powered efficiently. By adding cobalt to the inner surface of the battery, oxidation is reduced pro-longing the life in service of the battery. In this role, the only possible alternatives to cobalt chemically speaking are gold and silver however for economic reasons these are not viable alternatives (Cobalt Institute 2017; Tercero Espinoza et al. 2015).

Substitution of cobalt in Li-Ion batteries is potentially possible. Although LiCoO_2 is the preferred material for portable battery applications, both LiNiO_2 and LiMn_2O_4 can also be used for the same purpose. In addition, latest industry predictions indicate that many of the disadvantages of alternative materials have been overcome and although rechargeable battery demand is expected to increase rapidly in the next few years, cobalt demand in this application could remain stable or even decrease slightly (Cobalt Institute 2017; Tercero Espinoza et al. 2015).

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CATALYSTS

Cobalt plays a vital role in catalysing the removal of sulphur from oil, gas and petrochemical products such as petrol/gasoline, diesel, kerosene fuels and fuel oils. The second major use of cobalt catalysts is in the mixed cobalt acetate/manganese sodium bromide homogeneous catalyst for production of recyclable plastics (i.e. terephthalic acid (TPA) and di-methylterephthalate(DMT)). In addition, it is also used in the catalysis of gas to liquid processes (Cobalt Institute 2017). Finally, a potential emerging use (and subsequent increase in demand) of cobalt is as catalyst in hydrogen fuel cells (Tercero Espinoza et al. 2015).

With regard to its application for hydrodesulfurization, ruthenium, molybdenum, nickel and tungsten can be used depending on nature of the feed, instead of cobalt. Also alternative ultrasonic process can dispense with the use of cobalt, and rhodium can serve as a substitute for hydroformylation catalysts (USGS 2017b).

PIGMENTS

The unique combination of colour, solubility and stability make cobalt compounds into powerful colouring agents in a variety of applications. This ability of cobalt-containing minerals to impart colour has been important for thousands of years going back to the times of the Egyptians and Persians. These properties of cobalt produce light blue to black pigmentation for glass, porcelain, ceramics, paints, inks and enamelware, whereby the amount of cobalt oxide added to the final product depends on the required colour. The pigments used for colourants include cobalt in many formulations. In general, the pigments are prepared by mixing the ingredients as oxides before calcining (the treatment of a mineral product at a high temperature) them at 1100°C-1300°C and grinding back to a fine powder (Cobalt Institute 2017). The final colour depends on the application. For instance, in a glaze, further firing occurs which modifies the colour. As cobalt(II) acetate, it is used in the production of drying agents for inks and pigments (Tercero Espinoza et al. 2015).

Cerium, iron, lead, manganese, and vanadium can all be used as substitutes for cobalt for this application, unfortunately not necessarily with the same results (USGS 2017b).

SUMMARY

Generally, cobalt has limited options for substitution. In some applications, substitution for cobalt would result in a loss in product performance due to the unique properties of cobalt in superalloys and hard metals. Some examples of potential substitutes include cerium, iron, lead, manganese, or vanadium in pigments, but also leads to a decrease in performance; iron-phosphorous, manganese, nickel-cobalt-aluminium, or nickel-cobalt-manganese in lithium-ion batteries; cobalt as a catalyst may be substituted to some extent for hydrodesulfurization and hydroformylation processes (REMONDIS 2018; USGS 2017b).

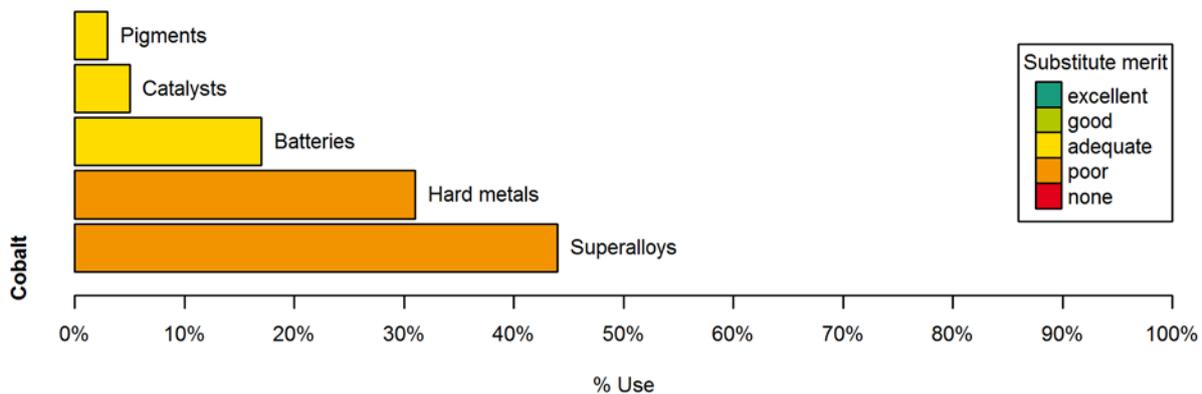


Figure 11: Summary substitutability assessment for cobalt.

COKING COAL

INTRODUCTION

Coking coals are sometimes referred to as metallurgical coals and are in general soft bituminous coal suitable for coking. Suitable coals for coke making can be identified by their characteristics as e.g. reflectance, swelling index etc. Coking coals are those coals that soften, swell and then solidify as they are heated through the temperature range 350°C to 550°C. These plastic properties are lacking in thermal coals. In general, approximately 4-8 coal types are mixed when coke is produced and in the selection of coals attention is on e.g. low ash content (1 – 10%), low contents of lime, alkali and iron in the ash, and volatile matter (VM) content in order to reach suitable amount in the blend.

The availability of high quality coking coal is limited and the price is strongly dependent on the economics of the global steel industry. When the steel business is doing well, the coking coal price is significantly increased. Therefore, there is research on how to replace some part of the coking coal with cheaper alternatives such as thermal coal and residues as e.g. plastics. Moreover, the focus on lowering of CO₂ emissions has resulted in activities for replacing fossil coal with bio-based alternatives.

Coking coal was introduced to the scope and classified as a Critical Raw Material for the EU in the assessment of 2014 but not in the latest 2017 assessment (European Commission 2014a, 2017b).

USES AND SUBSTITUTABILITY

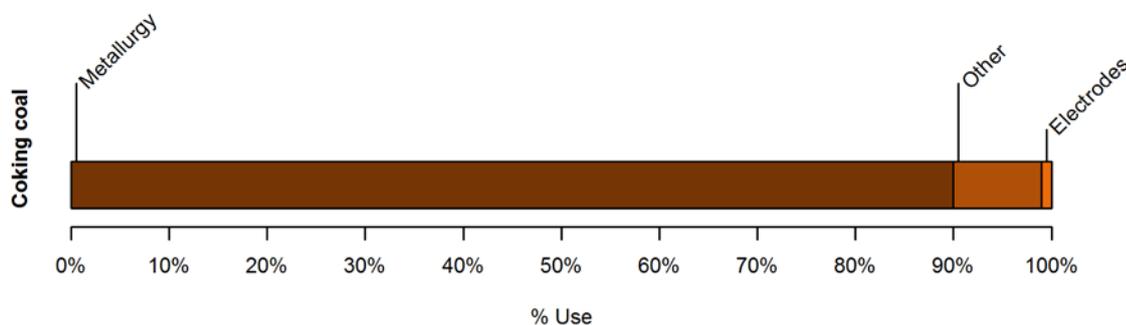


Figure 12: Distribution of recent coking coal demand for manufacturing in the EU (data from Bio by Deloitte 2015).

METALLURGICAL APPLICATIONS

Coking coal is mainly used for metallurgical applications. The production of coke in Europe was approximately 30 Mt in 2016. The amount of coking coal needed for the production of coke varies dependent on the volatile content but approximately 1250-1400 kg coking coal is needed for the production of 1 tone of coke.

High quality metallurgical coke is mainly used in blast furnace iron making but also in other metallurgical processes as e.g. ferroalloy production. Foundry coke can be used in low shaft furnaces and cupolas producing metals but in some cases also fibers for insulation.

Different methods have been explored to produce high-quality coke using materials other than coking coal.

- Stamp charging: By stamp charging slightly less high qualitative coking coals can be used while still producing high quality coke. Higher density of the blend may cause more swelling and thereby be a risk for the coke ovens, especially in case of high oven batteries. Additives as e.g. oil can make it possible to give the blend higher density (Madias & Córdova 2013).
- SCOPE21 process: Research and development of new coke-making process was conducted in Japan from 1994 to 2003 by the Japan Iron and Steel Federation (JISF).[1], [2] Pilot plant scale testing was successful and a type new coke oven battery was constructed and started up in 2008 at Nippon Steel Oita works. The coke production capacity is 1 million tonnes per year. At present, high quality coke has been produced in this process using high blending ratio (over 50%) of non- or slightly-coking coal. Such process can also give open possibilities for use of secondary materials (such as plastics).
- Calderon coking reactor: This is a two-step process with the same aim as scope 21 process, including carbonization at low temperature followed by calcination of the coke in a separate device with complementary hot gas cleanup system.[2], [3] This process shall also allow higher coking pressures than in conventional cokemaking.[4]
- Use of hypercoal as additive to coking coal blend: Research is on-going in order to increase the possible added amounts of thermal coals to the coal blend, in Japan this was enabled by addition of hypercoal[4]–[7] to the coal blend. Production of hypercoal involves a first step in which the carbon structure is dissolved into a solvent at elevated temperature and increased pressure. The solid ash is removed and solid carbon precipitated as the solvent is vaporized and collected for repeated use. In principle the hypercoal process can be used for producing material suitable in the coking coal blend using high ash containing coal that can be tailings from mining of thermal coals or coking coals.

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- Recycling waste plastics in coking coal: Waste plastics in coking coal blend has shown to be an alternative that can replace 1-2% of the coking coal and at the same time the coke quality is not lowered. Only 20% of the plastic will remain in the coke and the rest will report to the coke oven gas or chemicals collected in the gas treatment plant.

ELECTRODES

For making electrodes, natural graphite and synthetic graphite can replace coking coal. However, natural graphite is also listed as one of the Critical Raw Materials.

SUMMARY

Coking coal is mainly used for the production of metallurgical coke and high quality coking coal has its origin in Australia and USA. The ability to replace some coking coal with economically favourable alternatives (such as hypercoal and waste plastics) is in focus for steel producers globally and it is estimated that 5-10% of these alternatives can be used to substitute coking coal for metallurgical applications. Natural graphite and synthetic graphite can replace coking coal very well for making electrodes. The estimated substitute merit of coking coal in different applications at the moment is shown below.

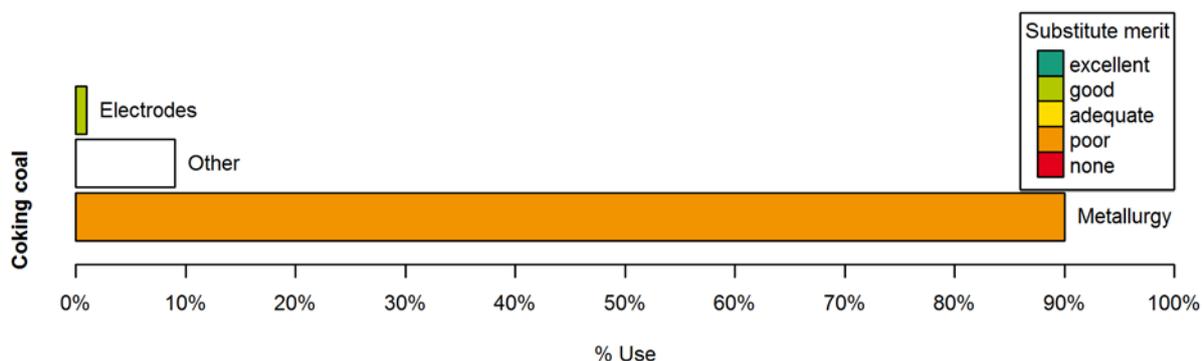


Figure 13: Summary substitutability assessment for coking coal.

FLUORSPAR

INTRODUCTION

Fluorspar, also known as fluorite (CaF_2), is a mineral compound consisting of 51% calcium and 49% fluorine when present in pure form. Fluorspar occurs naturally as mineral fluorspar and in smaller amounts in a number of other minerals e.g. in apatite and phlogopite (British Geological Survey 2011). The main usage of fluorspar is in the production of hydrofluoric acid which is in turn used to produce a number of other fluorinated chemicals including fluorocarbons, fluoropolymers, fluoraromatics and inorganic fluorine compounds (Bio by Deloitte 2015). Due to its low melting point, fluorspar is also added to metallurgical slags as a flux additive for smelting, as it reduces the viscosity, thereby increasing fluidity at lower temperatures. This is needed in the steel, aluminium or cement production (CRM Alliance 2017).

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Fluorspar has been classified as a Critical Raw Material for the EU since 2010 (European Commission 2010, 2014b, 2017b). The EU expects a modest demand growth rate of <3% per year until 2020 (European Commission 2014b). Substitutability of fluorspar was assessed by the European Commission (European Commission 2014c, 2017a), the US geological survey (USGS 2017b) and in the CRM_InnoNet project (Tercero Espinoza et al. 2015).

USES AND SUBSTITUTABILITY

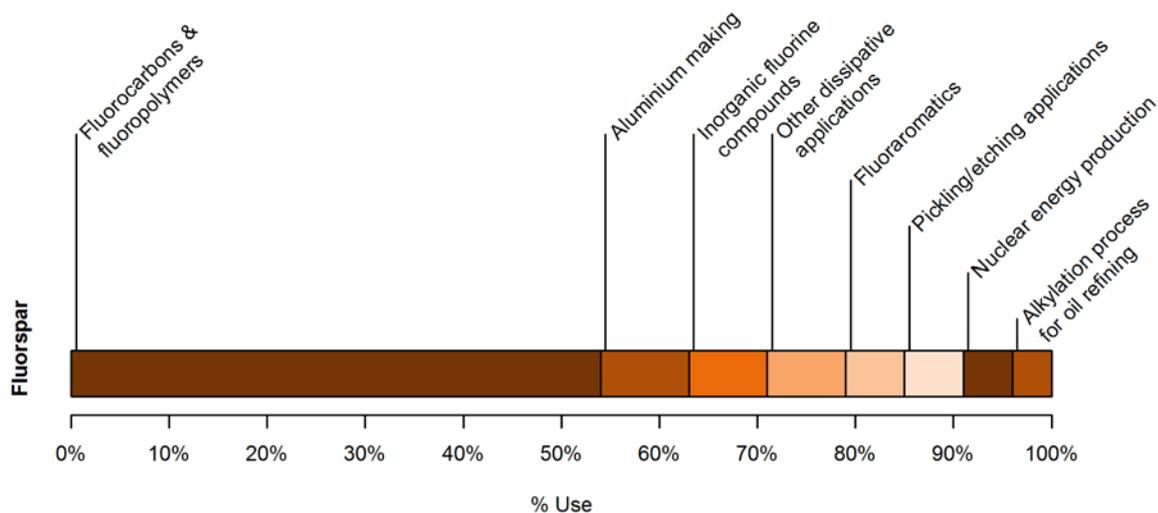


Figure 14: Distribution of recent fluorspar demand for manufacturing in the EU (data from Bio by Deloitte 2015).

FLUOROCARBONS & FLUOROPOLYMERS

Fluorocarbons (fluorinated hydrocarbons, HFCs) are mainly used as refrigerant in stationary and mobile air conditioners, heat-pumps, or organic Rankine cycles (ORC) for power generation from heat (EFCTC 2017). HFC's offer special advantageous properties as refrigerant: low toxicity, non- or low- flammability and a moderate global warming potential. Furthermore, HFCs show good thermodynamic properties and can be tailor-made to specific operation conditions required for process scalability, thereby increasing system efficiency. HFCs have been introduced to replace chlorofluorocarbons (CFCs), and hydrochlorofluorocarbons (HCFC) due to their higher ozone depletion potential (ODP) or global warming potential (GWP). Available substitutes for HFCs refrigerants are CO₂, ammonia, hydrocarbons and water (European Commission 2017). However, those may not be suitable for each application or as performant as HFCs as e.g. ammonia is toxic, hydrocarbons are flammable and CO₂ needs to be compressed to high pressures to be able to use it as refrigerant.

HFCs are also used as solvents for degreasing metal surfaces needed for precision coatings, in the optics and electronics sector (Robin 2014). HFCs specific properties make them valuable as solvent: high material comparability, excellent dielectric properties, low surface tension/viscosity, thermal and chemical stability, very low toxicity, non-flammability, zero-ODP and low GWP. Applications include landing gears in aerospace industry (to stop fracturing from trapped water), medical devices, heart valves, surgical needles (to obtain stringent infection free standards), fuel injectors, ABS brakes, switches, sensors, compressors, relays in the

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automobile industry, optical components and assemblies, lenses fiber-optics, displays, jewelry and watches. (EFCTC 2017; Robin 2014).

Due to HFC's very good insulating properties and non-flammability it is used as foam blowing agents for closed-cell foam structures, polyurethane foam (PU) and extruded polystyrene (XPS) as found in building insulations to reduce heat losses/heat gain for improving living comfort as well as in refrigeration applications (EFCTC 2017; European Commission 2017). Currently alternative fluorine based blowing agents, hydro-fluoro-olefins (HFO), are introduced to replace HFCs, due to their comparatively very low-GWP and better energy efficiency. HFC can be substituted by pentane. However, pentane is a flammable blowing agent not suited for most foam applications. Methylformate and dimethoxymethane may be potential substitutes for HFC in PU foams (Huntsman 2011).

Other applications of HFCs are in fire protection as fire extinguishant needed in cases where safety, space and speed are of special concern. As HFCs are clean, electrical insulating/non-conductive and do not leave residues, fire extinguishants using HFC are found in process control centers, computer/server rooms and telecommunication facilities (EFCTC 2017). HFC based fire extinguishants are employed for most effective fire protection systems concerning space and weight considerations.

Fluoropolymers have great strength, durability, heat resistance and versatility. Their main uses are in wire insulation for computer networks, automotive fuel hoses and semiconductor manufacturing equipment. Other applications comprise non-stick cook-/bakeware coatings, membranes for weather and chemical protective fabrics (European Commission 2017a; PKN 2012).

ALUMINUM MAKING

Hydrogen fluoride is used to produce synthetic cryolite (Na_3AlF_6) and aluminum fluoride (AlF_3) (Banks et al. 1994). Both materials are needed as additive to the electrolysis baths for the production of aluminum from electrolysis cells or in the electrolytic aluminum refining process (Aigueperse et al. 2011). Cryolite has the special property to dissolve fluorides and oxides of aluminum, thereby molten cryolite acts as electrolyte (Kvande & Drabløs 2014; Thonstad & Rolseth 2013). Cryolite serves as a bath controlling agent to create the right environment (temperature, viscosity, conductivity and density) for the electrolysis during aluminum production (Aigueperse et al. 2011).

Currently, there are no substitute options available for cryolite or aluminum fluoride in commercial aluminum production.

INORGANIC FLUORINE COMPOUNDS

Sulfur hexafluoride (SF_6) is used in electromechanical equipment where electrical insulation is needed. SF_6 shows good dielectric properties, inertness and is able to trap electrons during electrical arc blowing i.e. arc interruption (Aigueperse et al. 2011). Applications are high and medium-voltage circuit breakers, compact switchgear stations of high safety and which need little maintenance, and high power electric cable insulations through regions which have difficult environment or are protected (Aigueperse et al. 2011; EFCTC 2017). Minor usage of SF_6 is in the insulation of nuclear particle accelerators, X-ray equipment, microwaves and radar technology or thermoacoustic insulation of smart windows SF_6 helps to increase water repellency of kraft paper (Aigueperse et al. 2011).

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As SF₆ is an ozone depleting substance, substitute options have been developed. SF₆ may be substituted by CO₂ for medium voltage insulating switchgear applications. Also fluoroketone-based gas-mixtures can replace SF₆ in gas-insulated switchgears, however those substances also contain fluoride (Diggelmann et al. 2016).

FLUOROAROMATICS

Fluorinated aromatic compounds are presently key intermediate building blocks used for pharmaceuticals, but also for agrochemicals, advanced polymers/materials, reactive dyes and liquid crystals (Banks et al. 1994; Clark et al. 2018). Fluoroaromatics occur only very rarely in nature and if they do, they are very toxic. However, when fluoroaromatics are combined with biologically active compounds they show superior pharmacological properties with inherent pharmaceutical activity (Wakefield 2000). Pharmaceuticals based on these building blocks, so called effect chemicals, show increased efficacy which can lead to lower dosage and toxicity, broader spectrum of activity and unique physical properties (Clark et al. 2018). Typical fluorinated pharmaceuticals comprise antibacterials, antibiotics, antidepressants, nonsteroidal anti-inflammatory agents, anticancer drugs, antimalarials, tranquilizers and relaxants, and anaesthetics (Banks et al. 1994; Clark et al. 2018; Wakefield 2000).

Noninvasive medical diagnostic tools such as PETT (positron emission transaxial tomography) use ¹⁸F-radiopharmaceutical positron emitters in order to study metabolic pathways in living systems (Clark et al. 2018; Jacobson et al. 2015). Similarly, agrochemicals based on fluoroaromatic compounds with improved biological activity can be tailor-made to produce pesticides, fungicides or herbicides. Due to fluorine, very specific functionalization and selectivity can be realized which also manifests in a reduced dosage and increased crop safety (Banks et al. 1994; Clark et al. 2018). For the production of dyes, fluorine helps to fixate dye to fibers as a nucleofugal group and increases the reactivity of the dye to the fiber (Clark et al. 2018). Ferroelectric liquid crystal displays (FLCD) use aromatic substances containing fluorine substituents. The fluorinating groups are used to create large negative dielectric anisotropy, as needed in FLCDs, while at the same time maintain viscosity at a sufficient low level as opposed to non-fluorinating substituting groups (Clark et al. 2018).

PICKLING/ETCHING APPLICATIONS

Aqueous HF acid is used to produce pickling acid needed for surface treatment of metals. Other applications are in etching and polishing glasses (Banks et al. 1994). Furthermore, fluorine is used to prepare NF₃ used for etching of silicon, to produce polyolefin containers which are solvent-resistant or to enhance moisture transport in synthetic fiber applications namely, polyamide, polyester, polyolefin and polyacrylonitrile fibers (Jaccard et al. 2011).

NUCLEAR ENERGY PRODUCTION

Uranium hexafluoride (UF₆) gas is used for the separation of different uranium isotopes, namely U-235 from U-238. The natural abundance of isotope U-235 is scarce but it is needed in enriched form in order to be able to use as nuclear fuel for the fission reaction in the nuclear reactor to produce energy (WNA 2007). UF₆ is used as the only suitable chemical for the separation of uranium in the gas-diffusion or centrifugal separation process, because UF₆ has a high enough vapor pressure at room temperature such that uranium in gaseous form can be separated at low temperatures (Urenco 2018).

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Currently there are no substitute options available that use other substances than UF₆ for enrichment of U-235 (Urenco 2018). Alternative nuclear-fuel energy concepts which are currently developed can operate with transmuted U-233 as obtained from thorium-232 (Dolan 2017). However, separation processes for U-233 also rely on fluorinated compounds so far.

ALKYLATION PROCESS FOR OIL REFINING

Fluorine in form of hydrofluoric acid (HF) is used as alkylation catalyst in the oil refining (Aigueperse et al. 2011; Banks et al. 1994; European Commission 2017a). HF's capability to protonate alkenes is used to produce alkylate from isobutane and low-molecular weight alkenes, a blending component consisting of larger iso-paraffins for high-octane gasoline. Alkylates show excellent anti-knocking properties.

Substitute options for HF are available. It is possible to use liquid sulfuric acid instead of gaseous HF as alkylation catalyst which however requires altered process conditions and a different process itself (eia 2013).

SUMMARY

Fluorspar is mainly used to produce fluorocarbons and fluoropolymers besides a large variety of other fluorinated substances of smaller quantities. Substitute options are available in the oil refining segment with liquid sulfuric acid as alkylation catalyst, ammonia or CO₂ can be used as fluorine free substitute in the refrigeration segment of air-conditioning applications, but at altered process conditions and increase security risk in case of ammonia (European Commission 2017a). For some medium voltage insulating switchgear applications CO₂ can also be used instead of SF₆. However, no substitute options are currently available for UF₆ in uranium enrichment for nuclear energy production, for cryolite or aluminum fluoride in the aluminum production, or in the pharmaceutical sector for fluoroaromatics. Substitutes for fluorspar as flux additive (dissipative) such as borax, iron oxides, aluminum smelting dross, silica sand, calcium chloride and titanium dioxide have been used in the past. Solid fluoropolymers may be substituted by plastics, stainless steel, ceramics or aluminum.

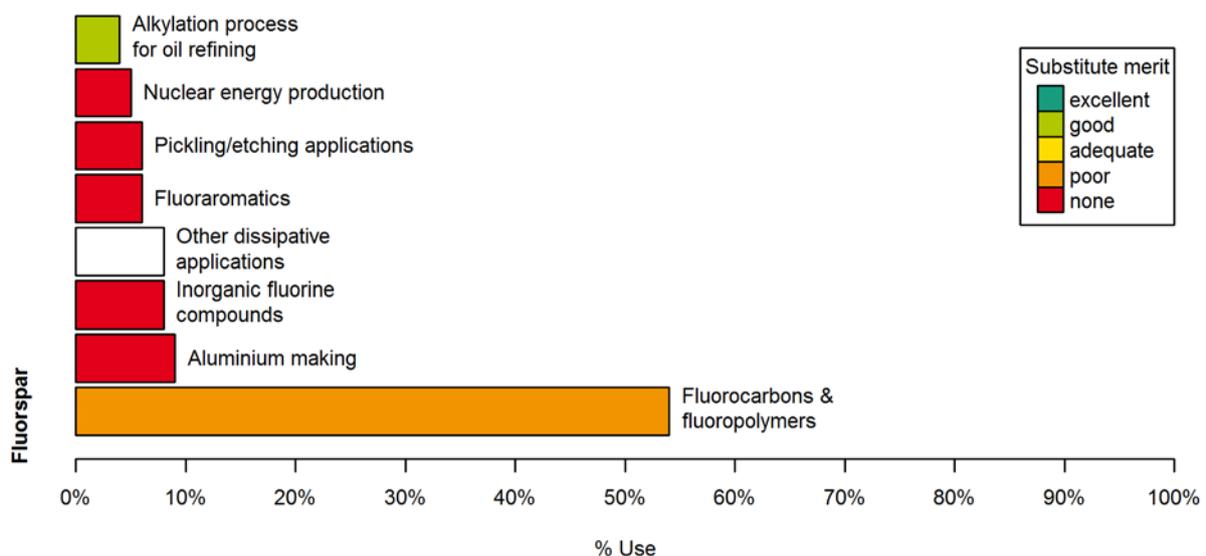


Figure 15: Summary substitutability assessment for fluorspar.

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GALLIUM

INTRODUCTION

Gallium is a silvery-white, soft metal, which is one of the rarer elements in the earth's crust. It is mainly found in enriched amounts suitable for economical use in ores of aluminum (bauxite) due to gallium's chemical similarity to aluminum, but also in ores of zinc (sphalerite) and in the fly ash of coal (Marscheider-Weidemann et al. 2016). Gallium is a low melting point metal and has one of the largest liquid ranges amongst all elements, as it melts already at 30°C and evaporates at 2403°C (Greber 2000). Gallium forms compounds with nitrogen (GaN) or arsenic (GaAs) exhibiting excellent semiconducting properties, which allows its use for high-frequency applications. The main use of gallium is in semiconducting form as GaAs and to a much lesser extend as GaN, due the comparatively difficult and costly production (European Commission 2017a). Currently, worldwide end uses for GaAs comprise integrated circuits (ICs), optoelectronic devices, including light emitting diodes (LEDs), laser diodes, photodetectors and copper-indium-gallium-selenium (CIGS) based thin film solar cells (USGS 2017b).

Within the EU the main share of manufactured gallium which is finished into products goes into sensor applications, mainly for military uses and in second place into applications using permanent magnets (Bio by Deloitte 2015). The EU Commission considers gallium as a critical raw material since 2010 due to the limited production potential as by-product during the aluminum refining process from bauxite, its growing use and importance for low CO₂ footprint technologies (European Commission 2014c; Licht et al. 2015; Løvik et al. 2015; Pavel et al. 2016b). It is forecasted that until 2020, the gallium demand will strongly increase by more than 8% annually, thereby showing the second largest demand growth rate of all classified critical raw materials after niobium in the EU. The substitutability of gallium was assessed by the European Commission (European Commission 2014c), the US Geological Survey (USGS 2017b) and in the CRM_InnoNet project (CRM_InnoNet 2015).

USES AND SUBSTITUTABILITY

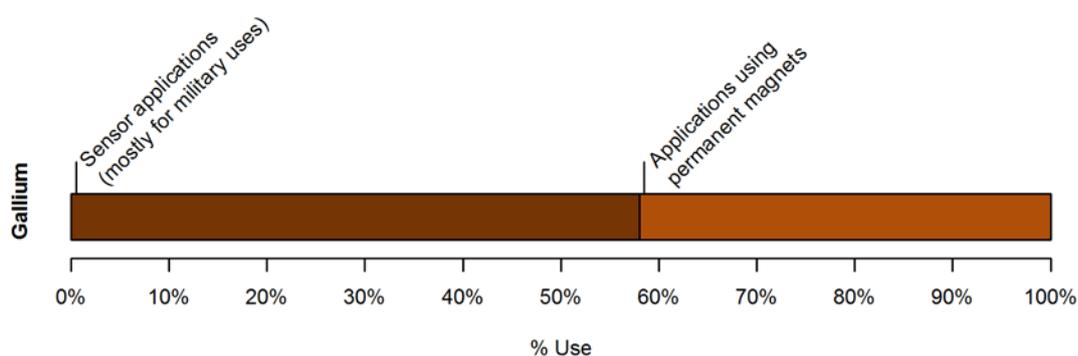


Figure 16: The distribution of recent gallium demand for manufacturing in the EU (data from Bio by Deloitte 2015).

SENSOR APPLICATIONS

The largest manufacturing field are gallium based applications using type III-V semiconducting compounds (GaAs, GaN, GaSb) for integrated circuits and sensors mostly for the military and defence sector in the EU (Bio

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by Deloitte 2015; CRM_InnoNet 2015). Ga-based sensors are used in radar technology, satellites, aerospace applications, for night vision or in high performance devices for wireless communication purposes (European Commission 2014b) due to their superior performance in handling high power, high frequencies, extended operational temperature range, smaller noise addition upon signal amplification, and operation at faster switching speeds (electron mobility) as compared to other conventional silicon based semiconductors. (Gallagher 2016; Gunn 2014). In particular, gallium is used in fibre-optic data communication units (optoelectronic ICs) consisting of optical transmitters to convert electrical into optical signals (LEDs and laser diodes) and optical receivers in form of photodetectors to re-convert light into electrical signals. Transmitter and receiver typically contain GaAs compounds enabling data transmission at high bandwidth over long distances in an electromagnetic interference protected way through optical fibres, also beneficial in hazardous environments. Wireless networks contain GaAs based field effect transistors (FET) or analogue integrated circuits (IC) also called monolithic microwave integrated circuits (MMIC) used for point-to-point radios and cellular communications (Gunn 2014). Modern night vision devices (NVD) use InGaAs and GaAs based photoelectrode sensors to convert invisible light in the near infrared (NIR) to shortwave infrared (SWIR) range into electrical energy in order to be able to generate visual light for the wearer (Gunn 2014; Photonics Online 2017). Phase array radars use high power semiconductors integrated as GaAs and lately GaN based MMICs (Keller 2015) for radio frequency (RF) power amplification. Thereby GaN based MMICs show >5-fold improved RF power densities as conventional GaAs based MMICs (Whelan et al. 2012), enabling smaller devices with less weight, larger sensitivity and extended ranges (Keller 2008; USGS 2013). Currently, there are no substitute options available, which could replace Ga-based sensors in military or defence applications without significant performance losses due to gallium's unique properties as semiconducting compound.

APPLICATIONS USING PERMANENT MAGNETS

Permanent magnets are the second largest manufacturing field for gallium-containing products in the EU (Bio by Deloitte 2015). Permanent magnets which require a high strength are used in various applications ranging from computers, wind turbines, electric and hybrid automobiles and several other automated and electronic equipment (Bell 2016b). When gallium is added in small amounts to neodymium-iron-boron (NdFeB) magnets, it increases the efficiency of the magnet and its corrosion resistance (European Commission 2014b, 2014c). However, the main reason for its addition lays in the manufacturing process where gallium acts as a molten lubricant in the hot forming process improving the fluidity of the alloy (Gunn 2014). This cannot be achieved with any other additive to date (Gauß 2018). Other benefits of Ga addition are the improved thermal stability/coercivity of the magnet material (Gauß et al. 2015; Pan 2013), benefits that can be achieved to a similar extent by addition of aluminum, niobium or dysprosium (Gauß 2018).

SUMMARY

Gallium is mainly used in semiconducting compounds as GaAs and increasingly as GaN for military and defense applications. Second largest demand segment for gallium are permanent magnets. In some electronic applications germanium can substitute GaAs (Gunn 2014). Silicon can be used as substitute semiconducting compound for Ga but not without significant performance and efficiency losses (Pavel et al. 2016b). There are no practical substitutes for gallium in the manufacturing of nano-crystalline neodymium-iron-boron magnets.

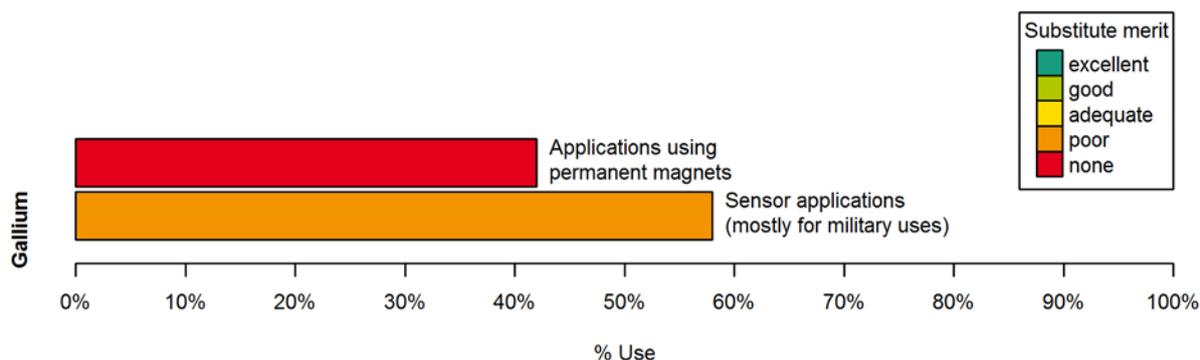


Figure 17: Summary substitutability assessment for gallium.

GERMANIUM

INTRODUCTION

Germanium is a silvery-white, hard, brittle n-type semiconductor and was only discovered in 1886. At 300 K it has a band gap of 0.67 eV, which was responsible for its earlier use in the semiconductor industry in transistors (Ashcroft & Mermin 1986; RSC 2017a; USGS 2017b). The abundance in the earth’s crust is about 1.6 ppm (g/tonne) in continents and 1.5 ppm in ocean’s crust (Gunn 2014). The primary source of germanium is from by-products of zinc and copper ore mining where zinc is associated with sphalerite as well as from coal and coal combustion fly ashes (Claeys 2007; Gunn 2014; Moskalyk 2004). Germanium is used mainly because of its good optical properties, i.e. transparency to infrared radiation, high refraction and dispersion indexes (RSC 2017a). Germanium has been considered critical to the EU since the original assessment in 2010 (European Commission 2010, 2014b, 2017b).

USES AND SUBSTITUTABILITY

The main germanium products in use are (Melcher & Buchholz 2012):

- GeCl_4 — fibre optics
- GeO_2 — PET catalysts, crystals (BGO) for γ -ray detection, medicine, phosphors,
- Ge metal (polycrystalline) — optical casting, IR lenses,
- single crystal Ge — IR lenses, solar cells, X-ray monochromator crystals,
- first-reduction metal – alloys and compounds.

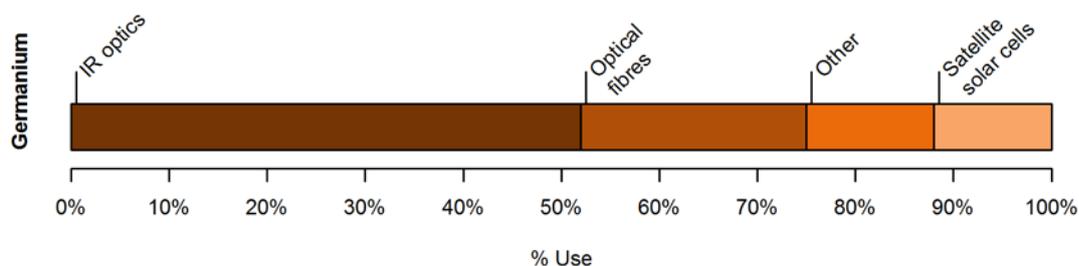


Figure 18: Distribution of recent germanium demand for manufacturing in the EU (Bio by Deloitte 2015).

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The shares in use by application are slightly different for for the world, the EU and the USA (Bio by Deloitte 2015; USGS 2017b).

INFRARED OPTICS

Both germanium and germanium oxide in glass form show very good transparency to infrared (IR) light in the 2-15 μm (mid-wavelength infrared, MWIR and long-wavelength infrared, LWIR) range of wavelength. Germanium other beneficial properties are a high refraction index as high hardness. This makes germanium ideal for building infrared optical elements for demanding applications (Edmund optics 2018b).

Infrared detectors and cameras utilize germanium in lenses and window panes. Ge is also incorporated in the detection sensors for IR to convert to electrical signals. In the military sector, they are used as surveillance, night vision devices, and satellite systems. In the civilian sector, the devices serve medical diagnostics, research equipment, satellite imagery, firefighting equipment (European Commission 2014b; Tercero Espinoza et al. 2015).

The IR optics market already offers— apart from germanium—several different types of lenses based on substrates such as, Black Diamond™ BD-2 ($\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$), ZnSe, ZnS, silicon, Vacuum UV Grade CaF_2 , Poly IR, CaF_2 , IG6 ($\text{As}_{40}\text{Se}_{60}$), GASIR®1, GASIR®5 chalcogenide glasses. They differ in spectral range of transparency, refractive index, dependence of transmittance on coating (Edmund optics 2018a, 2018b; II-VI Infrared 2016; Umicore 2018).

Zinc selenide or zinc sulphide substitute for germanium metal in selected applications like thermal imaging but with lower resolution (Tercero Espinoza et al. 2015; USGS 2018). Chalcogenide glasses especially tellurium-based is another possible substitute (Gunn 2014; Tercero Espinoza et al. 2015). Other chalcogenides such as $\text{Ge}_{30}\text{As}_{13}\text{Se}_{32}\text{Te}_{25}$ are a compromise between price and quality in broad spectral range from visual to LWIR. They have a high transmission from near IR (NIR) to LWIR and low glass transition temperatures and show potential in applications that need consistent performance, with minor defocusing, across broad temperature ranges. The use of a combination of lenses and chalcogenide lens molding technology can be especially successful in night vision applications (Park et al. 2015; Pleşa et al. 2015).

FIBRE OPTICS

Optical fibers transmit light signals at high rates. Among the many types of optical fibres, glass optical fibres are used to transport data across long distances, with high bandwidth and very low attenuation (< 0.2 dB/km). As such, they are used in the backbones of telecommunication networks including transatlantic undersea cables (Marscheider-Weidemann et al. 2016; Paschotta 2008c). This serves high-speed internet connections and telecommunications. The technology for glass optical fibres production is well established (Ungar 1990). Due to the high controllability of those processes, the optical properties of a fibre are easily modified through manipulation of amount of precursor gases. Leading producers of germanosilicate optical fibers in 2015 were: Fujikura Ltd., Furukawa Electric Co., Ltd., Sumitomo Electric Industries, Ltd. (all three in Japan) and Corning Inc. in the United States (USGS 2017a).

Germanium oxide, a high refractive index material is the preferred dopant in silica glass fibre core to form germanosilicate low-loss optical fibres used to make telecommunication cables (Kumar & Deen 2014). It is obtained from oxidizing GeCl_4 vapours at high temperature and co-deposition with silica vapours. However, various other dopants can modify the refractive index inside the fibre core and claddings. An increase in

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refractive index of the core can also be obtained by P_2O_5 (from $POCl_3$) or Al_2O_3 (from Al-based precursor) doping (Paschotta 2008a; Tercero Espinoza et al. 2015). The alternative is to decrease the refractive index n of cladding for example by using BCl_3 (for B_2O_3) and fluorine containing gas doping. Fluoride fibres would be more delicate by a smaller possible temperature range available to preform pulling (Paschotta 2008a). In 2015, a 22.65 km long, silica-core fluorine-doped cladding fibre with a large effective area for submarine applications was reported to have a “record-low” attenuation of 0.1460 dB/km. The fiber showed reduced Rayleigh scattering and attenuation coefficient in comparison with germanosilicate fibers (Makovejs et al. 2015).

Other types of fibres include fluoride glass fibres made of fluoroaluminate or fluorozirconate glasses (Le Verre Fluoré 2018). They exhibit high-optical transparency in MIR range but their attenuation is not as low as typical silica fibres. They find use in MIR spectroscopy, fibre-optic sensors, as well as thermometry and imaging (Paschotta 2008b). In addition, there are fibers using new geometries and different materials, e.g. photonic crystal fibres (PCF; also called hollow fibres, holey fibres, microstructure/microstructured fibres; Paschotta 2008d). In these fibres, the cladding is composed of a set of air holes surrounding the fibre core which effectively gives a lower refractive index (Gunn 2014; Paschotta 2008d). They are already commercially available. In terms of raw materials, these fibres are made of pure fused silica, but can be made from heavy metal soft glasses and polymers (Paschotta 2008d; Tercero Espinoza et al. 2015). Additionally, hybrid PCF are slowly being introduced (Markos et al. 2017). Theoretically, graphene-core optical fibres could exhibit better properties for telecommunication optical fibres than standard (germanium-doped) silica fibers (Das & Sahoo 2016). The above-mentioned non-standard fibres are mainly used in specialized applications, for example active fibres in fibre amplifiers and laser applications.

SOLAR CELLS FOR SATELLITES

Germanium has been used in solar applications in high-performance multi-junction solar cells mainly in space-based applications. The applications include PV panels used in satellite systems as well as terrestrial installations such as concentrated solar PV (CPV) systems. CPV systems utilize Fresnel lenses to decrease the operating area of a photovoltaic cell, and therefore lower the amount of materials and cost (European Commission 2014c; Tercero Espinoza et al. 2015). Germanium for solar cells are characterized by ease of production, robustness, and the absorption of longer wavelengths. Ge cells are also more efficient than silicon-based solar cells. However, their widespread application is limited by the high costs.

Possible substitutes are other cell types, such as combination of multi-junction cells for CPV systems. Substitute materials may include materials containing InGaP, AlGaInP, InGaAsP, InGaAs (all containing other CRM; Tercero Espinoza et al. 2015). A solution that can yield high efficiency would be Inverted Metamorphic Multi-Junction (IMM) solar cells, which are said to be the highest efficiency space solar cell in production (Sol Aero Technologies 2015, 2017). Apart from higher efficiency (32.3%), their core advantage is the lightweight design due to lack of rigid growth substrate (Pickerel 2017). They are initially grown preferably on GaAs, which is removed at the end of the process. They may also be grown on Ge or other suitable substrate which is then reusable (Lin et al. 2017). The product by SolAero Technologies is currently in the process of Space Qualification & Characterization (Sol Aero Technologies 2017).

OTHER USES

The use of germanium in electronics includes high brightness light emitting diodes (LEDs) in devices such as cameras and smartphone display screens. Si-Ge transistors are distinguishable by their high-speed switching

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characteristics utilized in high speed wireless telecommunications devices, as well as smaller energy consumption in comparison to Si-based transistors (European Commission 2014c; Tercero Espinoza et al. 2015). Silicon is the natural substitute in those applications but with inferior performance (Tercero Espinoza et al. 2015; USGS 2018).

Germanium dioxide is used as a PET polymerization catalyst to improve transparency. PET is used to produce plastic bottles, sheet, film and synthetic textile fibres. Germanium is found to remain at a very low concentration (tens of ppm) in the products (European Commission 2014c; Nishioji et al. 1993).

Due to high prices and their variation, the use of germanium in PET outside USA has been decreasing since 2011 (apart from Japan where it has increased after the disaster in Fukushima; European Commission 2014c; USGS 2017a). In addition, in 2015 the GeO₂-based PET resin production decreased by 8% in comparison with 2014 (USGS 2017a). Major producers in Japan have started using antimony and titanium-based products as substitutes for GeO₂ catalysts (Sb₂O₃; antimony triacetate an aluminium-based catalysts are potential substitutes Tercero Espinoza et al. 2015; USGS 2018). The disadvantages include potential carcinogenic effect from Sb-based catalysts (although they are reported safe under normal conditions), and a yellow tint imparted to plastic by Ti-based catalysts (Tercero Espinoza et al. 2015). These disadvantages are reportedly absent in commercially available aluminum-based catalysts (Plastics News Europe 2017).

Germanium is also used in the following applications (Melcher & Buchholz 2012; Tercero Espinoza et al. 2015):

- BGO crystals (Bi₂(GeO₃)₃) for γ-ray detection, medicine, phosphors,
- bismuth germanate oxide crystals (BGO – Bi₄Ge₃O₁₂) for various detection technology (scintillation, tomography, gamma spectroscopy)
- intrinsic Ge metal (polycrystalline) – optical casting,
- single crystal Ge – X-ray monochromator crystals,
- first-reduction metal – alloys and compounds as an alloying element (0.35%) for tin, or Al-Mg alloys, to increase their hardness, soldering material (12% Ge / 88% Au) for gold-based dental prosthesis.

SUMMARY

Germanium is mainly used in infrared optics, optical fibers and solar cells for satellites. Criticality, price and price variations of germanium compounds have encouraged intensive efforts in the search for efficient germanium substitutes. Substitution in infrared optics appears possible but still at the cost of performance. A recent announcement of a Ge-free optical fibre for undersea applications could lead to practicable substitution. The upcoming introduction of a Ge-free (inverted metamorphic multi-junction, IMM) high-efficiency solar cell could also lead to sizeable substitution in this important segment.

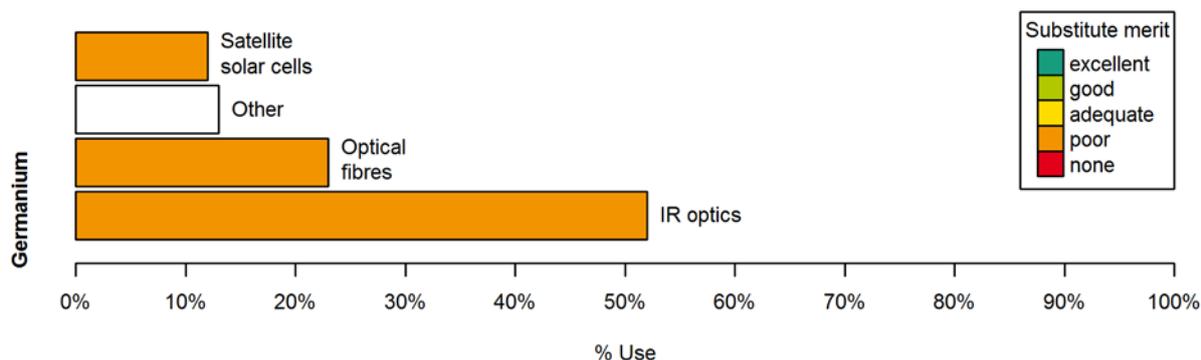


Figure 19: Summary substitutability assessment for germanium.

INDIUM

INTRODUCTION

Indium is a silvery-white soft metal with high ductility, which maintains its malleability even at cryogenic temperatures. The natural occurrence of indium in the earth crust is nearly equivalent to that of silver. Indium is found as a by-product in zinc ores and occurs in smaller amounts in copper and lead ores. Indium belongs to the low melting point metals with a melting point of only 156.6°C but possesses a quite high boiling point of 2080°C (Noël 2000). As alloying addition, indium can have considerable influence even at very low concentrations on strength, corrosion resistance or hardness of the alloying system (Noël 2000). Indium forms semiconducting compounds with antimony (InSb), arsenic (InAs) and phosphorus (InP) and has superconducting properties when cooled down to 3.37 K (Noël 2000). Particularly useful, indium forms together with tin a transparent indium tin oxide (ITO), which can be used as transparent conductive electrode in display technologies (CRM_InnoNet 2015). ITO is transparent to visible light but not to infrared light (Enghag 2004). The main uses of indium are in electronics applications, mainly in flat-panel displays (FPDs), automotive and architectural glasses (optoelectronic windows), lead-free solders, alloys addition, photovoltaics, alkaline batteries, and laser/light emitting diodes (LEDs; Bio by Deloitte 2015; Marscheider-Weidemann et al. 2016).

Since 2010 indium has been consecutively classified as critical raw material by the EU due to the large import dependencies and the limited recycling possibilities (European Commission 2010). It is predicted that within the EU indium will show a strong average demand growth rate of 4.5-8 % per year till 2020 (European Commission 2014b). This is mainly due to increasing demands in consumer electronics for display technologies (Bio by Deloitte 2015; Marscheider-Weidemann et al. 2016). The substitutability of indium was assessed by (Graedel et al. 2015) and in the CRM_InnoNet project (Tercero Espinoza et al. 2015) as well as in (USGS 2017b).

USES AND SUBSTITUTABILITY

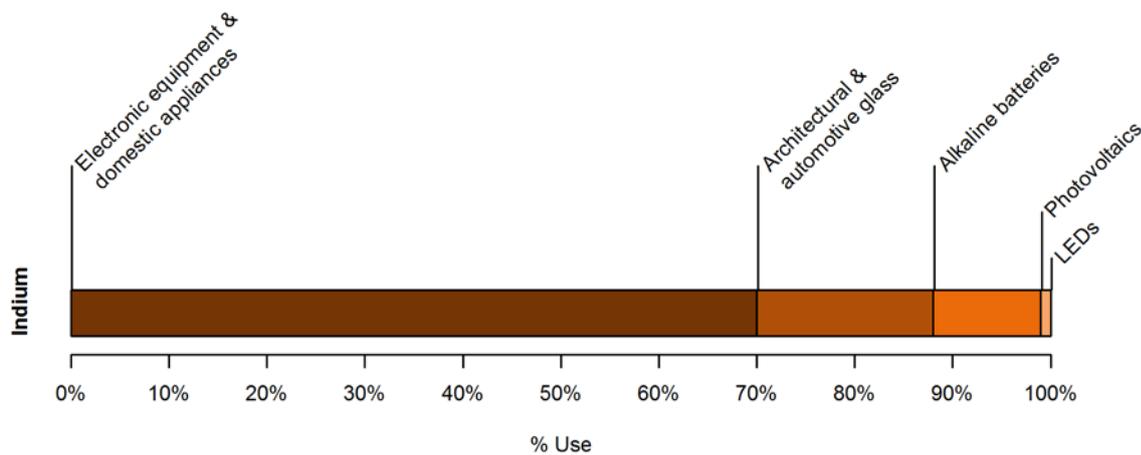


Figure 20: Distribution of recent indium demand for manufacturing in the EU (data from Bio by Deloitte 2015).

ELECTRONIC EQUIPMENT & DOMESTIC APPLIANCES

The most important use of indium in the electronic equipment & domestic appliances sector is in flat panel displays (FPD) including LCD TVs, monitors, notebooks, mobile phones and digital cameras (Polinares Consortium 2012). Indium is used in form of ITO, a transparent conductive oxide (TCO) material with high optical transparency and good electric conductivity which allows the voltage-triggered switching of individual pixels in displays (CRM_InnoNet 2015). As ITO material has excellent etching properties, needed to produce high-resolution displays, and is stable even under high atmospheric conditions, i.e. high durability, it is the material of choice.

Apart from FPDs, indium, alloys and compounds of it are used as thermal interface material (TIM; European Commission 2017a). Due to its extraordinary malleability, indium allows to connect different surfaces of electronic parts with large mismatch in thermal expansion coefficient by closing any microscopic gaps between the surfaces, thus improving the heat conductivity across the device, e.g. critically needed to prevent computer chips from overheating (CRM_InnoNet 2015; Indium Corporation 2016).

Alternatives to ITO based TCOs are aluminum doped zinc oxide (AZO) and fluorine doped zinc oxide (FZO). However, AZO and FZO have a 2-4 times lower specific electric conductivity and have less pronounced etching properties as compared to ITO which prevents their use in high-resolution displays (Tercero Espinoza et al. 2015). Furthermore, silver nanowires, carbon nanotubes, graphene, and metal mesh grids have been discussed as possible substitutes but are not ready to replace ITO in mass production and at the current ITO cost. They remain at academic research levels, although they may eventually find niche applications up to 10% of applications (CRM Alliance 2018).

Due to its low mechanical stability, ITO cannot be used in flexible display technologies. A possible non-ITO based alternative for future flexible display technologies could be based on the organic transparent conductive PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) consisting of a polymer mixture of two different ionomers. When PEDOT:PSS is assembled together with a grid printed on silver, it can be used as a substitute material for ITO for flexible organic LED (OLED) displays (CRM_InnoNet 2015). Bottleneck for commercialization of PEDOT:PSS based OLEDs is the limited durability in comparison to ITO.

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SMART WINDOWS

Other uses for indium are smart windows, applied in architectural and automotive glasses. Smart windows add specific functionalities to regular glasses, which result from the combination of electrical conductivity and high optical transparency of ITO and the integration of transparent sensors. Possible functionalities comprise (CRM_InnoNet 2015):

- light balancing from light transmission control via an electrochromic film
- temperature regulation via IR reflection
- low-emissivity coatings for reduced window heat losses
- defogging/defrosting capability for windscreens/headlights via integrated resistive heating of the ITO coating

ITO can be substituted by fluorine-doped tin oxide (FTO) in architectural glass. FTO is similar durable in atmospheric conditions as ITO but has a lower specific conductivity, which makes FTO suitable for low emissivity coatings where a lower conductivity is required. In moisture-protected applications e.g. inside double glazing, zinc oxide (ZnO) and aluminum-doped zinc oxide (AZO) can be used instead of ITO as well. Next generation TCOs, based on gallium-indium-tin-oxide (GIZO/IZGO), indium-zinc-oxide (IZO) or zinc-tin-oxide will contain much less or no indium and will have at the same time similar or improved properties as compared to ITO (CRM_InnoNet 2015).

ALKALINE BATTERIES

Alkaline-manganese-batteries use indium as an alloy addition for zinc in order to prevent corrosion of the zinc anode and subsequent formation of hydrogen gas, which leads to leakage of the battery cell (Trueb & Rüetschi 1998). Lithium-ion batteries with metallic anodes possess much larger anodic capacities and are thus promising future alternatives to intercalation based graphite anodes. However, metallic anodes based lithium-ion batteries typically suffer from dendrite growth which can lead to short-circuiting and are thus not yet market ready (Labo online 2017). For these possibly future battery systems indium may play a central role. When indium is used as a coating material for the lithium anode, it helps in preventing lithium dendrite growth during charging and improves cycle stability of the cell. This in turn reduces aging and leads to a prolonged state of health of the battery cell (Choudhury et al. 2017).

Nowadays, indium is widely used as a substitute material for mercury in alkaline-manganese-batteries, which was formerly used to inhibit the rate of corrosion of the zinc anode but is now mostly banned in batteries due to its hazardous impact on the environment and the potential health risk when leaked out (Trueb & Rüetschi 1998). Alternative substitute options for indium used in alkaline batteries are presently not available as in fact addition of mercury and cadmium to alkaline batteries shows similar effects but are highly toxic and are thus no real substitute options (Indium Corporation 2008).

PHOTOVOLTAICS

Indium is used in form of ITO as top transparent current collector electrode window layer in thin film photovoltaics (PV) and apart from that in the form of indium based semiconductor materials ($\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$) used as light absorber material in thin film solar cells (European Commission 2017a). Thin film light absorber materials are based on cadmium-telluride (CdTe), amorphous silicon (aSi) and copper-indium-gallium-

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diselenide (CIGS) or copper-indium-diselenide (CIS). CIGS is an ideal material for conversion of sunlight into electricity as CIGS thin film solar cells potentially lower manufacturing costs and have a better product integration as state-of-the-art silicon wafer based solar modules due to the possibility to make thin film solar cells. It is forecasted that future organic solar cells (OPV) and dye-sensitized solar cells (DSSC) will also preferentially use ITO as window material (CRM_InnoNet 2015).

A possible In-free substitute semiconductor material for CIGS is copper-zinc-tin-selenide/sulphide (CZTS). However, CZTS based solar cells have an efficiency of ca. 11.1% which is lower as in CIGS based solar cells with an efficiency of ca. 20.4% (CRM_InnoNet 2015). Thus, CZTS is presently not a commercial substitute option for CIGS (European Commission 2017a), but CIGS solar cells compete with other photovoltaic technologies in the market, which is still dominated by silicon solar cells. FTO and AZO can also substitute ITO needed for the top transparent electrode window layer in state-of-the-art thin film solar cells. Possible substitutes for ITO in flexible OPV modules are available in form of the organic transparent conductive PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate), a polymer mixture containing two different ionomers, when applied together with a printed silver grid (CRM_InnoNet 2015). However, PEDOT:PSS is not as durable as ITO.

LIGHT EMITTING DIODES (LED)

Less than 1% of the manufactured indium in the EU is used in LEDs in form of semiconductors (Bio by Deloitte 2015). For inorganic solid state semiconductor based LED displays, ITO is principally not required as each LED pixel can be individually controlled from the display backside, which makes the use of a transparent electrode unnecessary. The diodes' active component is made of indium-gallium-nitride (InGaN/GaN) for LEDs or indium-phosphide (InP) for laser diodes (European Commission 2017a). Depending on the mixture composition of indium to gallium ($\text{In}_x\text{Ga}_{(1-x)}\text{N}$), the semiconductor bandgap can be adjusted which allows for controlling the wavelength and thus the color of the emitted light (Anani et al. 2007). An exception in ITO containing LED based applications are rigid active-matrix organic LED displays (AMOLED) on glass, as lately used e.g. in smartphone displays (CRM_InnoNet 2015). For AMOLED displays, ITO is still in use, as OLEDs require a transparent conductive electrode, regardless of whether the display is rigid or flexible.

A possibly future alternative semiconductor material for indium used in LEDs is zinc oxide, which however is still under investigation due to its limited stability (CRM_InnoNet 2015).

SUMMARY

Indium manufactured in the EU is mainly used in form of ITO in various display technologies for electronic equipment and to a lesser extend in smart windows for architectural and automotive glasses. Other uses comprise alloy additions for batteries, solders and to a smaller fraction in semiconductor compounds for solar cells and LEDs. Substitute options are presently available for some indium containing applications (European Commission 2017a; USGS 2017b):

ITO is substitutable in LCDs by antimony-tin-oxide (ATO). However, antimony is no real substitute option as it is also classified as critical raw material (European Commission 2017a). For architectural glasses with low emissivity coating, ITO can be replaced by FTO. For smart window applications with double glazing (moisture protected) AZO or ZnO can be used for ITO. In thin film solar cells and flat panel displays, it is possible to use FTO or AZO as TCO instead of ITO, however not without a loss in performance with respect to conductivity and/or transparency. Furthermore, CdTe or a-Si based thin film solar cells can be used instead of CIGS/CIS

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based semiconductors in thin film solar cells. InP can be replaced in laser diodes by GaAs. However, Ga is also classified as critical raw material, which makes this substitute option obsolete. Tin-bismuth alloys can replace tin-indium alloys for low temperature bonding and soldering applications. Similarly, for cryogenic sealing applications, lead-based alloys can be used instead of indium and indium-tin alloys. Hafnium replaces indium in nuclear reactor control rods.

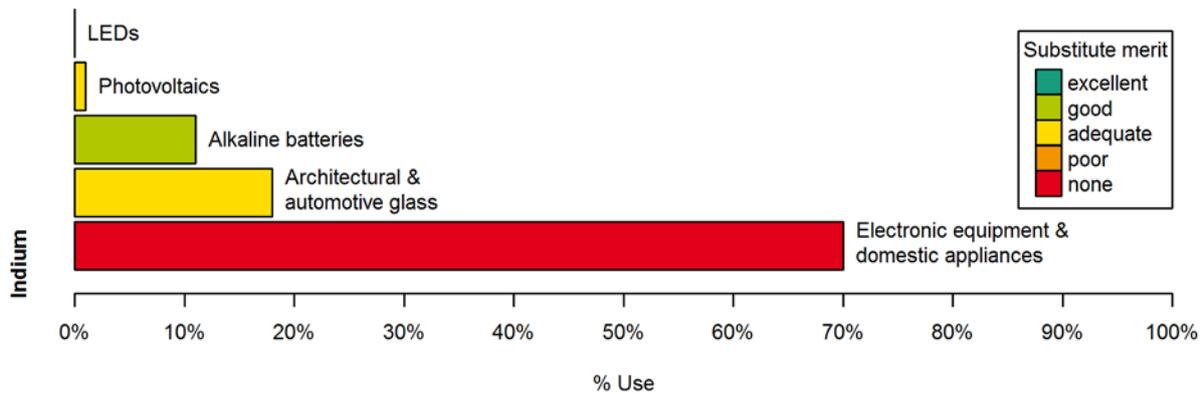


Figure 21: Summary substitutability assessment for indium.

NATURAL GRAPHITE

INTRODUCTION

Natural graphite is a crystalline mineral of pure carbon, which exists in the form of amorphous graphite, flake graphite and crystalline graphite. Natural graphite has important properties, such as chemical inertness, low thermal expansion and lubricity, which make it perfect material for certain uses such as refractories and steelmaking (AZO Materials 2002; European Commission 2017b; Kraus et al. 1989). Currently, the main use of natural graphite includes refractories, batteries, friction products and lubricant.

Natural graphite has been classified as a Critical Raw Material for the EU since 2010 (European Commission 2010, 2014b, 2017b). The substitutability of natural graphite was assessed by the European Commission (European Commission 2017b), the US Geological Survey (USGS 2017b), in the International Strategic Minerals Inventory Summary Report—Natural Graphite (Kraus et al. 1989) and in the CRM_InnoNet project (CRM_InnoNet 2013).

USES AND SUBSTITUTABILITY

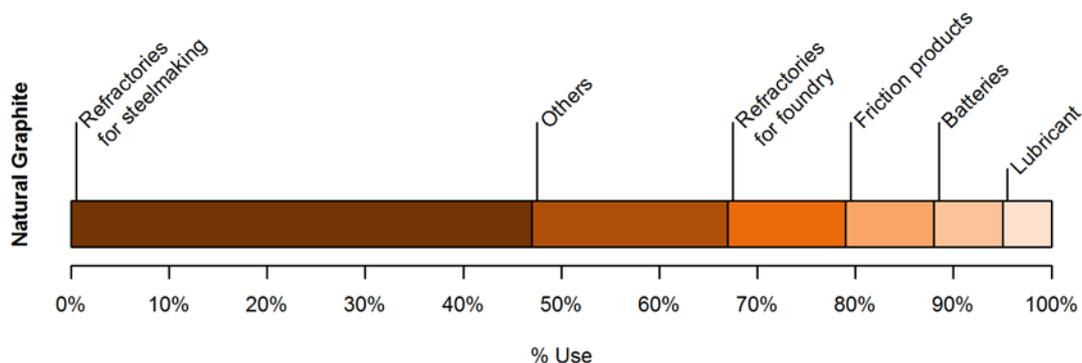


Figure 22: Distribution of recent natural graphite demand for manufacturing in the EU (data from Bio by Deloitte 2015).

REFRACTORIES FOR STEELMAKING AND FOUNDRY

Natural graphite has high durability, erosion resistance, thermal shock resistance and thermal conductivity; due to good combination of these properties it is selected as super refractory material for steelmaking applications. At the moment, there is no existing substitute for the use of natural graphite in steelmaking refractories (European Commission 2017a).

In foundries, graphite is mainly used as a facing. In this application, graphite and a small amount of clay, which serves as a suspension agent, are mixed in a carrier to produce a paint-like foundry facing. This facing is applied as a thin coating to mold surfaces thus providing a clean and easy mold release of the metal casting. Both amorphous graphite and low-quality crystalline flake graphite can be used in foundries; however, synthetic graphite powder, coke, talc, mica or zircon may be used as the substitutes (CRM_InnoNet 2013; European Commission 2017a; Kraus et al. 1989).

BATTERIES

Graphite is used as anodes in batteries due to its electrical conductivity. Synthetic graphite powder and secondary synthetic graphite from machining graphite shapes can be used to substitute natural graphite in battery applications (USGS 2017b).

FRICTION PRODUCTS

Natural graphite has high thermal conductivity for heat dissipation. Therefore, it is added to friction products, such as brake linings, brake pads and clutch facings, to provide lubrication and increased thermal transfer in order to improve operation at higher temperatures. Synthetic graphite can be used instead of natural graphite (European Commission 2017a), if the price of the synthetic graphite is acceptable.

LUBRICANT AND OTHERS

Natural graphite for lubricant application can be substituted by synthetic graphite and molybdenum disulphide; however, molybdenum disulphide is more sensitive to oxidizing conditions. Natural graphite is also used for

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recarburizing (increasing the carbon content of steel). Natural graphite for recarburizing can be substituted by using petroleum coke, synthetic graphite powder or scrap and anthracite, which are much cheaper. Natural graphite for pencils can be substituted by the use of pens and ink as well as coloured pigments or charcoal (CRM_InnoNet 2013; European Commission 2017a; USGS 2017b).

SUMMARY

Natural graphite is mainly used as refractory materials for steelmaking and foundries; the other applications of natural graphite include batteries, friction products, lubricants, etc. Although there are materials that may be able to compete with natural graphite in some applications, the unique combination of physical and chemical properties which qualifies graphite for industrial applications generally excludes the possibility of substitution by other materials (Kraus et al. 1989). Furthermore, the price of the substitution materials sometimes is also a hindrance for the economic substitution of natural graphite.

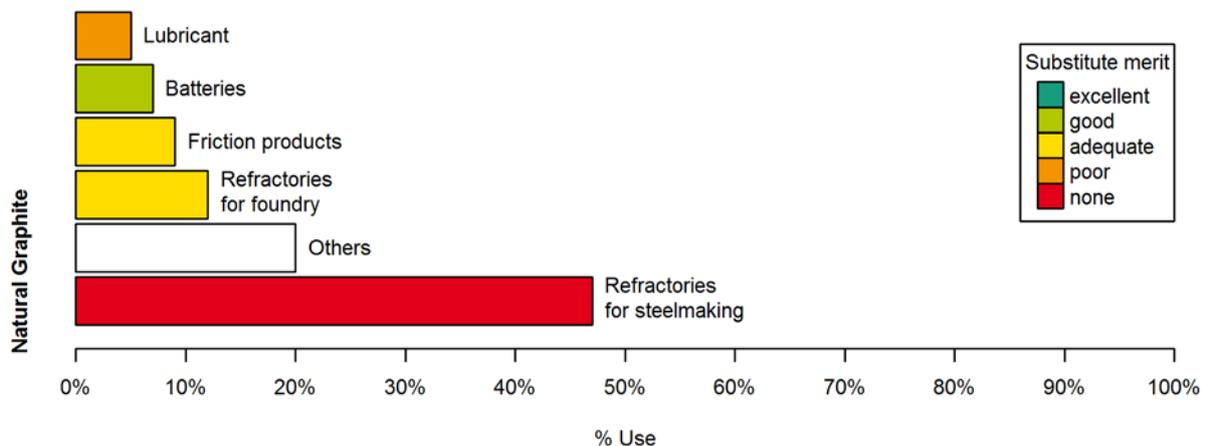


Figure 23: Summary substitutability assessment for natural graphite.

NIOBIUM

INTRODUCTION

Niobium is a soft greyish-silvery metal that resembles fresh-cut steel. It neither tarnishes nor oxidizes in air at room temperature because of a thin coating of niobium oxide. It does readily oxidize at high temperatures (above 200°C), particularly with oxygen and halogens. Some of niobium's characteristics and properties resemble several other neighbouring elements on the periodic table, making them, as well as niobium, difficult to identify. This is particularly true for tantalum, which is located just below niobium on the periodic table. Niobium is not attacked by cold acids but is very reactive with several hot acids such as hydrochloric, sulphuric, nitric, and phosphoric acids. It is ductile and malleable (Krebs 2006).

Niobium has been listed as a critical raw material for the EU since the original assessment in 2010 (European Commission 2010, 2014c, 2017b). Niobium principally is imported into the EU in the form of ferroniobium and niobium unwrought metal, alloy, and powder. The British Geological Survey listed niobium as one of the materials to most likely be in short supply globally (BGS 2015). The substitutability of niobium was assessed in

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the CRM_Innonet project (Tercero Espinoza et al. 2015) and MSP-REFRAM project (Bilewska et al. 2016; Cuesta López et al. 2017).

USES AND SUBSTITUTABILITY

Globally, 90% of the global Niobium production is used to produce Ferro-niobium, which is used in high strength low alloy (HSLA) steels. Niobium compounds and its alloys find use in various industrial sectors. The major consumer of niobium is the steel industry. It is mainly used as a micro-alloying element for carbon-steel or HSLA (High Strength Low Alloy) steels. Other minor consumers include aviation industry, superconductors etc.

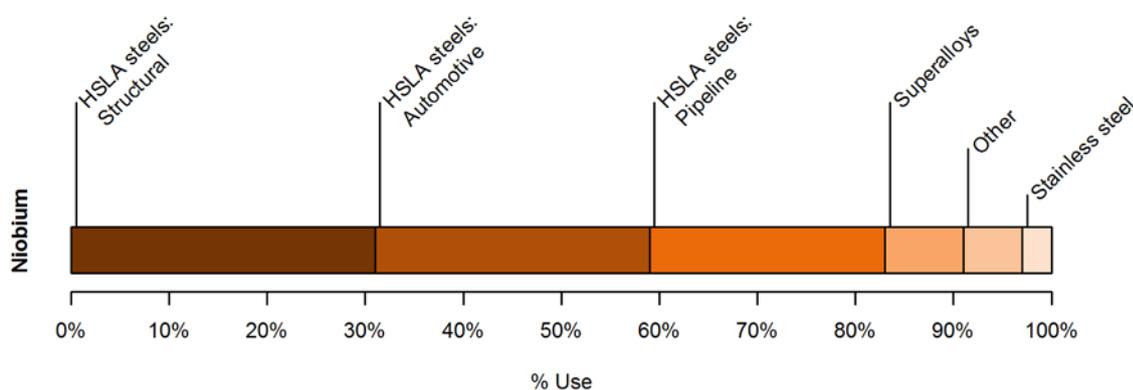


Figure 24: Niobium worldwide market distribution by type of material (European Commission 2014c; Oakdene Hollins & Fraunhofer ISI 2013).

HSLA STEELS

HSLA steels are known for its qualities of strength, fracture toughness, formability and weldability while being optimally priced (CRM_InnoNet 2013). Niobium is used as an alloying element in the production of HSLA (and stainless steels) to increase its overall strength and resistance towards corrosion and high temperatures. The principal markets of HSLA steels are automobiles, gas pipelines, construction and heavy engineering. Niobium has a 3-fold influence on the mechanical properties of steel (Klinkenberg 2007):

- Grain size refinement during thermomechanical hot forming.
- The lowering of Ar3 transformation temperature.
- Precipitation hardening.

The development of HSLA steels was possible through the use of niobium, vanadium (V) and titanium (Ti) as microalloying elements (IMO 2008). Niobium has the effect of lowering the γ to α (austenite to ferrite) transformation temperature. The γ to α (austenite to ferrite) transformation, which is a diffusion controlled process, is retarded more when the atomic size difference between base element and the other element in the solid solution is high. Compared to iron, niobium has the biggest atomic size difference of 15.6%. The size difference of other potential substitutes is Ti 14.8%, V 6.2% and Mo 9.4% (Hulka 2005). Therefore, possible (partial) substitutes for niobium in HSLA steels are vanadium, titanium and molybdenum (Oakdene Hollins & Fraunhofer ISI 2013; Tercero Espinoza et al. 2015; USGS 2017b).

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STAINLESS STEELS

Around 3% of the global demand per annum of niobium can be attributed to the production of various stainless steel grades. Niobium plays two important roles in cast and wrought austenitic stainless steels: as a stabilizing agent to reduce the risk of intergranular corrosion and as a strengthening agent. Considering its effect on corrosion, niobium addition will ensure that the chromium will remain in the metal matrix dissolve by the precipitation of NbC. This is because carbon has a higher affinity to niobium than chromium. Hence, higher amounts of chromium can participate in corrosion protection (Rodríguez Ripoll et al. 2016). In this case, the possible candidates for substitution are molybdenum, titanium and tantalum. Like before, the problems of increased weight and cost persist (CRM_InnoNet 2013).

The strengthening mechanisms are based on the precipitation of fine dispersed niobium carbide (NbC). Also, it is well known that stabilising the steel grade by Nb addition prevents the risk of intergranular corrosion in heat affected zones. The niobium content added depends on the carbon and nitrogen (ferritic types) levels. Hence, by controlling the amount of carbon and nitrogen in the steel grade, it is possible to change the amount of niobium required (Cunat 2004).

SUPERALLOYS

The properties required for superalloys can be obtained by alloying them with molybdenum, titanium and (or) tantalum (Tercero Espinoza et al. 2015). Ceramics are another class of materials that can be used for the same purpose. They offer reduced weight, strength and heat resistance but they are brittle and hence can shatter on impact. Composites of ceramic materials, especially ceramic matrix composites (CMCs) toughen the ceramics by incorporating fibres in them and thus exploit the good qualities of ceramics without risking a catastrophic failure. Since, a variety of ceramic materials may be used for the fibres and matrix, it is possible to engineer their properties to endure harsh mechanical and thermal load. This renders them useful in the sphere of superalloys (Raether 2013).

OTHER

A superconductor that can be put to practical use needs to possess superior high-critical-magnetic-field and high-critical-supercurrent-density properties coupled to high critical temperature with affordability and good workability. Niobium-titanium alloys are currently employed for this purpose. They are used in MRI, particle accelerators and colliders (CRM_InnoNet 2013; Cuesta López et al. 2017). However, there are two possible substitution alternatives for this purpose. Vanadium-gallium alloys, with a critical temperature of 14.2 K and the upper critical magnetic field over 19 Tesla. The structure of these alloys is similar to that of the niobium based superconductors. They are often used for the high field inset coils of superconducting electromagnets. Their properties can be improved by doping with high Z elements (Decker & Laquer 1969; Tedrow & Meservey 1984). Other substitution possibility is high temperature superconductors (HTS). They are ceramics which have higher critical temperature (Subramanian et al. 1988).

SUMMARY

Niobium, a grain refiner and precipitation hardener, enhances the steels' mechanical strength, toughness, high temperature strength, and corrosion resistance. This makes niobium pivotal to the automotive, construction and energy industries. Potential substitutes are titanium, vanadium, molybdenum, high nitrogen steels,

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ceramic composites and gallium alloys. While considering the substitution potential of Nb with other elements, it is important to factor in the global availability of those elements.

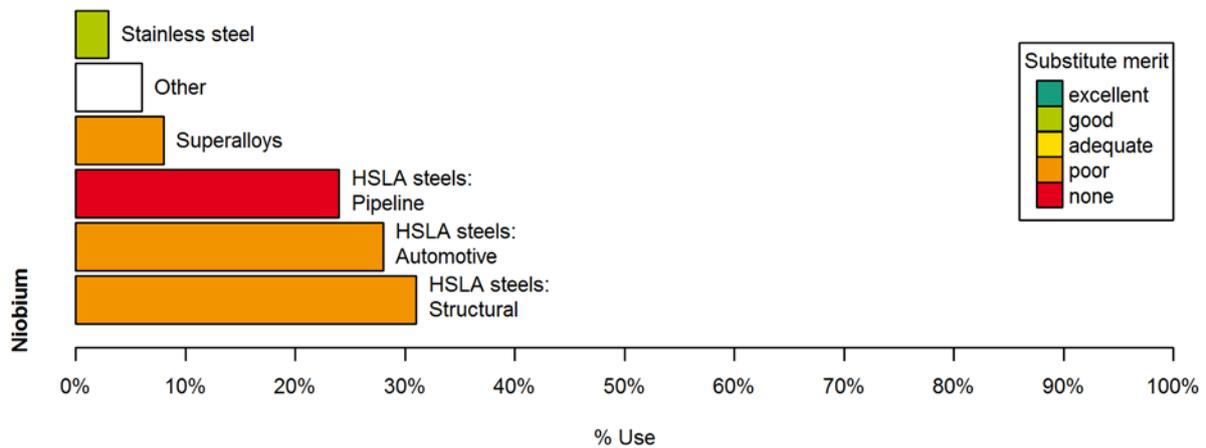


Figure 25: Summary substitutability assessment for niobium.

PLATINUM GROUP METALS (PGM)

INTRODUCTION

Platinum group metals (PGMs) are a group of metals comprising the commercially important platinum (Pt) and palladium (Pd), together with the less common rhodium (Rh), ruthenium (Ru), iridium (Ir) and osmium (Os). PGMs are chemically very similar and exhibit high density, electrical conductivity and melting points, coupled with a low reactivity (Tercero Espinoza et al. 2015). Due to their industrial importance, platinum and palladium are discussed in detail below.

Platinum group metals, either as a group or individually, have been considered critical to the EU since the original assessment in 2010 (European Commission 2010, 2014b, 2017b). The substitutability of PGMs has been examined by the EU (European Commission 2010, 2014b, 2017b), the CRM_InnoNet project (Tercero Espinoza et al. 2015), Graedel et al. (2015), and the USGS (2017b). Current demand trends including substitution are reported yearly by Johnson Matthey (2017).

USES AND SUBSTITUTABILITY

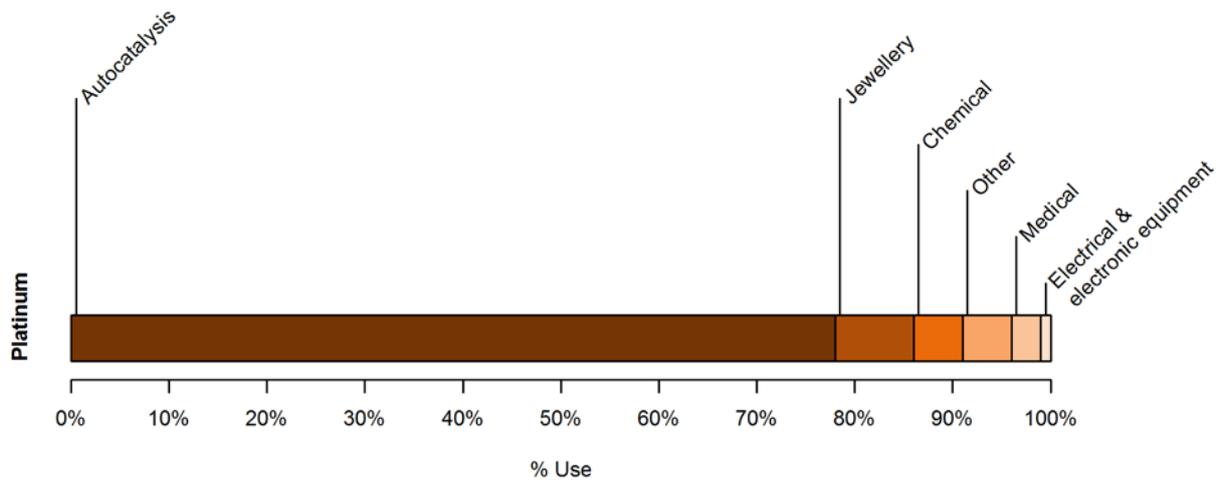


Figure 26: Distribution of platinum demand in the EU in 2016 (Johnson Matthey 2017).

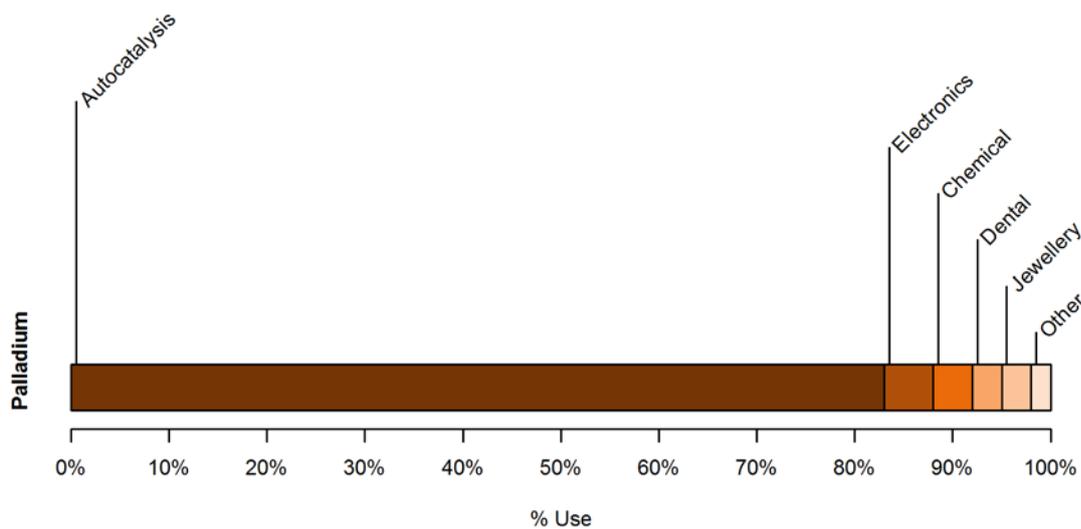


Figure 27: Distribution of palladium demand in the EU in 2016 (Johnson Matthey 2017).

AUTOCATALYSTS

Autocatalysts (catalytic converters) are the premier use for platinum group metals, chiefly Pt and Pd, but also Rh (Johnson Matthey 2017). Installed in the exhaust line vehicles with internal combustion engines, the catalytic converter has the function of converting pollutants including hydrocarbons, carbon monoxide and nitrogen oxides into carbon dioxide, nitrogen and water vapor, thereby reducing the toxicity and environmental impact of vehicle emissions. Because of the high price of both platinum and palladium, substantial efforts have been invested in finding substitute materials, but without success, as Pt and Pd can only substitute for each other (Johnson Matthey 2017; Langkau & Tercero Espinoza 2018; Tercero Espinoza et al. 2015).

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JEWELLERY

Being precious metals, PGMs are also used in jewellery. The main metal in this sector is platinum (>85% purity), with palladium being also used both in elemental form and as an alloying element, and rhodium for plating and decoration (Johnson Matthey 2017). Being decorative in nature, substitution in jewellery appears more closely tied to consumer preferences than to technical characteristics.

ELECTRONICS

Though electronics are a marginal market for platinum (mainly in hard disk drives), this sector is of larger importance for palladium (Johnson Matthey 2017). Pd is used for multilayer ceramic capacitors, and on the surfaces of printed wiring boards (PWBs) and on the copper wires used for bonding electrical components to the PWBs.

Multilayer ceramic capacitors (MLCC) are the largest single consumers of Pd in the electronics industry. MLCC with Pd electrodes are used for electrical components/devices for military, avionic and space equipment, and the automotive industry mainly in Europe and the Americas (Zogbi 2012). Since 1994, Pd electrodes in MLCC have been partially replaced by nickel and copper electrodes, thereby significantly reducing the amount of Pd used in this application (Manufacturers of passive electrical/electronic components 2018). In 2012, many of the specialty end-use market segments that required MLCC to operate in mission critical environments employed MLCC with palladium electrodes, and these specialty markets made up a significant portion of the palladium used for MLCC. In many instances, the high voltage, high-frequency and high-temperature MLCC being used in defense electronics, Class III medical devices, some downhole pump applications and many aerospace designs still required palladium because these capacitors are based on rigid and decades old military and industry specifications. The automotive markets are also large consumers of MLCC with palladium electrodes. Although the automotive industry in Japan and Asia had largely switched toward base metal, Pd-free MLCC in automotive circuits by 2012, the Americas and the European markets still preferred MLCC with Pd at that time (Zogbi 2012). There seems to be some dynamic for further replacement tied to the decommissioning of old designs of military and aerospace applications, and depending on whether the US- and European automotive industry follows the Asian lead in replacing their Pd-MLCC capacitors at least partially.

A further area of application of Pd in the electronics industry is in interconnection technologies for printed wiring boards (PWBs). The industry uses different technologies, each of which requires the surfaces to exhibit specific properties to enable reliable interconnections. A triple layer of nickel (Ni), palladium and gold (Au) provides a nearly universal surface that is compatible with almost all interconnection technologies (Oberender). In principle, this triple layer could be substituted by a thicker nickel and gold surface, a substitution that is hindered by the high gold price. While pure tin layers on PWB pads are generally applied where soldering is used to connect electrical and electronic components to the PWB, they are not appropriate for other interconnection technologies like wire bonding, or where very smooth and even surfaces are needed. In these cases, NiAu and Ni/Pd/Au surfaces are the best choice, with only the latter being appropriate for bonding with thin gold wires. A further benefit of Ni/Pd/Au surfaces is their long shelf life before assembly: The chemical stability and inertness of gold makes both Ni/Au as well as Ni/Pd/Au surfaces stable towards oxygen and other contaminants in the surrounding air, leading to reliable interconnects even after prolonged storage.

Since the prices of all precious metal based surfaces, in particular those containing Au and Pd, are higher than other surfaces, they are only used where the alternative surfaces are not viable, or if the longer shelf life or the

universal usability of Ni/Au and Ni/Pd/Au surfaces offer additional benefits which in the end may even save cost. Overall, it is not expected that the use of Pd for Ni/Pd/Au surfaces will considerably decrease in the coming years.

An emerging use of Pd in the electronics industry is in Pd-clad copper (Cu) wires which in parts replace Au wires for bonding, but additionally find their own application fields as well. These Cu/Pd wires are meanwhile used more frequently than pure Au wires and can be bonded to Ni/Au, Ni/Pd/Au and Pd/Au surfaces on the PWBs (Schneider-Ramelow 2018).

CHEMICAL

PGMs (Pt and Pd, but also Rh, Ir and Ru) are used both as homogeneous and heterogeneous catalysts in the chemical industry. The main use is in the production of silicones, where a Pt-Rh catalyst is used. Further uses are in the production of nitric acid, of precursors for polyethylene terephthalate (PET, used e.g. to make plastic bottles), and in petroleum refining (Johnson Matthey). Substitution options for PGM-containing industrial catalysts are extremely limited (Tercero Espinoza et al. 2015).

DENTAL

Palladium and to a lesser extent Pt are used in alloys to fabricate dental implants. The use of Pd-containing alloys varies widely from country to country depending on regulations and preferences. Therefore, PGM alternatives appear to be readily available in the market (Johnson Matthey; Tercero Espinoza et al. 2015).

MEDICAL AND BIOMEDICAL

The use of Pt in the medical sector comprises both pharmaceuticals and biomedical components. Pt in certain chemical forms is able to inhibit cell division, making it a good candidate for anti-cancer drugs, with some Pt-containing drugs already available and more being under development (Johnson Matthey). Furthermore, Pt is used in electrodes for pacemakers and similar devices because it is inert (does not corrode inside the body and very rarely leads to allergic reactions) while at the same time exhibiting good electrical conductivity, making it an ideal electrode material for heart implants.

SUMMARY

The main use platinum and palladium—the two industrially most important PGMs—is by far in autocatalysts. Here, there is no viable substitution option. Substitution also appears difficult to infeasible in catalysts, medical, and in the electrical and electronic industry, in some cases due to performance, in others due to costs. On the other hand, there are viable options for using other raw materials in jewellery and in dental alloys.

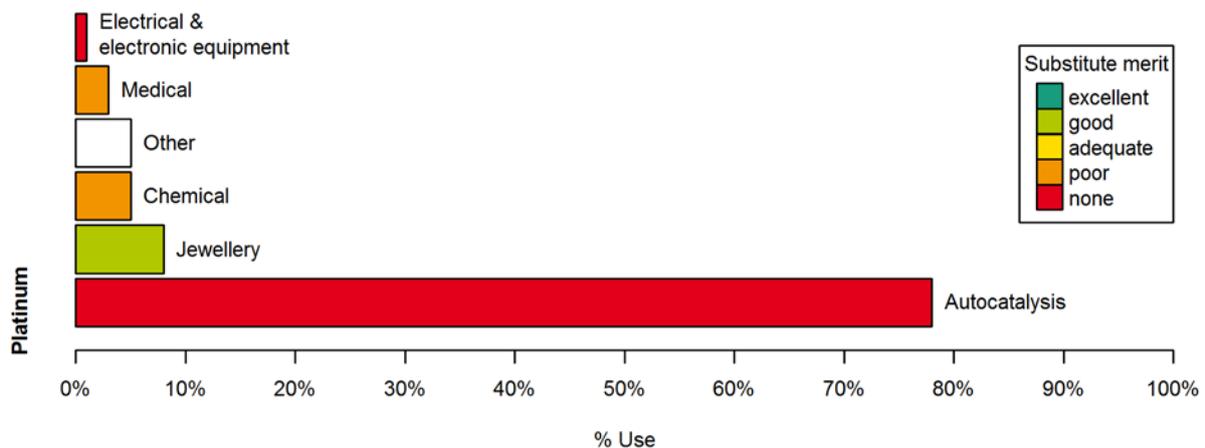


Figure 28: Summary substitutability assessment for platinum.

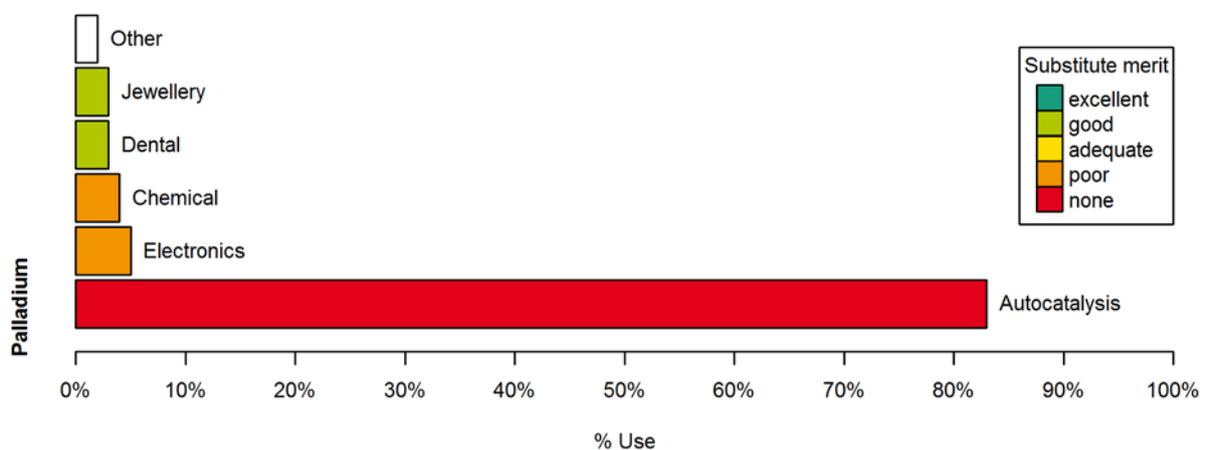


Figure 29: Summary substitutability assessment for palladium.

PHOSPHATE ROCK

INTRODUCTION

Phosphorus is vital for all living creatures, animals and plants due to its essential role in supplying the organism with energy (Enghag 2004) and as a component in DNA. Phosphate rock denotes a range of ca. 300 phosphorus-bearing minerals and is the main source of phosphorus (Bio by Deloitte 2015; European Commission 2017a). Phosphate rock is primarily obtained from mining as unprocessed ore or when subsequently processed as concentrate (Jasinski 2017). Two main types of phosphate rock deposits exist, namely sedimentary and igneous phosphate rock (van Kauwenbergh S. J. 2010), with sedimentary deposits (phosphorites) being the most important source for phosphate rock (Kongshaug et al. 2011). The content of phosphorus pentoxide (P_2O_5) in the deposits determines its marketable use to produce e.g. phosphoric acid, fertilizers or elemental phosphorus (USGS 2017b). Phosphate rock needs to be treated in order to obtain water-soluble and plant-available phosphate in form of fertilizers. Smaller quantities are used to produce

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detergents as well as nutritional supplements for animals or pure phosphorus as a feedstock for the chemical industry.

Phosphate Rock was assessed as a new Critical Raw Material for the EU in the criticality assessment of 2014 (European Commission 2014c) and was again classified as critical in 2017 (European Commission 2017c). The substitutability of phosphate rock was assessed by USGS 2017b and European Commission 2014c, 2017a.

USES AND SUBSTITUTABILITY

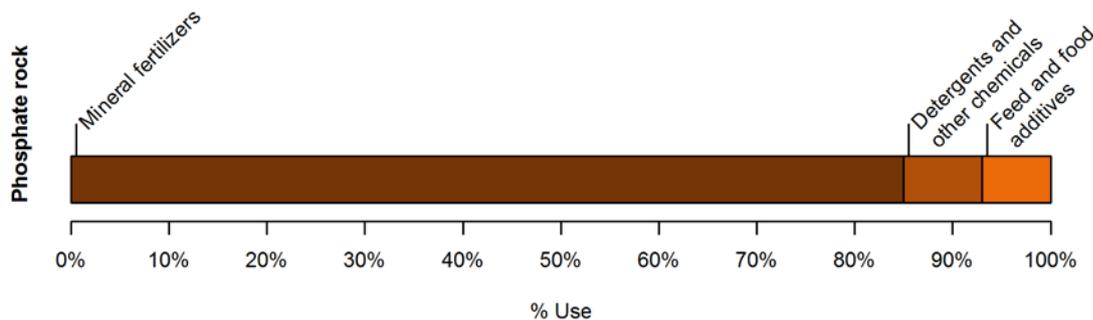


Figure 30: Distribution of recent phosphate rock demand for manufacturing in the EU (data from Bio by Deloitte 2015).

MINERAL FERTILIZERS

The main use of worldwide mined phosphate rock (about 91%) is the production of mineral phosphate fertilizers. A share of 85% of European demand is for this purpose (Bio by Deloitte 2015).

Alternative sources for producing phosphate fertilizers besides Phosphate rock such as Guano, bone meal or other organic sources are less economically viable due to higher costs per unit but also because of the insignificant potential to supply the overall amount of material needed to produce the fertilizers (van Kauwenbergh S. J. 2010). Phosphorus is a vital component that plants need. There are numerous plant functions where phosphate plays a role, e.g. it is a constituent of the nuclei acids, phospholipids and of coenzymes containing phosphorus compounds. The main function of phosphorus is to start the photosynthesis process by capturing the sun's energy (Minerals Education Coalition 2017).

There exist no substitutes for phosphate rock in the agricultural sector (USGS 2017b).

DETERGENTS AND OTHER CHEMICALS

A minor part of phosphate rock demand in the EU (about 8%) is for detergents and other chemicals (Bio by Deloitte 2015).

Different detergents exist based on their application purpose; phosphate is contained in laundry and dishwasher detergents. It is used as detergent builder mainly in form of sodium tripolyphosphate (STPP). However, its use therein was strongly reduced as rising levels of phosphorus in surface waters in the 1970s led to the occurrence of eutrophication. STPP builder requirements for detergents are manifold: reducing the water hardness, developing the optimal water conditions for operation, enabling solubilisation of other detergent components, providing the skeleton for the powder grains in the detergent and others. Phosphate

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based detergents can be cost-effectively substituted by Zeolite A (European Environment Directorate 2002). Zeolite A is an aluminosilicate which is non-toxic to the water environment and the human body.

A further use of phosphate rock is to produce chemicals. These comprise elemental phosphorus in its white, and red forms. White phosphorus P_4 serves as a base chemical for the production of very pure phosphoric acid, pharmaceuticals, phosphohalides, metallic phosphides, red phosphorus, flame retardants, oil additives, plastic additives, catalysts. To date, the EU has no P_4 production (European Commission 2017a). Some of the white phosphorus is used as an intermediate for metal extraction typically in the cobalt industry, and for surface treatment of metals (Diskowski & Hofmann 2011; European Commission 2017a). Red phosphorus is used for the match industry (Enghag 2004). Substitutability of white phosphorus is not given as applications are specific to the phosphorus chemicals and no substitutes are available to date (European Commission 2017a).

FEED AND FOOD SUPPLEMENTS

A smaller fraction of phosphate rock (approx. 7%) is processed into nutritional supplements for animal feed chiefly in form of mono- and dicalcium phosphate (MCP/DCP; Bio by Deloitte 2015; Scholz et al. 2014). The main use of phosphorus in the animal body is in skeleton formation (approx. 80% of phosphorus in the body; Vitti, D. M. S. S. & Kebreab 2010), the smaller fraction is involved in phospholipids, amino acids, and as a constituent of the DNA and RNA. It is possible to enhance the efficiency of phosphorus uptake to the animal organism through improved digestion of rather indigestible organic phosphorus compounds present in plants by co-feeding the phosphatase enzyme phytase (Scholz et al. 2014). Phytase enables the release of a usable form of inorganic phosphorus to the organism.

However, phosphorus by itself cannot be substituted in the nourishment of animals, as it is a vital component participating in the various metabolic functions of the animal organism (European Commission 2017a).

SUMMARY

Phosphate rock is mainly used to produce mineral phosphorus fertilizers for the agricultural industry. Smaller fractions are used to manufacture feed supplements for animal nutrition. In none of both uses can phosphorus be replaced by other substitutes due to the physiological and metabolic way plants and animal organisms work (European Commission 2017a; USGS 2017b). For non-feed and non-agricultural purposes as in the case of detergents, sodium tripolyphosphate can be effectively substituted by zeolite A. For uses of other chemicals related to elemental phosphorus P_4 , no effective substitutes are available to date due to the specific phosphorus chemical properties, e.g. phosphorus based flame retardants (European Commission 2017a).

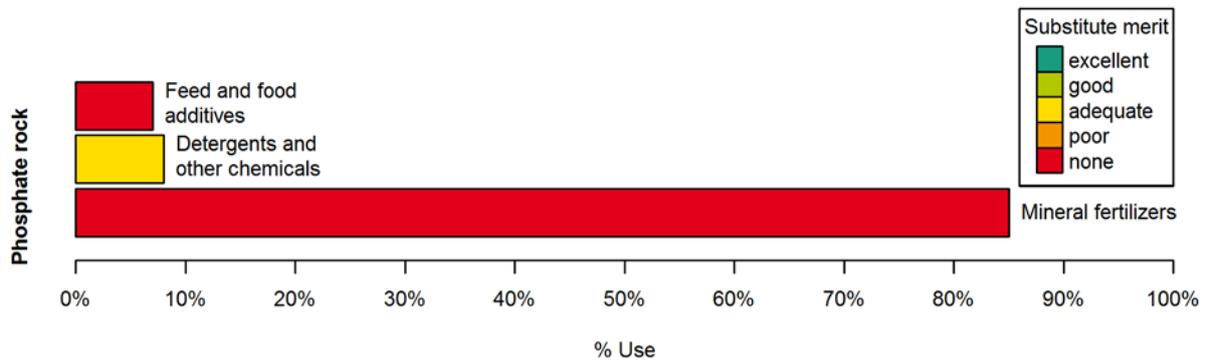


Figure 31: Summary substitutability assessment for phosphate rock.

RARE EARTH ELEMENTS (HEAVY)

INTRODUCTION

Rare earth elements (REEs) include 17 chemical elements with atomic numbers 65-71– lanthanoids, scandium and yttrium. REEs are divided into two groups according to the atomic number. Heavy rare earth elements (HREEs) comprise the lanthanide elements europium through to lutetium and yttrium, because of their similar chemical and physical properties (Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y). The European Commission has classified HREEs as critical since the original criticality assessment (European Commission 2010, 2014b, 2017b).

USES AND SUBSTITUTABILITY

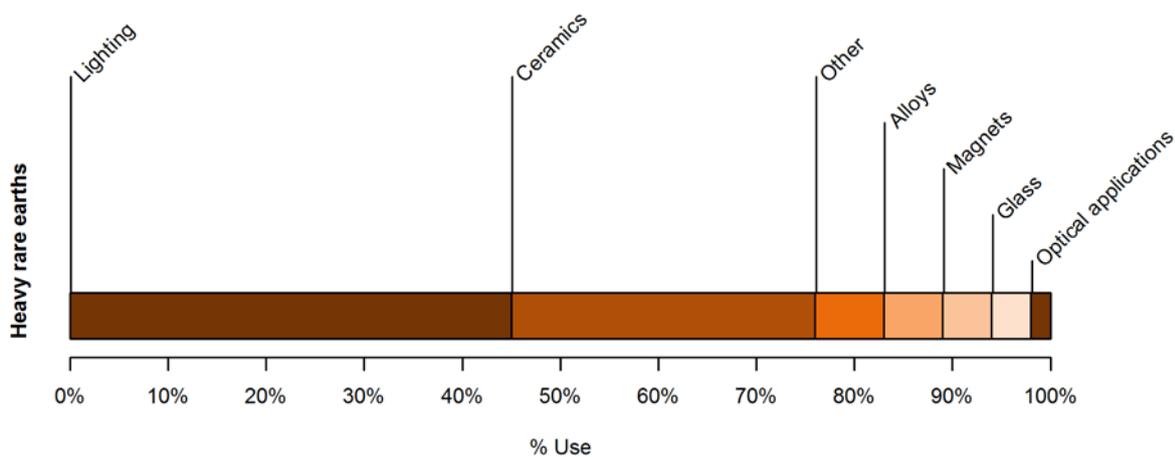


Figure 32: Distribution of recent heavy rare earth demand for manufacturing in the EU (data from European Commission 2017a).

LIGHTING

HREEs are widely used in the lighting sector. Yttrium is the most commonly used REE for the production of luminophores (70%-80%). Y is used in fluorescent and also LED lamps. Lanthanum, cerium, europium, erbium, terbium are rare earth oxides (REOs) used for lighting phosphors and fluorescent lamps.

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While there are no substitutes for Eu, Tb and Y in phosphors that can be used in commercial fluorescent lighting applications (Tercero Espinoza et al. 2015), the widespread adoption of light-emitting diodes (LEDs) implies a strong reduction in the need for HREE. LED also uses HREEs phosphors, but the amount of phosphor in LED is 1000 times lower than in fluorescent lamps (2 mg of phosphor powder/LED instead of 2g/LFL or CFL). Rare earths efficacy in term of lumens (lm) produced per gram of REE is about 18 times higher for LED compared to fluorescent lamps. The lifetime of LED is 40,000-50,000 hours, while for fluorescent lamps only 10,000-25,000 hours (Guyonnet et al. 2015). This causes a reduction in the demand for HREEs by 15 to 20 times in LEDs (DERA 2014). The most promising substitute for HREE in lighting was manganese, but it was not competitive with Eu and Y phosphors. A silicon-based phosphor that could replace HREE in LED is still in the research stage (Smith Stegen 2015). Other free-REE alternatives are organic light-emitting diodes (OLED), but their product efficiency and lifetime have to be improved. In OLED, REE are substituted by organic compounds and indium-tin oxide (Pavel et al. 2016a).

CERAMICS

The largest use of yttrium after phosphors are wear-resistant ceramics - yttrium-stabilized zirconia. Y is also used in electronics for the manufacture of oxygen sensors in vehicles. No substitutes exist for ceramics application of yttrium (Tercero Espinoza et al. 2015).

METALLURGY

Some HREEs, primarily yttrium are used in magnesium (Mg) alloys. Due to the high solubility in the solid state in Mg, yttrium is added to Mg-alloys to increase its creep strength at elevated temperatures up to 300°C (European Commission, 2017).

MAGNETS

The main application of dysprosium (Dy), terbium (Tb) and gadolinium (Gd) is as alloying elements in NdFeB permanent (hard) magnets. Because of their strong coercivity, permanent magnets are used in wind generators and electric traction motors. The role of Dy and Tb is to preserve the magnetic performance of the magnet at elevated temperature – up to 200°C. The amount of Dy and Tb in high-temperature magnets can reach 3-7% in wind turbines and 9% in electric vehicles. However, since the high-price phase at the turn of the decade, great efforts have been made to replace or reduce amount of Dy and Tb in magnets. Two basic approaches to achieving this are controlling working temperature (thus allowing for reduced specifications of the magnets) or attaining the same specifications with a reduced HREE requirement.

One of the techniques positions Dy atoms at the grain boundaries of the NdFeB, which allows to use less of this element (Shin-Etsu 2007). TDK produced a NdFeB magnet without Dy addition with a higher intrinsic coercive force (TDK 2013). Siemens, which is a leading turbine manufacturer in the offshore segment, begun to design wind turbine exempt of Dy using a cooling system to reduce the temperature of the use. The JRC expects the extensive use of dysprosium-free magnets in wind turbines and of magnets with reduced Dy-content in electric vehicles (Pavel et al. 2016a). Japan's Rare Metal Substitute Materials Development Program targets a 30% reduction in the Dy and Nd content of permanent magnets through grain refinement and nanostructure techniques, and REE-less/free alloys or other elements (Lacal-Arántegui 2015).

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GLASS

Erbium is one of the most used HREEs in the glass industry. Er is used as pink colour additive in glass, and there is currently no substitute for this (European Commission 2017a). Erbium-doped optical silica-glass fibres are the active element in erbium-doped fiber amplifiers (EDFAs), which are widely used in optical communications (Nakahara et al. 2006). Yttrium oxide is added to the glass used to make camera lenses heat and shock resistant.

SUMMARY

HREEs are mainly used in lighting technologies, glass and ceramic industry. The most frequently used element from this group is yttrium, which is primarily used in phosphors, ceramics and electronics. In most of this application there is no substitute for Y. Alternative is LED technologies, which uses less amount of REEs. There is no possibility of replacing yttrium in zirconia (yttrium-stabilized zirconia). Dy and Tb are used in magnets. Currently, magnets without these additives are appearing on the market but research into reduced use of HREE has proved more fruitful than research into new magnetic materials with comparable properties.

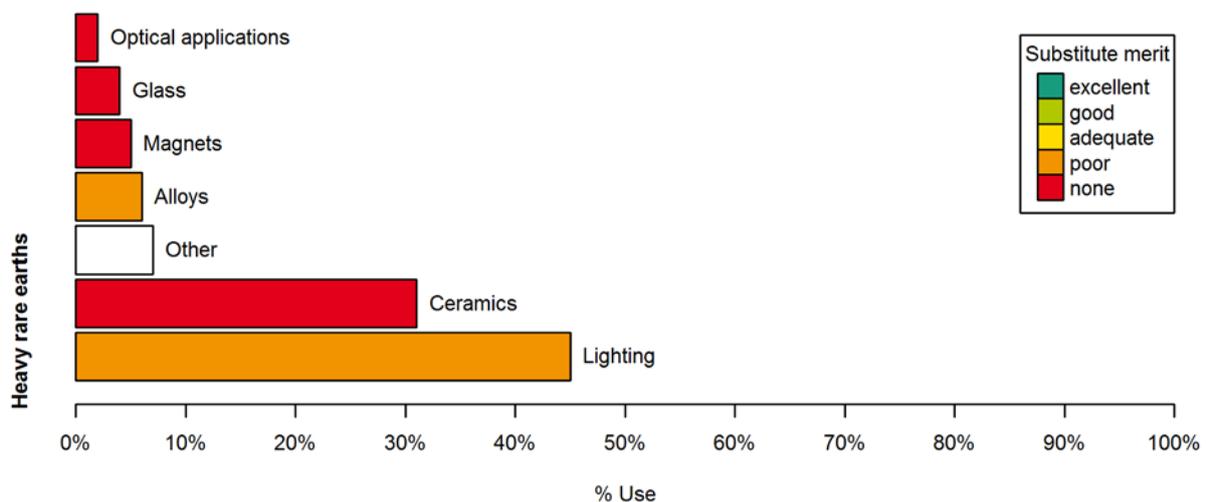


Figure 33: Summary substitutability assessment for the heavy rare earth elements.

RARE EARTH ELEMENTS (LIGHT)

INTRODUCTION

The group of the rare earth elements (REEs) include 17 chemical elements with atomic numbers 65-71–lanthanoids, scandium and yttrium. REEs are divided into two groups according the atomic number. Light rare earth elements (LREEs) are defined as the lanthanide elements lanthanum through to samarium (lanthanum/La, cerium/Ce, praseodymium/Pr, neodymium/Nd, samarium/Sm). The main markets for LREEs are magnets (Pr, Nd, Sm), catalysts (La, Ce), metallurgy and glass/polishing (Ce) (European Commission 2017a).

USES AND SUBSTITUTABILITY

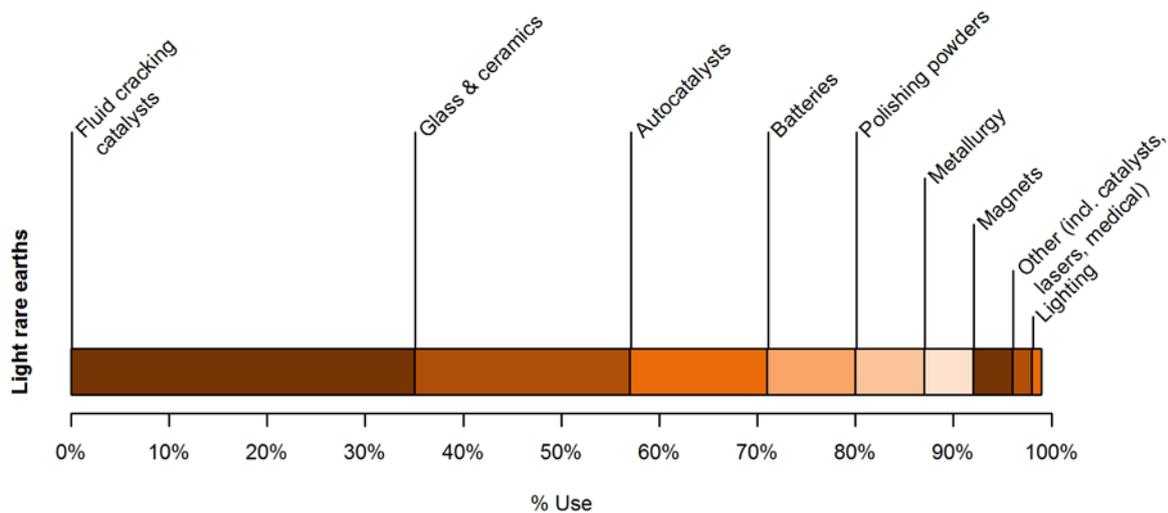


Figure 34: Distribution of recent light rare earth demand for manufacturing in the EU (data from European Commission 2017a).

FLUID CRACKING CATALYSTS

The largest application of light rare earths is in fluid cracking catalysis (FCC) for the petroleum industry. Both lanthanum and cerium are used in these catalysts to increase the activity and stability of the zeolite, which is the most active component in the catalysts. There are commercially available low rare earth and rare earth-free FCC based on the Z-21 zeolite (e.g. REplaceR and REDuceR catalysts by Grace Davison Refining Technologies). For some applications, these catalysts can completely replace rare-earth using FCC, for resid FCC, a blend of rare earth free and rare earth catalysis (up to 50%) have been successfully used (Digital Refining 2011).

GLASS AND CERAMICS

Cerium oxide is widely used as additives for glass, display faceplates, preventing solarisation in sunglasses, bottles. Lanthanum oxide is also used in the glass industry to increase refractive index. REE are also used for coloring glass, for example Nd colours glass red, Pr – green (Gupta & Krishnamurthy 2005).

LREEs are used as pigments in ceramics: neodymium is mainly used as a blue, praseodymium as a yellow pigment (Yoldjian 1985). LREEs are widely used in advanced ceramics. Cerium oxide is added to ceramics as stabilizer and sintering aid, which reduces sintering temperature. Another application of REO are functional ceramics – semiconductor sensors, dielectric and piezoelectric ceramics. Rare earths cannot be substituted in most of these applications (Tercero Espinoza et al. 2015).

AUTOCATALYSTS

The main application of cerium carbonate and cerium oxide are catalyst substrates and component of the converter's oxidising catalyst system (Castor & Hedrick 2006). Cerium can be substituted by lanthanum, neodymium and praseodymium—all rare earths—in these applications (European Commission 2017a).

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BATTERIES

Lanthanum is the main LREE used in nickel metal hydride (NiMH) rechargeable batteries. Neodymium and praseodymium are also used in NiMH batteries, as a part of the batteries' cathode, although this use is declining due to competition mainly from lithium-ion batteries (Higgins 2016; Umicore 2016). Other alternatives are NiCd or lead-acid batteries (Tercero Espinoza et al, 2015).

POLISHING

Due to its high hardness, cerium-oxide has been widely used for polishing since the 1930s. It is used mainly for glass (display panels, flat glass, optical glass) and electrical components polishing. Cerium is suitable as a polishing agent because it removes glass by mechanical abrasion and also by chemical dissolution, which is very efficient (Tercero Espinoza et al. 2015). Demand for cerium can be lowered by using shorter polishing times, smaller amounts of slurry and slurry re-use. Cerium can be substituted by iron oxide or alumina powder. Cerium oxide powders often includes also lanthanum oxide which can be replaced by iron oxide and alumina powders (European Commission 2017a).

METALLURGY

The LREEs most commonly used as an alloy additive in cast iron are cerium and lanthanum. They are used to modify the graphite morphology from flake to nodule (Tercero Espinoza et al. 2015). REEs bind sulphur and form stable precipitates in the alloy, which improve its mechanical properties. Alternative additives based on magnesium are already available. Lanthanum can be substituted by cerium, neodymium, gadolinium and calcium (European Commission 2017a).

Cerium is necessary for certain grades of stainless steel in order to improve oxidation resistance, erosion corrosion resistance and oxide spallation resistance (Tercero Espinoza et al. 2015).

LREEs are also used as alloying elements in magnesium (Mg) alloys in the form of rare-earth mischmetal consisting of Ce, La, Pr. Up to 3% of Ce and Nd is added to cast magnesium in order to create low melting eutectic phase. This improves castability of Mg alloys. REE increases the strength of alloys at elevated temperatures and reduces the tendency for cracks in the joint and porosity in castings. Alloys containing REE are used only in application where high properties are required – aerospace, high-end automotive. LREEs can be partially substituted by calcium in these applications (European Commission 2017a; Tercero Espinoza et al. 2015). LREEs are also commonly added as alloying elements in superalloys, which are group of heat resistant alloys used in high-temperature oxidizing environments (Gupta & Krishnamurthy 2005).

MAGNETS

Neodymium-iron-boron (NdFeB) magnets are the strongest type of permanent magnet commercially available. They are characterized by highest energy density, which is why they are used especially in high-performance applications where acceptable size and weight are limited. The main application for neodymium magnets include industrial motors, hard drives, automobiles and wind turbines. So far, no other material with superior qualities has been developed for large-scale applications. NdFeB magnet contains about 29–32% Nd/Pr, which might decrease to 25% by 2020 and even to 20% by 2030 (Lacal-Arántegui 2015).

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There are two possible ways to reduce amount of neodymium/praseodymium in permanent magnets, one of them is material substitution and the second one is using alternative magnet technology. In recent years, a number of promising research initiatives regarding this topic have begun. For now, no promising results have been announced regarding the substitution of rare earths in commercial NdFeB magnets or the discovery of new magnets with a similar properties. For example, information about the possibility of replacing a part of neodymium (by about 20%) in magnets by using cerium and cobalt appeared (Pathak et al. 2015). Alloys co-doped with cerium and cobalt have very good high-temperature properties, but these materials are still in R&D stage. In some applications, NdFeB magnets could be replaced by other permanent magnets like ferrite or SmCo magnets, which could be used in some electric motors, but due to their lower magnetic performance they are not designed to high technology applications. Other existing types of magnets still continue to be developed, for example, ferrites modified with La and Ce (TDK 2013), anisotropic SmFeNi bonded magnets or combination of iron nitrides with hard ferrites in nanoscale (KomMa 2014). Producers are re-designing machines in order to make them compatible with ferrite magnets (servo motors in cars and motors in industrial applications; ERECON 2015). There are many alternatives for permanent magnet synchronous generators (PMSG) in wind turbines that require less or no REE: doubly-fed induction generator (DFIG), electrically excited synchronous generator (EESG), squirrel-cage induction generators linked to a full converter, PMSG substitution with high-temperature superconductors (HTS; Pavel et al. 2016a). Permanent magnets are widely used in electric vehicles in highly efficient PM synchronous-traction motor (PSM). There are some alternative electric motors: Tesla S uses an asynchronous motor (ASM), the Renault Zoe has an electrically excited synchronous motor (EESM). Another substitute for PSM are: ASM with high rpm, PMS with low-cost magnets, hybrid motor, the transversal flux motor (TFM) and the switched reluctance motor (SRM, still in research phase; Pavel et al. 2016a).

LIGHTING

Less than 10% of La supplies are used for lighting phosphors. Also cerium is used in phosphor powders in linear fluorescent and compact fluorescent light bulbs. There is no substitute to La in fluorescent lamps, but the alternative lighting technology, light-emitting diodes (LED), requires less or no REEs (Tercero Espinoza et al. 2015).

SUMMARY

LREEs are widely used in catalysis, glass and ceramics and magnet technologies. Lanthanum and cerium are the most frequently used elements from this group. There some alternatives for REEs in catalysis and metallurgy. Substitutes of NdFeB magnets generally do not exhibit sufficiently good magnetic properties. The alternative may be re-design of wind turbines or new solutions for the construction of electric motors, which are currently under development.

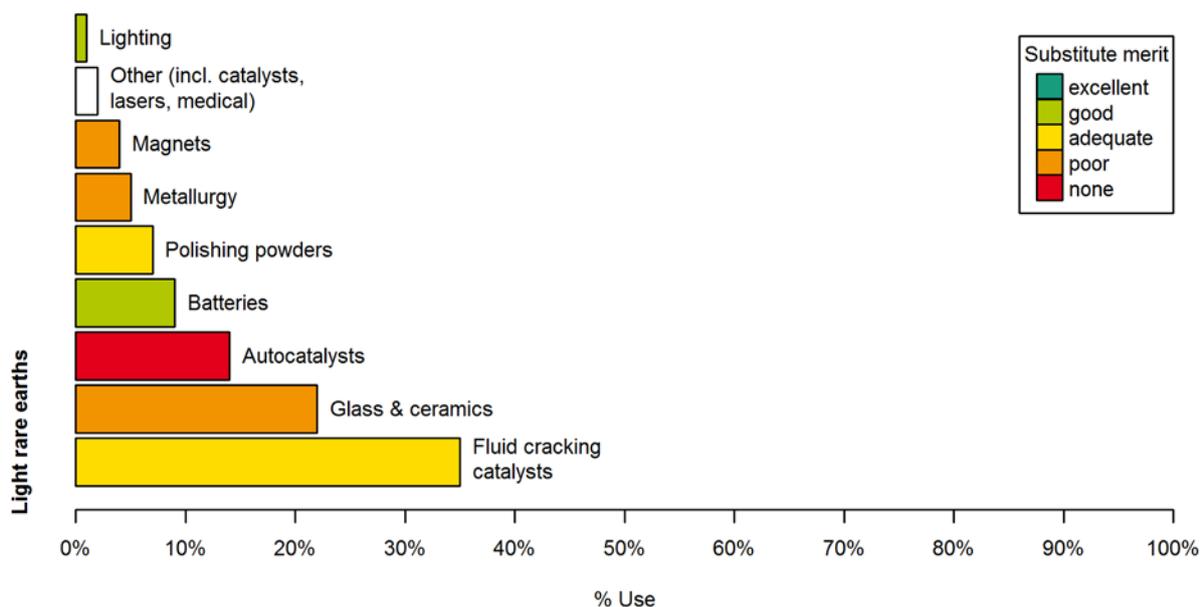


Figure 35: Summary substitutability assessment for the light rare earth elements.

SILICON METAL

INTRODUCTION

The element silicon has been known for time immemorial (Enghag 2004) in form of quartz (SiO_2) and silicates. It is the second most abundant element in the earth's crust with (27.5%; Zulehner et al. 2011). Silicon is a semi-conductive metal with a dark grey colour and bluish tinge; it is lustrous and brittle and has good electrical conductivity (Holleman et al. 2007). Larger amounts are used for alloys and as raw material for the production of chemical compounds in the chemical industry e.g. silicones and silanes. Furthermore, larger quantities of silicon are used in form of ferrosilicon as a reducing agent in the aluminum and steel production. Only smaller quantities are needed for computer chips in electronic devices and in photovoltaic cells but of ultra-high purity (BGS 2016).

Silicon was included in the List of Critical Raw Materials for the EU in the assessment of 2014 (European Commission 2014b) and was again classified critical in 2017 (European Commission 2017c). The non-EU country imports of silicon metal consumed by the EU amounts to 73% (European Commission 2017a). The average demand growth for silicon metal in the EU till 2020 is expected to be modest (<3%; European Commission 2014b). However, there is no functional recycling of silicon in products that are at their end of life (Bio by Deloitte 2015). The substitutability of silicon metal was assessed in European Commission (2014c) and USGS (2017b).

USES AND SUBSTITUTABILITY

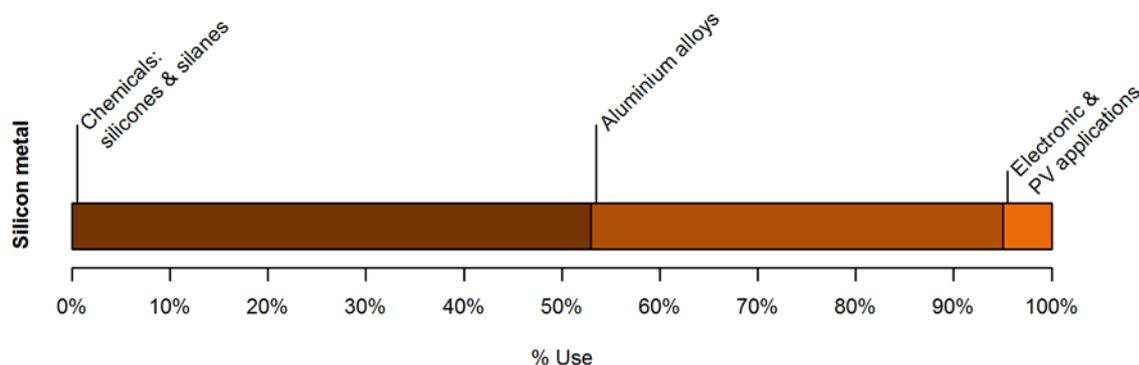


Figure 36: Distribution of recent silicon metal demand for manufacturing in the EU (data from Bio by Deloitte 2015).

CHEMICAL INDUSTRY

The largest use for silicon metal in the EU are applications related to the chemical industry (Bio by Deloitte 2015), containing a wide range of different products (Flörke et al. 2011; Wacker 2017), comprising mainly silanes, silicones and synthetic silica.

Silanes are chiefly used as building blocks for the production of various types of silicones (Wacker 2017) but are also used for glasses, ceramics, foundry and in the painting industry (European Commission 2017a). Due to the metallic character of silicon, silicones have remarkable thermo-oxidative and thermal resistance and are, compared to organic plastics, electromagnetic and particle radiation resistant (Wacker 2017). Silicon rubbers show no physiologically harmful effects and are used for sealing, in coating applications and for electrical insulation. Fluidic silicones are used as hydraulic and transformer oil in lubricants, antifoam agents, dielectrics, impregnating agents for leathers and textiles, and as release agents for laser printers and photocopiers. Silicone resins are perfectly suited as binders for temperature resistant coatings due to their excellent thermal stability and are also applied to fiberglass laminates and electrical windings.

Synthetic silica, such as fumed or pyrogenic silica improves flow characteristics (fluidity) and reduces agglomeration of powders used e.g. in fire extinguishers, cosmetics powders, pharmaceuticals, foods, paints or inks and toners (Flörke et al. 2011; Wacker 2017). Pyrogenic silica acts as an anti-settlement agent, preserving facile dispersibility, and aids in improving rheological properties such as spreadability of paints, coatings, sealants and adhesives. Most important application for pyrogenic silica when added to silicone elastomers or rubbers is its use as reinforcement filler for adjusting mechanical properties (hardness, tear and tensile strength, abrasion resistance) for shoe soles, cable sheathing, tires and technical rubbers. Precipitated silica is superior to natural or mineral reinforcing fillers and can also be used for white or coloured rubbers instead of carbon blacks. Other applications include the use as cleaning agents and toothpastes due to the efficient cleaning properties at a low scratching tendency.

Substitutability of silicon metal in applications of the chemical industry depends on the desired properties of the final product, e.g. thermoplastics do not equally perform as silicon based materials (European Commission 2014c). Thus, no practical substitutes are currently available for silicon metal in the chemical industry (European Commission 2017a).

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ALUMINUM ALLOYS

The second largest use of finished products containing silicon metal manufactured in the EU is in the automobile and construction industry sector, in particular in aluminium alloys (Bio by Deloitte 2015). The application of the alloy depends on the content of silicon and the co-alloying elements.

Silicon acts as viscosity reducer for aluminium melts, reduces the melting temperature (AlcoTec 2017) (ca. Si <17%), improves the hot tear resistance and solidification cracking (Kaufman & Rooy 2010). Silicon added to aluminium also improves aluminium alloy mechanical properties e.g. the abrasion resistance and leads to a reduced coefficient of thermal expansion. Co-alloying elements typically used besides silicon are Cu (Al-Si-Cu) and Mg (Al-Si-Mg; Kaufman & Rooy 2010). The main use of these alloys is in casting parts for the automobile sector with Si contents of about 7-12% due to reduced weight and excellent casting properties. Other uses comprise wrought alloys with Si contents between 0.5-1% (European Commission 2017a).

Effective substitutes for silicon metal as used for metallurgical purposes are not available (European Commission 2017a).

PHOTOVOLTAIC AND ELECTRONICS

Silicon metal is used to manufacture silicon wafers for the production of n-type and p-type semiconductors, integrated circuits (VLSI - Very-Large-Scale-Integration; Sitzmann 2004b), diodes and photo elements used in the solar cell industry. Single crystal silicon based electronic devices makeup more than 95% of all electronic devices worldwide (Zulehner et al. 2011). Instead of silicon, semiconductive properties can also be obtained by germanium or by phosphide, arsenide and antimonide compounds together with gallium or indium (GaP, GaAs, GaSb and InP, InAs, InSb; Enghag 2004). However, the semi-conductive characteristic of germanium disappears at lower temperatures (>100°C) as compared to silicon (>200°C). Highest purified grade silicon is used to manufacture the most common commercially used type of silicon solar cells with purities >99.99% (Bio by Deloitte 2015; European Commission 2017a). Polycrystalline silicon photovoltaic (PV) cells make up >50% of the globally produced PV energy, while single crystal silicon cells contribute by ca. 35% (Bell 2017).

It is possible to replace silicon in semi-conductor and IR-applications by GaAs and Ge (USGS 2017b).

OTHER APPLICATIONS

Additional applications of silicon metal include ceramics, refractories and explosives.

SUMMARY

Silicon metal is mainly used as metallurgical grade silicon for the aluminium industry where there is no practical substitute. It is also used for synthetic silica, silicones and silanes in the chemical industry, which comprises a wide variety of different products with different requirements. Here, substitution is only partially possible (e.g. thermoplastics for silicones) but with loss of performance. Therefore, from the perspective of the chemicals industry as a whole, no practical substitute is available.

Small quantities of high-grade silicon are used for the production of computer chips, solar cells and electronic devices in general. For semiconductor and IR applications, it is possible to use GaAs and Ge as principal

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substitutes for silicon. In this case, substitution is not only limited by the properties of the substitutes but also by their physical availability as the markets for Ga and Ge are much smaller than that of Si.

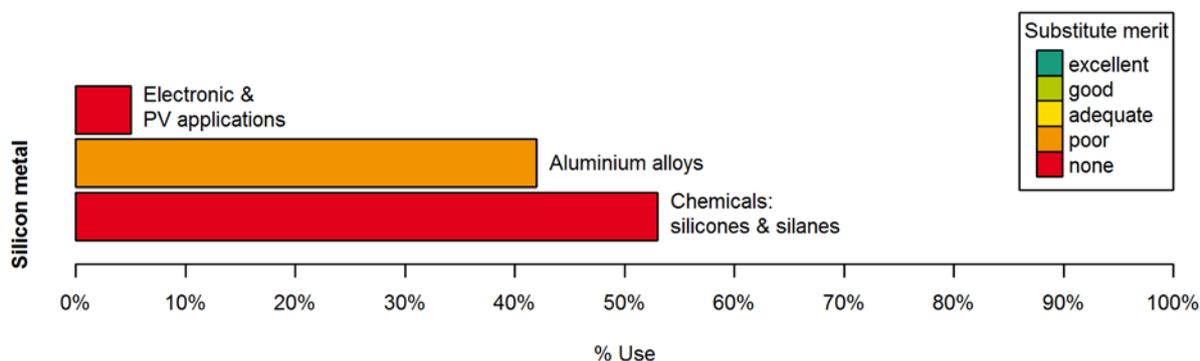


Figure 37: Summary substitutability assessment for silicon metal.

TANTALUM

INTRODUCTION

Tantalum is a shiny, silvery metal with malleable and ductile properties. Tantalum is very resistant to corrosion due to an oxide film on its surface. It is a very good conductor of heat and electricity and has a high melting point (2996 °C). Tantalum causes no immune response in mammals, so has found wide use in the making of surgical implants and other medical applications. Tantalum also has near-zero electric resistance at low temperature, shape memory properties and high capacitance (Tercero Espinoza et al. 2015).

Due to these unique properties, tantalum ensures its increasing usage in different areas such as electronics, mechanical, aerospace, chemical machinery, process industry, vacuum techniques, optic and other applications (Agulyansky 2004). One of the main uses of tantalum is in the production of electronic components (i.e. automotive electronics, mobile phones and personal computers), mainly tantalum capacitors. Alloyed with other metals, tantalum is also used in making carbide cutting tools for metalworking and in the production of superalloys for turbine blades, rocket nozzles and nose caps for supersonic aircraft.

Tantalum was classified as a Critical Raw Material for the EU in the criticality assessments of 2010 and 2017 (European Commission 2010, 2017b). In the list of 2013 tantalum was moved out of the EU critical material list due to a lower supply risk (European Commission 2014b).

USES AND SUBSTITUTABILITY

Tantalum is mostly used in capacitors, cemented carbides and super-alloys for aerospace, automobile, defence and turbine applications (Tercero Espinoza et al. 2015). The greatest demand for tantalum is in capacitors (powder or wire form) for the electronic industry. Second largest demand is in superalloys in metal industry and in sputtering targets in electronics. Other notable application areas are carbides, mill products and chemicals (Bilewska et al. 2016; Cuesta López et al. 2017).

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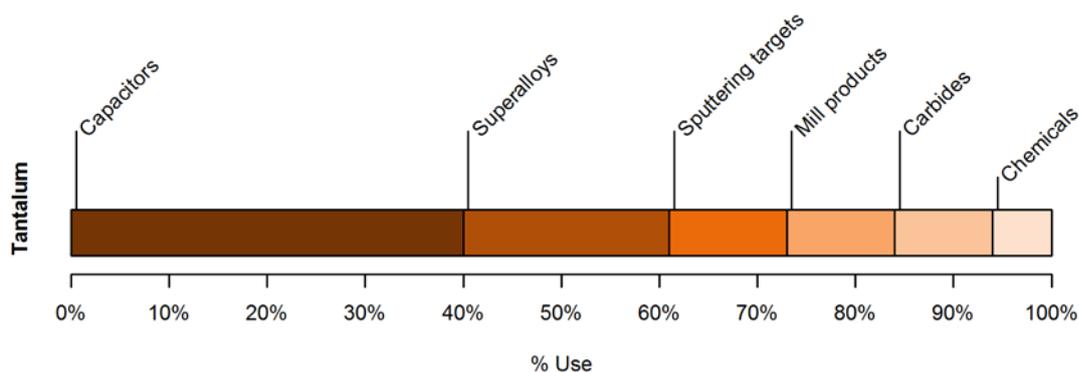


Figure 38: Main end-use global markets for tantalum in 2013 (data from Bilewska et al. 2016; Cuesta López et al. 2017).

CAPACITORS

The major use of tantalum powder is in capacitors, thanks to its high capacitance coefficient that enables smaller components for miniaturized and portable electronics. These components are also robust, temperature tolerant, and with low failure rate. Applications using tantalum capacitors take advantage of their low leakage current, high capacity and long term stability and reliability (automotive electronics, portable electronic boards, mobile phones, medical electronics, etc; BGS 2011a).

In terms of substitution, niobium (also considered a critical raw material) can be used to produce capacitors at lower cost, but they are usually larger and have a shorter life-span (Bilewska et al. 2016; Cuesta López et al. 2017). Despite of its lower cost, and higher raw material availability, aluminium capacitors are more sensitive to harsh and hot operating conditions. Ceramic capacitors are also an option and have a lower cost, smaller size and/or reliability. The superior performance and robustness of tantalum capacitors remains, however, the best choice in applications where size and/or security matters (e.g. automobile anti-lock brake systems, airbag activation systems, etc. Tercero Espinoza et al. 2015).

SUPERALLOYS

Tantalum super-alloys are used mostly in aerospace (75% of super-alloy demand, including jet engine and rocket engine nozzles) and defence applications (e.g. missile parts). These are typically Ni-based super-alloys with a tantalum fraction, but can also be tantalum-based super-alloys. These super-alloys are also used in other turbine-type equipment (e.g. gas turbines). Tantalum-ruthenium alloy is used in the military for its oxidation resistance and shape memory properties (Tercero Espinoza et al. 2015).

In steel super-alloy applications where strength is required at high temperature, tantalum addition can be replaced by vanadium or by molybdenum. Other possible substitutes for high-temperature applications can be hafnium (CRM), iridium (CRM), molybdenum, niobium (CRM), rhenium and tungsten (CRM; USGS 2018). Although this substitutability is possible, it normally implies higher cost and/or loss of performance (Bilewska et al. 2016; Cuesta López et al. 2017).

SPUTTERING TARGETS

Tantalum sputtering targets are used in the semiconductor thin film industry. They make thin coatings via a sputtering process for copper interconnect metallization, magnetic recording media, inkjet printer heads, flat panel displays, optical and industrial glass, battery chargers, power rectifiers, game consoles, and thin film resistors (H.C. Starck 2018a, 2018b). Tantalum acts as a barrier to prevent copper from polluting silicon. This separation is necessary because the presence of copper in silicon leads to device degradation and failure. Tantalum is suitable for this purpose because it (and its nitrides, which are no longer of industrial importance) do not form any compounds with copper (Albrecht et al. 2012; Kaloyeros et al. 2000; Lambert 2007; Tercero Espinoza 2012). Because of this combination of properties and the continued use of tantalum despite supply, price and image concerns, substitution of tantalum in semiconductors appears impractical.

MILL PRODUCTS

The main use of tantalum mill products (mostly sheet and foil, but also bar, rod, plate and forging billets) is in structural parts and cladding in applications that require high corrosion resistance, especially at high temperatures. These mill products are used in heat exchangers, condensers, coils, columns, vessels, reactors, bayonet heaters, furnace parts, etc. In mill products, the substitutability is possible with high cost and/or loss of performance (Bilewska et al. 2016; Cuesta López et al. 2017). Some of these substitutes can be glass, titanium and niobium.

CARBIDES

Tantalum carbide is an extremely hard refractory ceramic which can be used for the production of high-speed cutting and boring tools, or other environments with high levels of stress and temperatures. Teeth for excavator buckets, mining drills and high-performance bearings are possible applications. These carbides are also used in refractory parts and coatings for furnaces and nuclear reactors.

In carbides applications, possible substitution of tantalum by niobium (CRM) is possible, as well as the use of tungsten (CRM) and titanium carbides (TiC) and nitride (TiN) are also possible, even at a lower cost (Tercero Espinoza et al. 2015).

CHEMICALS

Tantalum's corrosion resistance and high temperature resistance properties provide many benefits to the chemical process industry and make it a valuable material in a large number of chemical applications. For this reason, tantalum is used in the production of reactor coatings, heat exchangers, boilers, condensers, pressure reactors, distillation columns, pipelines, etc. Tantalum is also used to produce dimensionally stable anodes that can be used in extreme environments such as in the production of chlorine and soda in systems with ion exchange membranes (Tercero Espinoza et al. 2015). Possible corrosion-resistant substitutes are glass, platinum (CRM), titanium and zirconium (USGS 2018).

OTHERS

With regards to its bio-compatibility, tantalum alloys are used in invasive medical applications such as surgical tools, pacemakers (coating and capacitors), prosthesis devices either as metal or coating (e.g. hip joints, skull plates, stents for blood vessels), as foil or wire it connects torn nerves and as woven gauze it binds abdominal muscle (RSC 2017b).

Some orthopaedic applications of tantalum in prosthetics can be substituted by titanium and ceramics, but some specific applications cannot be substituted, for example porous tantalum alloys used in prosthetic body parts, or pacemaker coating. Chromium/nickel steel alloys can be used for surgical equipment (e.g. stents and pinches), but with lower durability of the oxide coating layer and a lower malleability (Tercero Espinoza et al. 2015).

Other applications involve the use of tantalum oxide in lenses, as it provides high index of refraction. It is used in spectacles, digital cameras and mobile phones. In some cases, it can be substituted by niobium (also a CRM; Bilewska et al. 2016; Cuesta López et al. 2017).

Other applications of tantalum have been identified, though no information regarding possible substitutes has been found. For instance, tantalum is used in cathode protection systems for large steel structures (e.g. oil platform, bridges, water-tanks), and corrosion-resistant fasteners (e.g. nuts, bolts). Since it is a very good conductor of electricity, it is used in LED applications, solar cells, transistors and integrated circuitry as tantalum nitride (Tercero Espinoza et al. 2015). Yttrium tantalite phosphor reduces X-ray exposure and enhances image quality in X-ray film (Bilewska et al. 2016; Cuesta López et al. 2017).

SUMMARY

Due to the physical and chemical similarities of niobium and tantalum, both metals can be substituted for each other in a large number of applications, for example in cemented carbides, corrosion resistant coatings, optics and hard disc drives. In cases where strength at high temperature is required in steel, metals such as molybdenum and vanadium could be used to substitute tantalum. In superalloys hafnium, iridium, molybdenum, niobium, rhenium and tungsten could substitute tantalum (Bilewska et al. 2016; Cuesta López et al. 2017).

All in all, though there are substitutes available for most applications of tantalum and its compounds, the use of these substitutes often incurs a cost or performance penalty or less versatility. The core use of tantalum in capacitors has several possible substitutes (aluminium, ceramic or niobium-based capacitors) that are likely to answer most common needs (Tercero Espinoza et al. 2015). However, it is expected that tantalum capacitors will remain first-choice for applications requiring high reliability and resistance to elevated temperature where cost is not a primary consideration. Substitutes are also available in the case of mill products (e.g. glass, titanium, niobium) and high-temperature applications (e.g. niobium, tungsten, hafnium). The use of tantalum in carbides is in long-term decline (Tercero Espinoza 2012; USGS 2018).

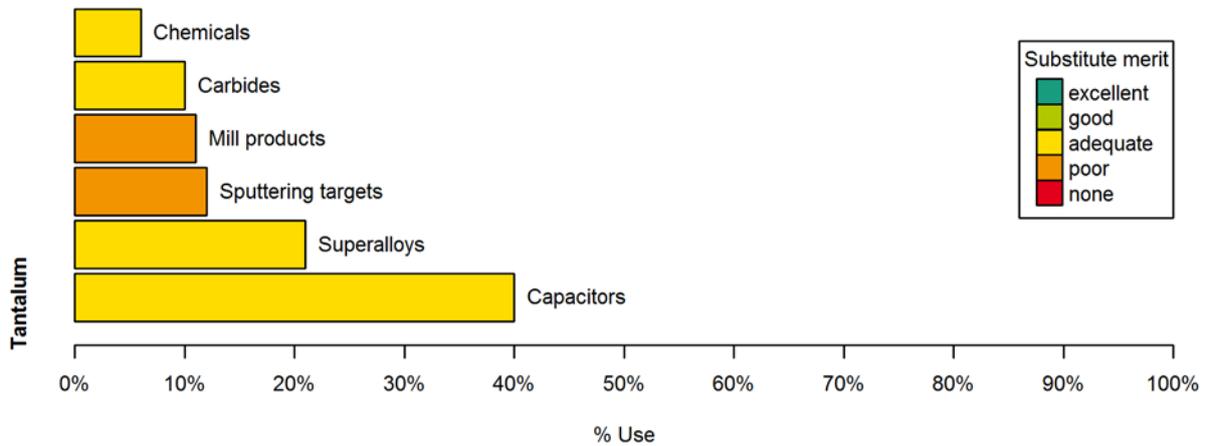


Figure 39: Summary substitutability assessment for tantalum.

TUNGSTEN

INTRODUCTION

Tungsten special properties include the highest melting point, the lowest coefficient of thermal expansion and the lowest vapour pressure of any non-alloyed metal (BGS 2011b). In addition, tungsten is the heaviest metal with a density similar to that of gold and presents a high modulus of compression, high wear resistance, high tensile strength and high thermal and electrical conductivity (ITIA 2011c). These properties make it extremely important for a variety of products, in particular in cemented carbides.

Tungsten has been listed as a critical raw material for the EU since the original criticality assessment in 2010 (European Commission 2010, 2014b, 2017b). Europe has mines of tungsten in its territory but the mine production still does not meet the demand of the European industries. The British Geological Survey's risk list ranked tungsten in the top ten materials facing potential supply disruptions (BGS 2011c, 2012, 2015). The substitutability of niobium was assessed in the CRM_Innonet project (Tercero Espinoza et al. 2015) and MSP-REFRAM project (Bilewska et al. 2016; Cuesta López et al. 2017).

USES AND SUBSTITUTABILITY

Cemented carbides, steel and alloys, mill products, and chemicals and specialists are the main applications of tungsten.

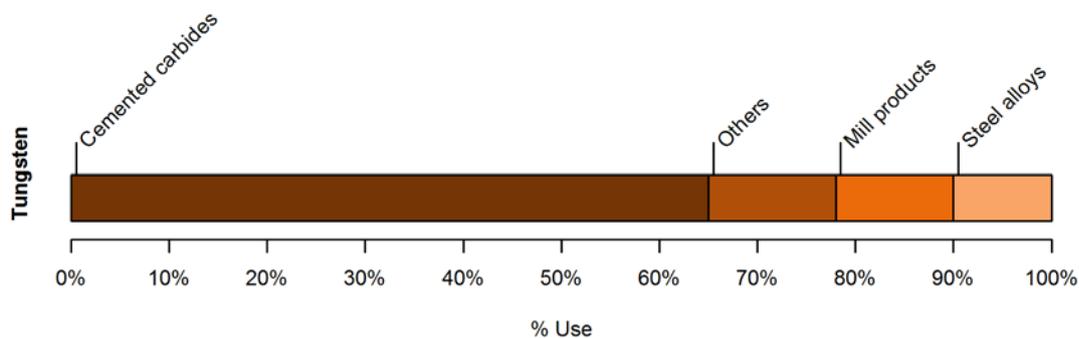


Figure 40: Distribution of recent tungsten demand in the EU (data from Argus Media 2016).

CEMENTED CARBIDES (HARD METALS)

Cemented carbides are the most important usage of tungsten today. The main constituent is tungsten cemented monocarbide (WC, making up 85-95% of the hard metal). Cemented carbides are materials made by "cementing" very hard tungsten monocarbide (WC) grains in a binder matrix of a tough cobalt or nickel alloy by liquid phase sintering. The high solubility of WC in the solid and liquid cobalt binder at high temperature provides a very good wetting of WC and results in an excellent densification during liquid phase sintering and in a pore-free structure (ITIA 2011a; Tercero Espinoza et al. 2015).

WC plays a crucial role in hard metals as it combines high hardness and strength with good toughness within a wide property range (hardness, toughness), and thus constitute the most versatile hard materials group for engineering and tooling applications. Hardness increases with decreasing grain size and binder content and hardness increases fracture toughness decreases and vice versa. In sliding abrasive applications, hardness is a good measure of wear resistance.

Tungsten carbide can be substituted by niobium carbide, molybdenum carbide, titanium carbide, titanium carbonitride in metallic binder phase (Ni and/or Co) possible with toughening additives, ceramics and ceramic metallic composites. As an advantage TiC microstructure that contains a complex carbide phase (K-phase) forming a frame around each carbonitride particle core and providing a strong bond between these hard phase particles and ductile binder metal. TiC is also more lightweight, useful in tribotechnical and machining applications. TiC hard metal grades shows a higher hardness and fracture toughness. Several research studies have concluded that TiC hard metals grades are potential candidates to substitutes tradicional WC-Co in certain applications where high hardness and fracture toughness is needed, but at an increased cost of the final product. Therefore, the main drawbacks of the substitutes are the increment of the final product cost and in some other cases, the loss of product performance (Bilewska et al. 2016; Cuesta López et al. 2017; Ishida et al. 2011; Lindroos et al. 2015; Tercero Espinoza et al. 2015; Zhang 1993). The replacement of hardmetal machinery by an alternative system or product appears unrealistic (Cuesta López et al. 2017).

MILL PRODUCTS

Tungsten in mill product provides extremely high melting temperature (3414 °C), low vapor pressure, high stiffness and excellent creep resistance at elevated temperature. Tungsten mill products are either tungsten metal products, such as lighting filaments, electrodes, electrical and electronic contacts, wires, sheets, rods, etc., or tungsten alloys.

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Evolution of lighting and heating industry in the latest years has led to the development of new devices and products that may evolve to a drastic reduction and event total substitution of tungsten in lighting and heating technology. Carbon nanotube filaments, induction technology and light-emitting diodes are potential substitutes for tungsten-containing products in these applications (Wei et al. 2004).

The tungsten filaments used for lighting equipment, such as lamps and household light bulbs has been substituted in Europe by light-emitting diodes (LEDs). The benefits of LED technology regarding the use of W are clear as they completely dispose this element. Substitution of incandescent / fluorescent bulbs with more advanced light-emitting diode (LED) technology also decreases the demand for europium, tungsten and yttrium, though, demand for gallium and indium will increase (Pavel et al. 2016b). Nevertheless, the new OLED offers new possibilities to substitution as it relies in one critical raw material only: Indium.

Tungsten filaments used for heaters due to high temperature and corrosion resistance and lower thermal expansion can be substitute by electromagnetic induction, a method of heating electrically conductive material such as metals (Rudnev et al., 2017). The benefits of this technology are related with quick heating and higher rates than tungsten heaters, energy saving, less scale loss, fast start-up and high production rates, but at a higher cost.

STEEL ALLOYS

Tungsten significantly improves the hot hardness and hot strength of steel and leads to increased yield strength and tensile strength without adversely affecting ductility and fracture toughness. Tungsten is used for high speed steels, hot work tool steels, cold work tool steels, plastic mould tool steels, heat and creep resistant steels, corrosion resistant stainless steels and valve steels (ITIA 2011b).

Tungsten in steel increases the amount of undissolved and excess carbide in the hardened steel and the eutectoid point is shifted towards lower carbon concentration. The consequence is the precipitation of fine or very fine grained carbides evenly distributed in the steel matrix. Good wear resistance is the most important property of tool steels, and tungsten, next to vanadium, is the most effective carbide forming element for increasing wear resistance (ITIA 2008).

Substitutes for tool/high speed steels are molybdenum combined with alloying with chromium, vanadium and nickel, ASS (alumina, silicon nitride, and sialon), AZS (alumina, zirconia, silicon carbide). Summary of advantages: Better performance (addition of 5-10% of Mo increase the hardness and toughness), Mo combined with V prevents softening and embrittlement of steels at high temperature, ASS can increase productivity and AZS can improve wear and corrosion resistance (U.S. Congress OTA 1984).

SUPERALLOYS

The role of tungsten in superalloys is to provide high temperature strength, high thermal fatigue resistance, good oxidation resistance, excellent hot corrosion resistance, air melting capability. W alloyed nickel- and cobalt-based super-alloys are used in aircraft engines, marine vehicles, turbine blades and vanes, exhaust gas assemblies and as construction material for furnace parts (Tercero Espinoza et al. 2015).

In the case of super-alloys, potential substitutes are molybdenum, ceramic matrix composites (CMCs) made from a silicon carbide/nitride matrix toughened with a coating of silicon, tantalum fiber-reinforced super-alloys

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(turbine blades). CMC durability has been validated through significant testing in customer gas turbine engines accumulating almost 30,000 hours of operation (General Electric GE).

SUMMARY

As a summary, the consumption of W continues to increase as the amount of carbide tool production increases with the expansion of markets in developing countries. For tungsten's main application, WC-based cemented carbides, substitution is appears technically possible but implies higher costs and, in some cases, a decrease in performance. Titanium carbides (TiC) and nitride (TiN) are potential substitute but the technology is not competitive at the moment. Tungsten can be replaced by other refractory metals such as niobium (CRM) or molybdenum in steel products. In other application areas, possible substitution of tungsten is affordable, as super-alloys substituted by Ceramic Matrix Composites (CMCs) made from a silicon carbide/nitride matrix for gas turbine engines. Also, substitution with nanostructured n-alloys such as FeTa, is could be possible in 10 year since current TRLs are very low (TRL 3-4). Substitution in the lighting sector is well underway (Bilewska et al. 2016; Pavel et al. 2016c; Tercero Espinoza et al. 2015).

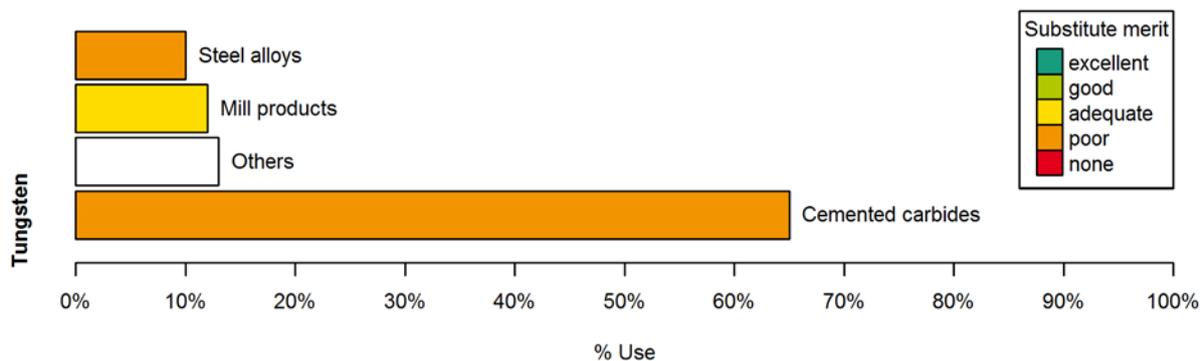


Figure 41: Summary substitutability assessment for tungsten.

VANADIUM

INTRODUCTION

Vanadium is a hard, silvery grey, ductile and malleable transition metal. Its melting point is 1910°C and its boiling point is 3407°C. Vanadium occurs in many minerals (phosphate rock, titaniferous magnetite, bauxite as well as in deposits of fossil fuels such as oil and coal) and is basically obtained as a by-product from the production of steel. Vanadium resists corrosion due to the formation of a protective oxide film on the surface. Vanadium is mainly used as additive in HSLA (high-strength-low-alloyed) steel and special alloys to improve their strength and resistance to corrosion. Vanadium oxide is also used as chemical for catalyst production (European Commission 2017b; USGS 2017b).

Vanadium has been classified as a Critical Raw Material for the EU since 2017 (European Commission 2017b). The substitutability of vanadium was assessed by the European Commission (2017b), the USGS (2017b), and in the CRM_InnoNet project (Tercero Espinoza et al. 2015).

USES AND SUBSTITUTABILITY

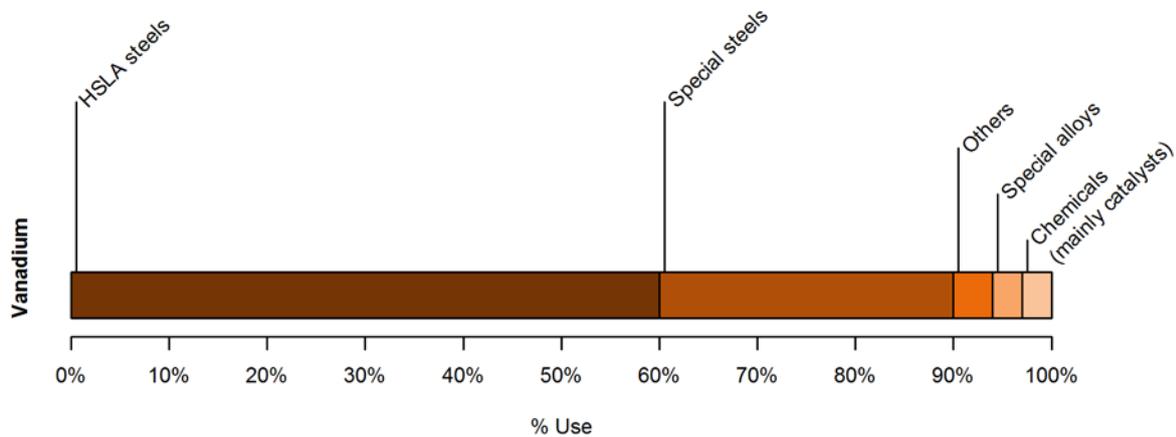


Figure 42: Distribution of recent vanadium demand for manufacturing in the EU (data from European Commission 2017b).

HSLA STEELS AND SPECIAL STEELS

Vanadium is an important alloying element in HSLA steels, tool steels and certain types of other steels. The formation of vanadium-rich carbides and nitrides gives strength to steel, even when a few kilograms of vanadium per ton of steel is added. Furthermore, vanadium also inhibits corrosion and oxidation of the steels.

The substitution of vanadium in all types of steels is possible. However, the substitution is limited to only a few degrees by certain elements, such as columbium/niobium. For example, niobium can partially substitute vanadium in tool steels. However, niobium cannot completely substitute vanadium, as niobium can hardly contribute to the secondary hardness of tool steels during the heat treatment. Replacement of vanadium with other elements requires significant technical adjustments of the steel production process to ensure the product specifications and at the same time to ensure that the quality of the steels is not compromised. Therefore, substitution for vanadium is normally not considered for short-term changes in market conditions because of the considerable effort involved in implementing the change (European Commission 2017b; USGS 2017b, 2017c; Wilmes & Zwick 2002). Another concern that may limit the substitution of vanadium in steel is that the substitution element, niobium, is also listed as one of the critical raw materials by EU.

SPECIAL ALLOYS

Vanadium, when combined with titanium, produces a stronger and more stable alloy, and when combined with aluminium produces a material suitable for jet engines and high-speed airframes. At the moment vanadium is irreplaceable for its role in aerospace applications because vanadium-titanium alloys have the best strength-to-weight ratio of any engineered materials (USGS 2017c).

CATALYSTS

For catalytic uses, platinum and nickel can replace vanadium compounds in some chemical processes. However, platinum is also listed as one of the critical raw materials by EU (European Commission 2017b; USGS 2017b, 2017c).

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SUMMARY

Vanadium is mainly used for the production of HSLA steels, special steels, special alloys and catalysts. Vanadium in steels can be substituted by other elements. However, the substitution is limited due to either the criticality of the substitutes or the poor performance of the substitutes in the steels. In special alloys, vanadium is irreplaceable. In catalysts, vanadium can be replaced in some cases by other elements, such as nickel and platinum, the latter being also listed as a critical raw material by EU.

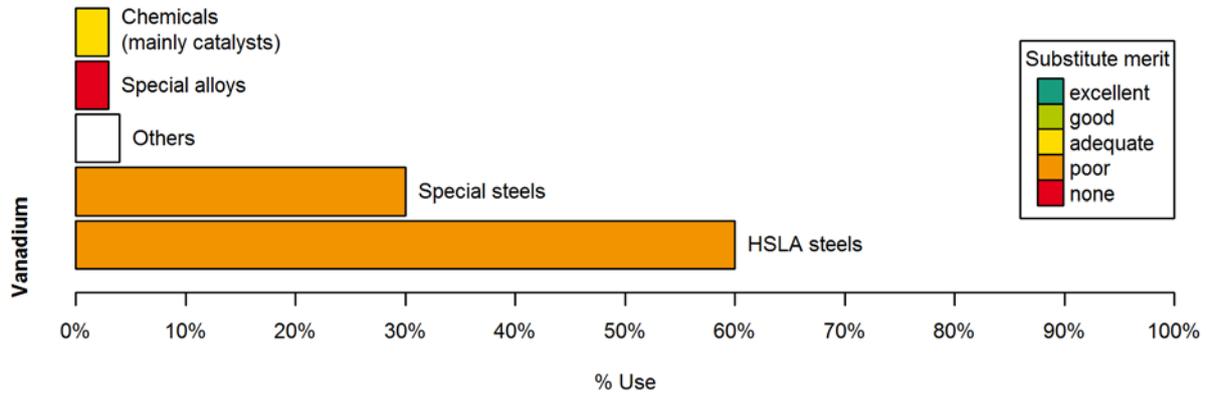


Figure 43: Summary substitutability assessment for vanadium.

SUMMARY VIEW OF CRM SUBSTITUTABILITY

This report examined the substitution options available for selected critical raw materials in 20 substitutability profiles. Figure 34 shows a summary of the substitutability assessments shown in the individual profiles. Inspection of this figure reveals that, while not in their entirety non-substitutable, a significant fraction of critical raw material demand is for applications where they play a key function not currently attainable by other means or without being detrimental to competitiveness.

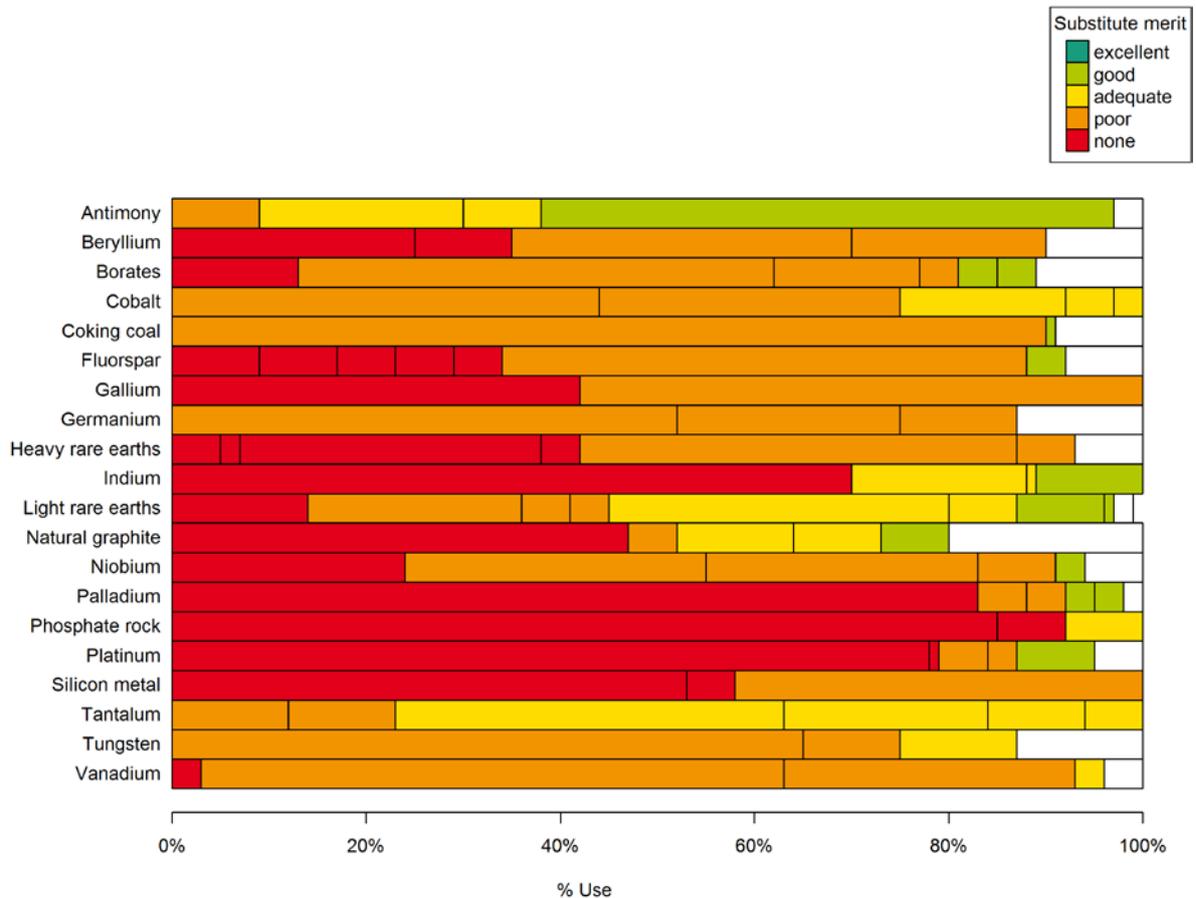


Figure 44: Summary substitutability assessment for the raw materials examined in this report.

Figure 44 also gives a first impression as to the relation of different end-use applications, their shares in demand for the selected raw materials, and their substitutability. Table 2 gives a detailed overview of which end-use applications require these raw materials.

Table 2: Shares (in %) of the different end-use application areas for each of the raw materials examined in this report. The sum of each column equals 100 (excluding rounding errors). The color coding is the same as in Figure 34.

	Antimony	Beryllium	Borates	Cobalt	Coking coal	Fluorspar	Gallium	Germanium	Heavy rare earths	Indium	Light rare earths	Natural graphite	Niobium	Palladium	Phosphate rock	Platinum	Silicon metal	Tantalum	Tungsten	Vanadium
Aerospace / Defence		10																		
Alloys	59							6									42			
Autocatalysts										14			83		78					
Batteries			17						11	9	7									
Capacitors																		40		
Catalysts			5																	3
Ceramics								31												
Chemicals		4												4	5		6			
Chemicals (fluoroaromatics)						6														
Chemicals (fluorocarbons/polymers)						54														
Chemicals (inorganic)						8														
Chemicals (silicones & silanes)																	53			
Dental														3						
Detergents															8					
Electrical & electronic equipment	21									70						1				
Electrical (wire & cable)	8																			
Electrodes					1															
Electronics														5						
Electronics & PV																	5			
Electronics (auto)	20																			
Electronics (telecom)	35																			
Feed and food additives															7					
Fertilizers			13												85					
Fluid cracking catalysts											35									
Friction products												9								
Frits and ceramics																				
Glass			15						4	18										
Glass & ceramics			49									22								
Hard metals				31														10	65	
Industrial components		25																		
Integrated circuits																		12		
IR optics								52												
Jewellery														3		8				
LEDs																				
Lighting									45		1									
Lubricants												5								
Magnets									5		4									
Medical																3				
Metallurgy			4		90	9					5									
Mill products																		11	12	
Nuclear						5														
Oil refining						4														
Optical applications																				
Optical fibres																				
Other	3	10	11		9	8		13	7		2	20	6	2		5			13	4
Permanent magnets							42													
Photovoltaics											1									
Pigments				3																
Polishing powders												7								
Refractories (foundry)																				
Refractories (steel)																				
Satellite solar cells																				
Sensors																				
Special alloys																				3
Steel																			10	
Steel (automotive)														28						
Steel (HSLA)																				60
Steel (pipeline)														24						
Steel (special)																				30
Steel (stainless)																	3			
Steel (structural)																	31			
Superalloys				44										8				21		
Surface treatment						6														
Textiles	9																			
Wood preservatives			4																	

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