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Report on refractory metal reduction potential ? potential substitutes

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Summary

Report on refractory metal reduction potential ? potential substitutes

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REFRACTORY METAL REDUCTION POTENTIAL – POTENTIAL SUBSTITUTES

MSP-REFRAM D5.1

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CONTENT

INTRODUCTION TO SUBSTITUTION

The idea of critical raw material substitution has emerged as a by-product of critical raw materials initiative brought up by European Commission. Secure and sustainable supply of raw materials was identified as an important issue in European economy and substitution is seen as one route to improve the raw materials supply chain for Europe. Other strategies involve search for material with higher resource efficiency, repair, remanufacturing, reuse, recycling for waste reduction and increase in European mine production or extraction of by-products.

MOTIVATION

There are a handful of causes for a certain material to possibly be substituted urgently. The causes are preferably focused example around health, environment and economy of supply chain. Health is the most important issue related with the impact that a material exerts on, not only the end-users but also people involved in all stages of the supply chain, especially during mining, processing and end-product development stages. Environmental issues exist such as limited or no recyclability or local availability may cause increase in costs of transport, waste storage and waste management concerns or high energy intensity of the solution. Furthermore, economical reasons most often put materials into consideration in terms of their substitution; there the role of manufacturer and solution owner is essential. On top of that the value chain of a material or technology is important for societies in general and social responsibility is regarded as necessary to maintain good balance between economies and ecosystems they are working in. Substitution is one of the routes to address these issues.

As a background, the British Geological Survey's (BGS) risk list in 2012 ranked e.g. tungsten as number two in a supply critical index list mainly due to alleged political instability in supplying regions and its limited number of substitutes [BGS 2012]. However, in 2015, BGS ranked tungsten as number eight with a relative supply risk index of 8.1 being China the leading producer and the top reserve holder [BGS 2015].

Element	Rank	Top producer	Top reserve holder
REE	9.5	China	China
Sb	9.0	China	China
Bi	8.8	China	China
Ge	8.6	China	
V	8.6	China	China
Ga	8.6	China	
Sr	8.3	China	China
W	8.1	China	China
Mo	8.1	China	China
Co	8.1	DRC	DRC
In	8.1	China	
As	7.9	China	
Mg	7.6	China	Russia
PGE	7.6	South Africa	South Africa
Li	7.6	Australia	Chile
Ba	7.6	China	China
Graphite	7.4	China	China
Be	7.1	USA	
Ag	7.1	Mexico	Peru
Cd	7.1	China	
Ta	7.1	Rwanda	Australia
Re	7.1	Chile	Chile
Se	6.9	Japan	China
Hg	6.9	China	
F	6.9	China	South Africa
Nb	6.7	Brazil	Brazil
Zr	6.4	Australia	Australia
Cr	6.2	South Africa	Kazakhstan
Sn	6.0	China	China
Mn	5.7	China	South Africa
Ni	5.7	Indonesia	Australia
Th	5.7		USA
U	5.5	Kazakhstan	Australia
Pb	5.5	China	Australia
Fe	5.2	China	Australia

Table 0.1. Risk List 2015-Current supply risk for chemical elements or element groups which are of economic value-British Geological Survey

The research developed by Leal-Ayala, et al., 2015 gathers information from the literature about how to secure supply strategies of tungsten [1]. However, supplementary information contains an overview of supply security mitigation strategies for many of other minerals. This information is presented in the table below. They report that some of the most common strategies could be mineral resource exploration incentives for supply diversification, material substitution, recycling systems and technological improvement, material re-use and waste reduction. However, the authors believe that the potential development and application of such approaches is usually hindered by the lack of transparency and data availability that exists across the supply chain of these materials, which limits the analysis of each strategy's potential material benefits and overall economic and technical feasibility.

Study	Materials covered	Mitigation proposals
Critical Material Strategy *[2]*	Li, Y, Co, Ga, In, Te, La, Ce, Pr, Nd, Sm, Eu, Tb, Dy	**General** ▪ Expand or vary number of producers across industry. ▪ Invest in material substitution R&D. ▪ Follow material efficiency strategies: recycling, reuse, and improved yields. ▪ Increase transparency and data availability across supply chain.
Critical Raw Materials for the EU *[3]*	▪ Sb, Be, Co, Ga, Ge, In, Mg, Nb, Pt, Pd, Rh, Ru, REEs, Ta, W, Fluorspar and Graphite.	**General** ▪ Periodical review of critical elements list (five year intervals). ▪ Increase transparency and data availability across supply chain. ▪ Encourage the use of life cycle analysis. ▪ Investigate future demand forecasts, including new technological advances. ▪ Incentivise resource exploration and supply diversification. ▪ Improve collection and recycling systems. ▪ Invest in material substitution R&D.
Critical metals for future sustainable technologies and their recycling potential *[4]*	▪ Pd, Pt, RE, Te, In, Ge, Ga, Ru, Li, Ta, Co	**Recycling** ▪ Enlargement of recycling capacities ▪ Development of new recycling technologies ▪ Improvement of international recycling infrastructures **General** ▪ Promote UNEP and EU research and policy on short-risk metals. ▪ Promote R&D on rare earth elements. ▪ Promote R&D on metals with serious technical recycling problems. ▪ Promote R&D on recycling technologies of specific products (e.g. solar panels & LCD monitors) ▪ Legislation measurements and evaluations (WEEE, etc.) ▪ Encourage regional (EU) and international organizations (UNEP, OECD) to improve monitoring and controlling of illegal scrap-exports containing critical metals. ▪ Promote know-how transfer and international cooperation regarding the increasing stocks of used products in developing countries
Minerals, critical minerals, and the US economy *[5]*	▪ Cu, PGMs, REs, Nb, Ga, In, Li, Mn, Ta, Ti mineral concentrates, Ti metal, V	**General** ▪ The US federal government should continue and enhance its data collection, dissemination, and analysis of minerals data and information. ▪ The US federal government should enhance its data collection and analysis ▪ The USGS Minerals Information Team should have greater authority and autonomy, as well as sufficient resources to carry out its mandate. ▪ The USGS Minerals Information Team should establish formal mechanisms for communicating with users, governmental and nongovernmental organizations or institutes, and the private sector, on the types and quality of data and information it collects, disseminates, and analyses. ▪ The USGS Minerals Information Team should be organized to have the flexibility to collect, disseminate, and analyse additional, non-basic data and information, in consultation with the users, as specific minerals and mineral products become relatively more critical over time (and vice versa). ▪ Promote R&D to encourage innovation in the critical minerals and materials area, including global mineral availability and use.

Study	Materials covered	Mitigation proposals
Critical metals in strategic energy technologies *[6]*	▪ Te, In, Sn, Hf, Ag, Dy, Ga, Nd, Cd, Ni, Mo, V, Nb, Cu, Se, Pb, Mn, Co, Cr, W, Y, Zr, Ti	**Mitigation strategies** ▪ Supply-chain analysis ▪ Expanding primary output ▪ Promote reuse, recycling and waste reduction ▪ Promote substitution **Specific recommendations** ▪ Improve data collection and analysis on demand, supply and price trends ▪ Support and sustain the existing rare earths supply chain in Europe ▪ Fast-tracking exploration and permitting of European rare earths deposits ▪ Engage in dialogue with zinc, copper and aluminium refiners over by-product recovery ▪ Incentivise by-product recovery in zinc, copper and aluminium refining in Europe ▪ Promote R&D of recycling technologies and end-of-life collection systems ▪ Invest in alternative technologies to substitute technologies that rely on critical materials ▪ Promote R&D into indium and tin oxides substitution ▪ Encourage substitution of tellurium use in low-value applications
Materials critical to the energy industry *[7]*	▪ Cd, Cr, Co, Cu, Ga, Ge, In, Li, Mo, P, Pt, K, REE, Rh, Ag, Te, W, U, V	**No recommendations given**
Energy critical elements: securing materials for emerging technologies *[8]*	▪ La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Tb, Lu, Sc, Y, Ru, Rh, Pd, Os, Ir, Pt, Ga, Ge, Se, In, Te, Co, He, Li, Re, Ag	**General** ▪ Established group of experts to supervise energy critical elements. ▪ Increase transparency and data availability across supply chain. ▪ Improve collection and recycling systems. ▪ Invest in material substitution R&D.
Material Security: Ensuring Resource Availability for the UK Economy *[9]*	▪ Au, Rh, Hg, Pt, Sr, Ag, Sb, Sn, Mg, W, Bi, Pd, Ni, B, Mo, Zn, Ho, Tb, CaF2, As, C, NH3, Co, Eu, Gd, Os, Nb, Kyanite, Be, Ru, Ge, Cr, C, V, Ba, Te, Pb, Ga, In, I, Cu, Fe, Zr, Se, Lu, Br, Si, Re, BaSO4, Na2CO3, H2Mg3(SiO3)4, Al2SiO5, B(OR)3, Asbestos, Vermiculite, Diatomite,	**General recommendations** ▪ Substitution ▪ Minimisation of material use ▪ Closing substance loops ▪ Minimisation of dispersal of residuals into the environment **Recommendations for policy makers** ▪ Incorporate social costs of environmental impact into mining and metal production ▪ Assist developing nations with environmental and social regulation of industries ▪ Encourage aggregation rather than dispersal of insecure metals to the environment ▪ Promote recycling and recovery of environmentally beneficial metals **Recommendations for business** ▪ Promotion of products mined and produced using green strategies ▪ Voluntary codes and agreements to incorporate environmental externalities ▪ Product design to discourage dispersal to the environment and easier recovery ▪ Adopt Life-Cycle management policies

	Mica, Feldspar, Bentonite, Perlite,	**Recommendations for innovation funders** ▪ Encourage projects that develop substitutes for the least secure metals ▪ Consider displacement effects of "green" technologies using insecure materials ▪ Encourage technologies that generate substitutes for insecure materials ▪ Encourage "mining" of waste streams for insecure metals ▪ Stimulate sustainable design approaches that consider overall life-cycle issues

FORMS OF SUBSTITUTION

In substitution there are two main components – a component for which there is a need to withdraw and replace (i.e. substituted) and a component which comes in its place – i.e. a substitute. Technically substitution can be addressed in many different routes. One can substitute

- an element for an element,
- a product (material/compound) for a product (material/compound),
- a product for a service,
- a product for a product,
- a system for a system.

The choice of the route depends on economic viability, sustainability, environmental friendliness and health safety, and last but not least the quality of the proposed solution in terms of performance.

APPROACH AND METHODOLOGY

Work Package 5 of MSP-REFRAM project addresses the concepts and scenarios of substitution for selected elements: tungsten, tantalum, molyblenum, niobium and rhenium. The primary objective is to analyse the map of substitution potential for each refractory metal with respect to their properties and applications that are most relevant in the EU industry. The criteria of choice depend on the social, economic and strategic importance of a discussed component of raw material (RM) value chain. Such a map is to be considered a guideline in defining and prioritizing actions towards whole RM value chain, especially the supply and recycling/waste management strategies.

The analysis was oriented towards defining the reduction and increase potential of refractory metals in their value chain which is covered in the Work Package deliverables 5.1 and 5.2 respectively. The value chains are viewed with respect to the applications and volumes and evaluated based on the literature and expert discussions. The outcome of Work Package 1 is a background for further analyses. The potential for both reduction and increase of RM use is considered for four possible scenarios:

1. The use of RM is reduced in considerable volume or substituted.
2. The potential and realistic substitutes are found in order to maintain demand in current level, increase of usage.
3. The present usage continues, no potential substitutes are found, and refractory metal demand will increase.
4. The refractories will substitute the less performing elements in large amounts.

The present deliverable, D5.1, outlines the potential substitutes of refractory metals based on analysis of the properties, applications, value chain and potential subsitutes. On the other hand, subsequent deliverable D5.2 is focused on a search for new application areas for RM, where they can substitute other, less performing materials.

On methodology wise, the report refers to the prior methodology and indexing; **the substitutability index is given as a result of evaluation of performance and price [10,12].** Still the driving forces for substitution can alter at time and place e.g. the ethical issues, the conflict material, the environmental issues.

The procedure for estimation of ability of substitution of many raw materials is given briefly in many documents on identification and assessment of profiles, economy and risks related to critical raw materials [10, 11, 12]. The substitutability index is a comparable quantified measure where all this information is concentrated. The substitutability index σ_s is first estimated for an element with respect to certain application to account for the element's functionality in a certain end-use sector. The estimated values are combined into an overall substitutability index σ_{RM} of an element by calculating a weighted sum of sector indexes with weight given by the sector consumption share of an element in the total element's consumption:

$$\sigma_{RM} = \sum_{s} A_{RM,s}\sigma_s$$

where $A_{RM,s}$ is the net consumption share (in %) of a given RM (refractory metal) in a given end-use sector. The values of substitutability index are subjected to experts' judgement and estimated by them. The values of occur between 0 and 1 where selected values mean:

0.0 – easily and completely substitutable at no additional cost
0.3 – substitutable at low cost
0.7 – substitutable at high cost and/or loss of performance
1.0 – not substitutable.

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CHAPTER 1. TUNGSTEN

1.1 TUNGSTEN PROPERTIES, APPLICATIONS AND PRODUCTION

1.1.1 PROPERTIES OF TUNGSTEN

Tungsten (W) is a greyish-white lustrous metal, which is a solid at room temperature. Tungsten has the highest melting point and lowest vapor pressure of all metals, and at temperatures over 1650°C has the highest tensile strength. It has excellent corrosion resistance and is attacked only slightly by most mineral acids [1]. Table 1.1 gathers the information about tungsten properties[2].

Table 1.1. Tungsten properties

Property	Tungsten, W
Natural state	Hard, dense, silvery-white, lustrous meta. Tungsten-containing ores are scheelite and wolframite
Atomic number	74
Atomic mass	183.84 amu
Density	19.3 g/cm^3
Melting point	3414 °C
Boiling point	5555 °C
Hardness	7.5 Mohs
Specific heat capacity	133.89 J/kg
Crystal structure	Body Centred Cubic

Figure 1. Tungsten metal

1.1.2 APPLICATIONS OF TUNGSTEN

Tungsten special properties include the highest melting point, the lowest coefficient of thermal expansion and the lowest vapour pressure of any non-alloyed metal [3]. 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 [4]. These properties make it extremely important for a variety of products. In particular, tungsten's use in cemented carbides represents its most important application as it is showed in Figure 2 for the year 2015 [4].

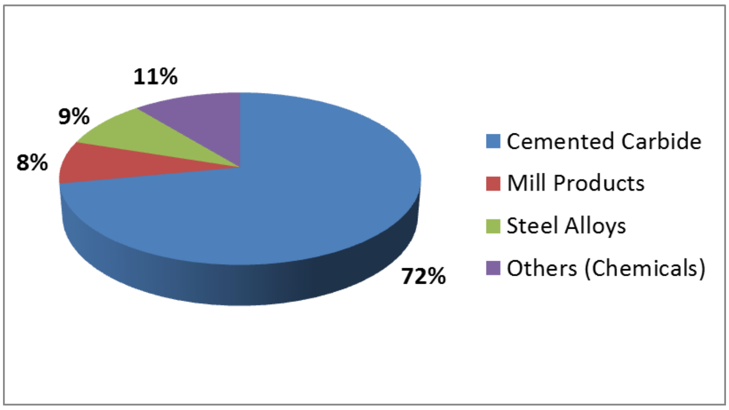


Figure 2. Figure of tungsten applications: Primary use of tungsten in Europe for the year 2015.

1.1.2.1 CEMENTED CARBIDES (HARDMETALS)

Cemented carbides represent a group of hard and wear resistant refractory composites in which hard carbide particles are bound together or are “cemented” by a ductile and tough binder matrix. Due to the high cost of tungsten, it is only utilised where the operative parts come into direct contact with the material being worked (wear parts) [5].

Tungsten carbides are widely employed in the mining, petroleum, construction and metal-working industries in drill bits and in machine tools for shaping metals, wood, composites, plastics and ceramics (e.g. punches, stamping dies, bushes, rollers, milling inserts and tile and glass cutters among others).

1.1.2.2 STEEL ALLOYS

Tungsten in steel contributes to increased hardness and wear resistance. Grain refining can further increase toughness [4]. These highly alloyed steels are used primarily in the working, cutting and forming of metal components [4]. Tungsten is commonly alloyed with steel, especially in high speed steels (HSS) that allow high productivity levels in metal curring and in superalloys with applications in the aerospace, industrial gas turbine and marine turbine industries due to high resistance to corrosion and wear.

Tungsten metal is also applied in thermal and radiation shields of space vehicles, electrodes for welding in noble gas atmosphere, X-ray emitting cathodes, heating elements for industrial furnaces, and others. It can be also used as an alloy component for production of various steels i.e. high-speed, tool and matrix as well as corrosion- and thermal-resistant superalloys.

The high temperature properties and high density of tungsten explain why there are so many tungsten based alloys. The hardness and high temperature properties of the respective tungsten carbides make them an important component in steels, stellites, superalloys and diamond tools [4].

1.1.2.3 MILL PRODUCTS

Pure tungsten mill products are used as light bulb filaments, vacuum tubes and heating elements. Metal tungsten powder is used in electric and electronic industry (tungsten wire in light bulbs and vacuum tubes) and some of its alloys with Cu and Ag for electrical contacts production.

In the lamp industry, tungsten filaments have been used since the beginning of the 20th century and continue to be used today. Tungsten electrodes are used for gas discharge lamps and tungsten is used in many different types of incandescent lamps. The most common types are general household lamps, automotive lamps, and reflector lamps for floodlight or projector applications. There are also many thousands of specialty lamps, which have a broad range of applications, such as audio-visual projectors, fibre-optical systems, video camera lights, airport runway markers, photoprinters, medical and scientific instruments, and stage or studio systems [4].

For the electronic and electrical industry, tungsten is practically the only material used for electron emitters. Although other, more electropositive, metals would yield higher emission rates, the advantage of tungsten is its extremely low vapour pressure even at high temperatures [4].

1.1.2.4 CHEMICALS

Tungsten chemical compounds can be found in paints, dyes, enamels, painted glass, catalysts, chemical compounds and others.

Different tungsten applications are presented in Figure 3.

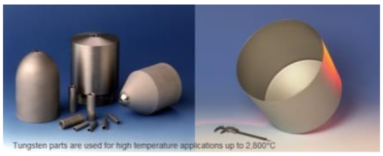
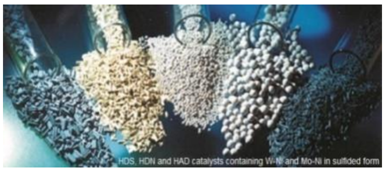
		
Hardmetals-cutting materials manufacturing	Mining and Construction	High Temperature applications
		
Lamp industry	Turbine blades	Catalysts

Figure 3. Tungsten applications

1.2 THE SUPPLY CHAIN OF TUNGSTEN

1.2.1 PRODUCTION

Mineral deposits can be found on all continents but it is estimated that China ranks first in the world in terms of tungsten ore resources and reserves and has some of the largest deposits [6]. Tungsten is considered to be a rare element, with and average abundance of tungsten in the Earth's crust estimated as 1.25-1.55 ppm [7]. In 2010, tungsten was included in the critical raw materials list published by the Ad-Hoc Working Group on Defining Critical Raw Materials [6].

It appears in nature as an oxide, not as a pure metal and is combined mainly with calcium (scheelite group) and manganese (wolframite) group. Figure 4 represents the world distribution of tungsten mining and primary tungsten products [8].

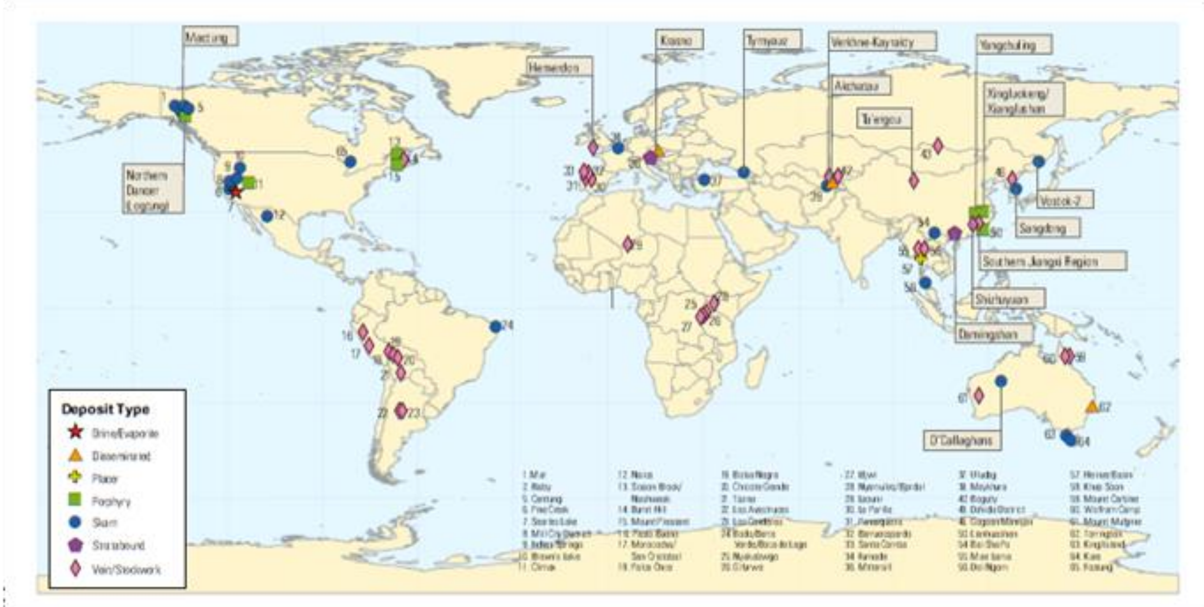


Figure 4. Tungsten Mining & Primary Tungsten Producers 2009

Following the USGS tungsten publication the reserve amount is presented in Table 1.2 [7].

Table 1.2. World mine reserves [7]

Country	Tones
Austria	10000
Bolivia	
Canada	290000
China	1900000
Portugal	4200
Russia	25000
Rwanda	
Spain	32000
United Kingdom	51000
Vietnam	100000
Other Countries	670000
Total	**3300000**

According to the most recent US Geological Survey report on the metal, world tungsten production reached 87 000 of tones in 2015, from which China produced 71 000 of tonnes [7]. In 2015, about 81% of the world's tungsten production came from China (Figure 5), followed by Vietnan (5000 tonnes, 6%) and Russia (2500, 3%). China is not only the most important supplier of tungsten but also its largest consumer.

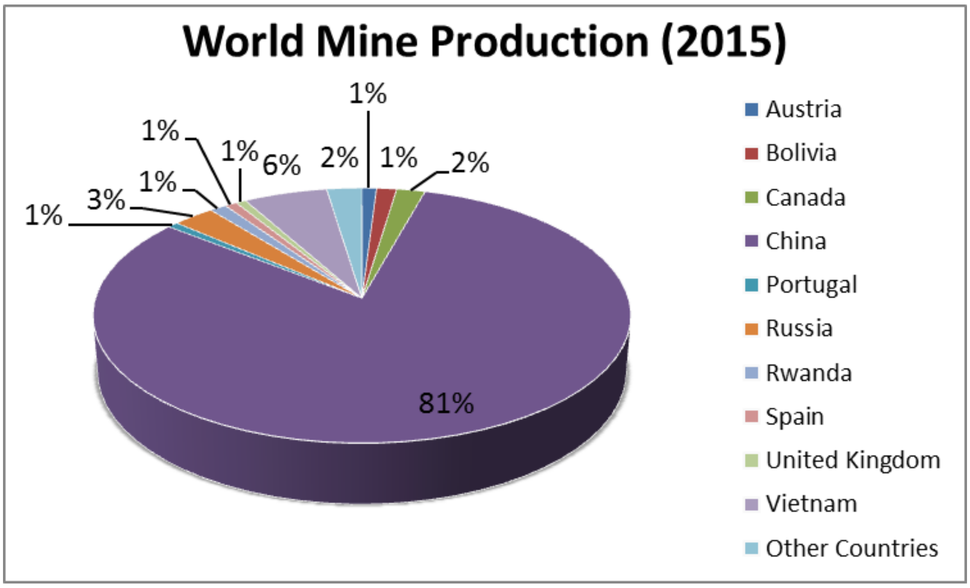


Figure 5. Geographic distribution of the 2015 production of tungsten concentrates (percent of the total world production).

Tungsten has been considered economically important throughout the last century. Figure 6 shows how the different supply and demand situation worldwide influenced tungsten prices. Tungsten prices have been stable during the 1980s and 1990s and have climbed in 2005/2006 reaching values of 300 dolars per tonne, when global demand increased while Chinese export declined [9], [10].

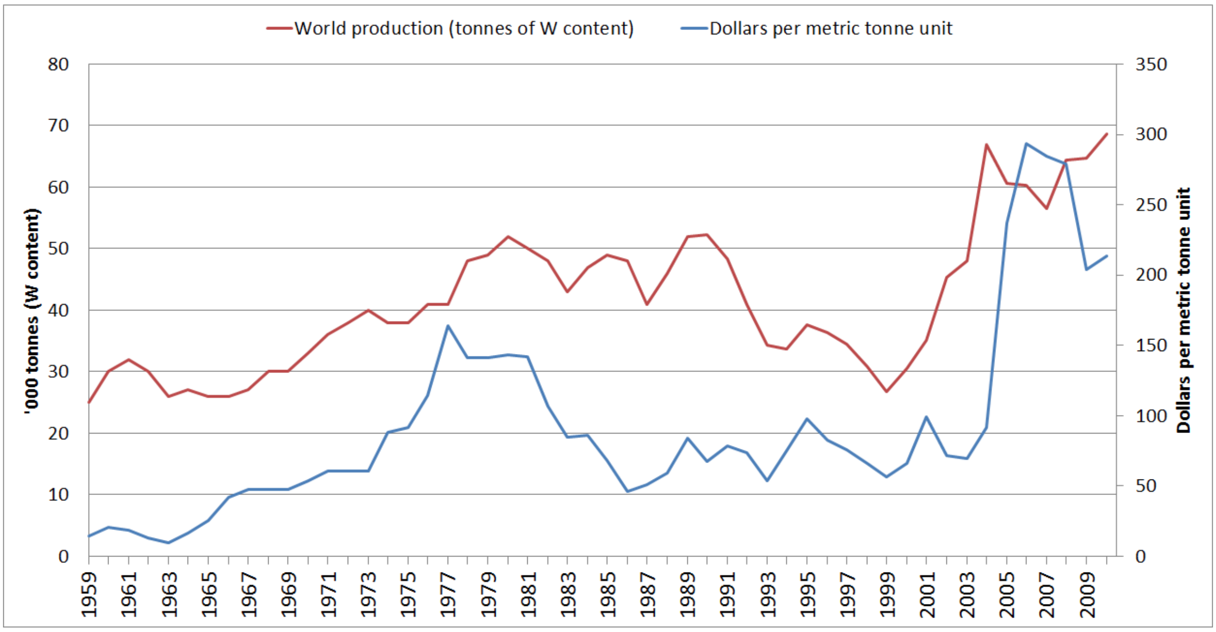
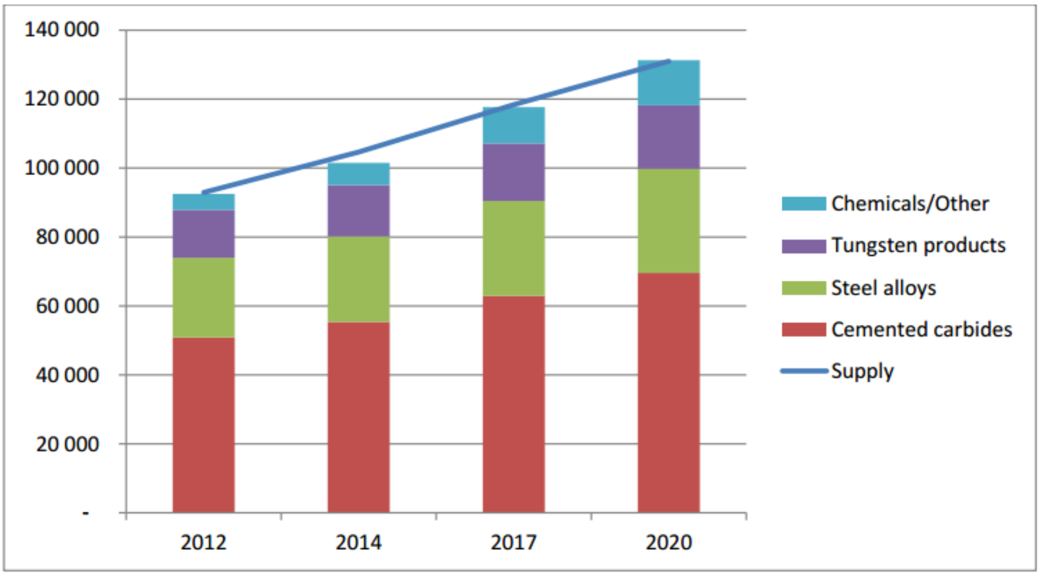


Figure 6- Historical tungsten production and unit value 1905-2010. [10].

1.2.2 CONSUMPTION

The global demand for tungsten increase from 62.550 tonnes in 2005 to 82.500 tonnes in 2015. In 2015, China was the highest consumer of tungsten (64%) followed by Europe (14%), USA (9%), Japan (7%) and other (6%) [11]. Following the report on critical raw materials from the EU [9], the market for tungsten is expected to remain roughly in balance, with a small surplus opening up by 2014, as some new mines reach the market.

However, by 2017 and 2020, demand is expected to catch up again with these scheduled production increases. Data from Roskill information Service for 2013 CRM study is presented in Figure 7.



Source: Roskill Information Services for 2013 CRM study

Figure 7. World total tungsten supply and end-use forecast to 2020

The consumption of tungsten by applications is mainly due to cement carbides followed by steel alloys, mill products and finally chemical and others. However, there is a significant variation in consumption by end-use between countries and regions Figure 8. China is the main consumer of tungsten for steel alloys, Europe the main for cemented carbides and USA for mill products.

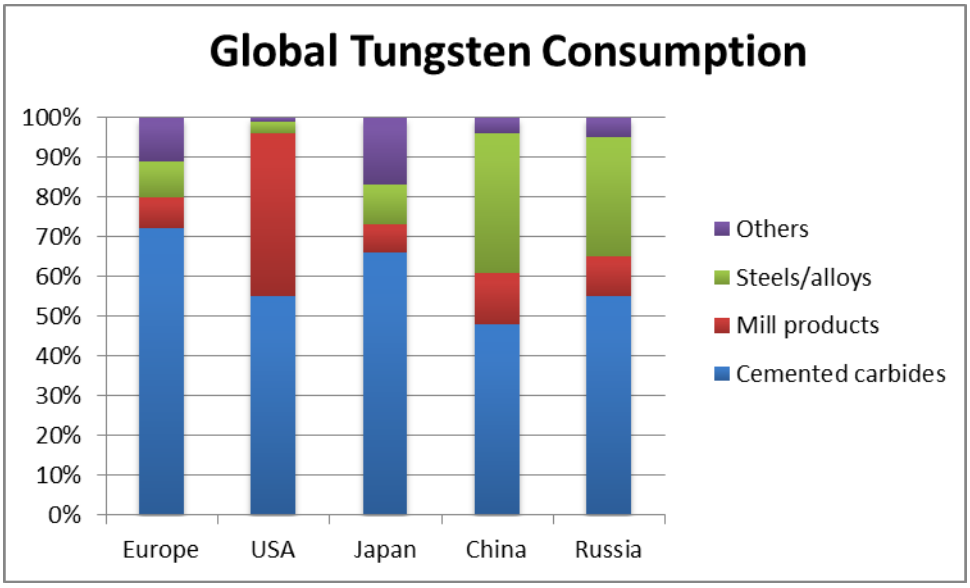


Figure 8. Tungsten consumption by application and main consumer countries

In Europe, data from Eurostat-Material flow acoounts in raw material equivalents-modelling estimates, gathers information about the total imports and exports of W in Europe from 2004 to 2013 [12]. This information shows that W exports are lower than W imports. Data is presented in Figure 9.

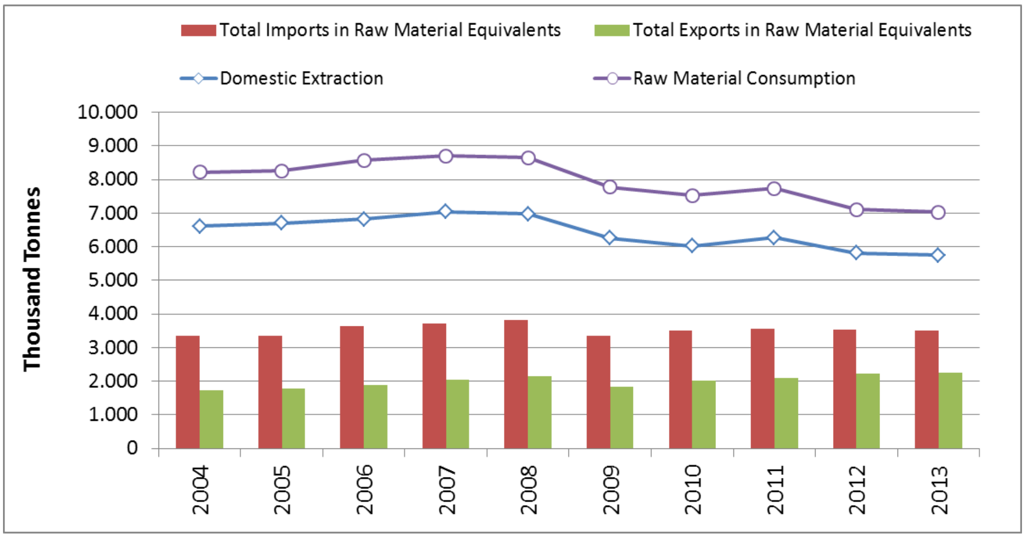


Figure 9. Total tungsten imports and exports in Europe

1.2.3 TUNGSTEN MASS FLOW

D.R. Leal-Ayala et al. elaborated a global mass flow analysis of tungsten to discuss key supply security oportunities. The paper gathers a complete methodology to perform the mass flow for different categories : mining and extration, recycling routes, fabrication of intermediate products and finished sectors, tungsten grades and processing energy consumption.

Figure 10 presents the global mass flow of tungsten through its entire supply chain in 2010, as well as the energy requirements of key transformation processess and the materials grades of main flows [10].

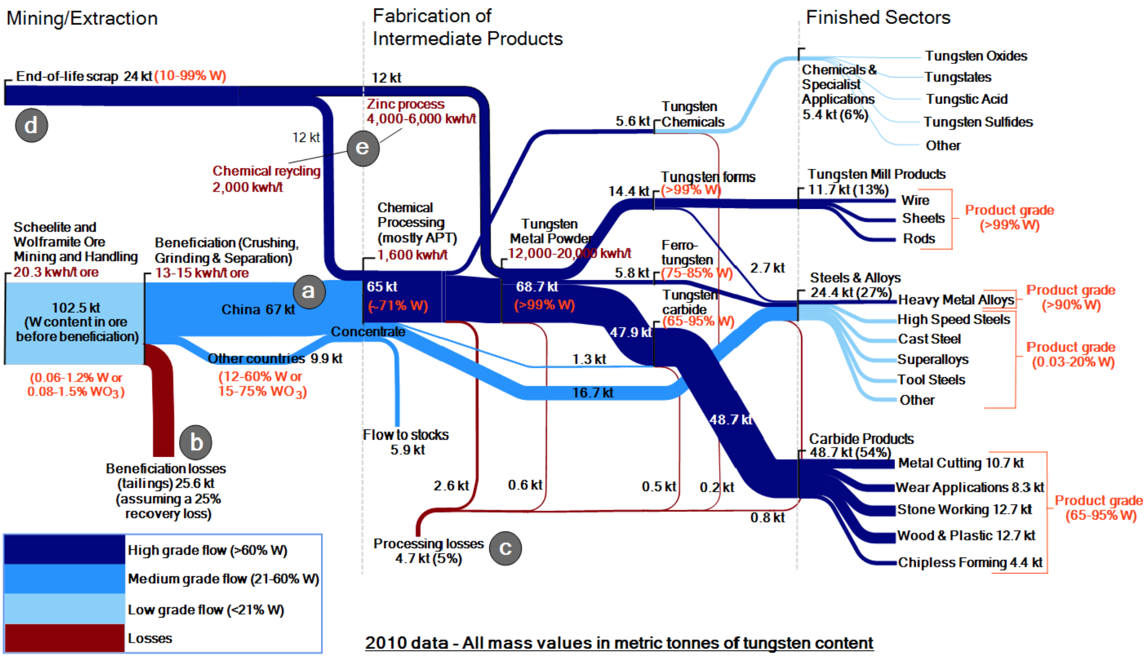


Figure 10. Global mass flows of tunsten in 2010. The grade of different flows and the energy consumption of selected processes are indicated with orange and red text respectively.

The conclusions for the mass flow presented are :

- In 2010, China accounted for about 87% o all mine production

- Tungsten's beneficiation process leads to considerable losses (10-40% of the tungsten content of the ore may be lost
- Processing losses during the fabrication of intermediate products are comparatively lower (<5%). In addition, nearly three quarters of all tungsten are processed through powder metallurgy and about half of total tungsten is used to manufacture carbide products.
- Roughly 25% of total tungsten upply came from end-of-life scrap
- Based on their processing energies, tungsten recycling is less energy intensive than primary production.

1.2.4 TUNGSTEN SUPPLY RISK

In the case of tungsten, it will be difficult to satisfy the growing economic demand in the future. This has been evidenced by its inclusion in the European Union's (EU) raw material supply criticality list which was motivated by its high economic importance, wide range of applications, its lack of viable substitutes, the EU's dependence on imports and trade concerns arising from China's dominant market position [13].

The Bristhis Geological Survey's risk list in 2012 ranked tungsten as number two in a supply critical index list mainly due to alleged political instability in supplying regions and its limited number of substitutes [14]. However, in 2015, BGS ranked tungsten as number eigh with a relative supply risk index of 8.1 being Chinea the leading producer and the top reserver holder [15].

The conclusions from the European Commision to include tungsten in the list of critical raw materials at EU level are [13]:

- raw material supply (APT, oxide) dominated by China which also has the largest reserves of tungsten ore worldwide, that means high risks of quantitative and price disruption.
- growing risks of "predatory" behaviour of China on the tungsten scrap market
- substitution possibilities limited by cost of alternative materials/technologies, lesser performance, and less environmental friendly alternatives.
- worldwide loss of know-how if EU tungsten value chain is destroyed as it is the leader in the development of many tungsten products development for automotive, aerospace, medical, lighting applications. Disappearance of EU tungsten industry would result in full dependence of several key industries on imports from abroad.

1.3 POTENTIAL SUBSTITUTES OF TUNGSTEN

1.3.1 ROLE OF TUNGSTEN IN DIFFERENT APPLICATIONS

1.3.1.1 ROLE OF W IN CEMENTED CARBIDES (HARDMETALS)

Cement Carbides are the most important usage of tungsten today. The main constituent is tungsten cemented monocarbinde (WC, making up 85-95% of the hardmetal). 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 a excellent densification during liquid phase sintering and in a pore-free structure [16] [17].

WC play a crucial role as they combine high hardness and strength with good toughness within a wide property range, and thus constitute the most versatile hard materials group for engineering and tooling applications. As it is presented at Figure 11, hardness increases with decreasing grain size and binder content. Hardness increases fracture toughness decreases and vice versa. In slidign abrasive applications, hardness is a good measure of wear resistance.

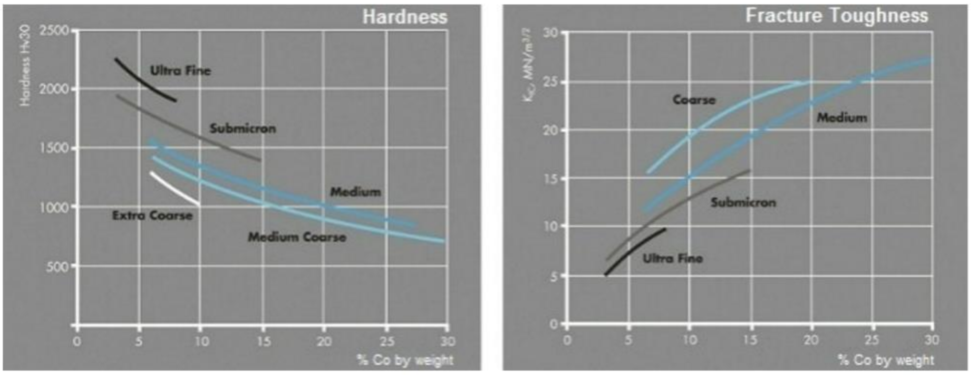


Figure 11. Main properties of Cemented Carbides [16]

Cemented carbides havetheir high modulus of elasticity (about three times that of steel), their extremely high compressive strength (up to 8,000 MPa) making them ideal tool material for high pressure diamond synthesis, and an excellent thermal conductivity.

1.3.1.2 ROLE OF W IN 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. Alloying element in steels 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 [16]. The effect of tungsten alloying on hardness during tempering is schematically shown in Figure 12 [18].

Tungsten has the highest melting point of all metals and is alloyed with other metals to strengthen them. Tungsten and its alloys are used in many high-temperature applications, such as arc-welding electrodes and heating elements in high-temperature furnaces.

Tungsten in steel increase the amount of undissolved and excess carbide in the hardened steel and the eutectoid points 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.

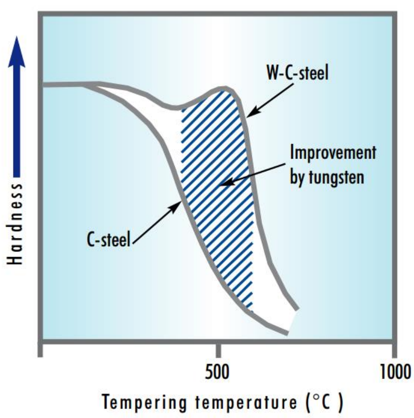


Figure 12. The effect of tungsten alloying on hardness during tempering [18]

The content of tungsten in steel changes from different applications as it is presented in Table 1.3.

Table 1.3. Tungsten content in steel

Steel	W content
High Speed Steels	1,5%-20%
Hot Work Steels	1,5%-18%
Cold Work Steels	0,5%-3%
Plastic Mould Steels	~1%

1.3.1.3 ROLE W IN SUPER-ALLOYS

The role of tungsten in Super-alloys is to provide high temperature strength, high thermal fatigue resistance, food oxidation resistance, excellent hot corrosion resistance, air melting capability. W alloyed nickel- and cobalt-based super – alloys are used in aircraft engines, marine vehicle, turbine blades and vanes, exhaust gas assemblies and as construction material for furnace parts [17].

1.3.1.4 ROLE W IN MILL PRODUCTS

Tungsten in mill product provides extremely high melting temperature (3414 ºC), low vapor pressure, high stiffness and excellent creep resistance at elevated temperature W used in the form of wires, coils and coiled coils incandescent lamps and as electrode in low-and high pressure discharge lamps [17].

1.3.2 POTENTIAL SUBSTITUTES

1.3.2.1 TUNGSTEN SUSTITUTABILITY

Tungsten substitutes for most application results in a loss of performance or in an increase of cost. In cemented carbides and other applications, W and its compounds can be replaced by Mo, Ti, ceramics depleted uranium or hardened steel. For lightning equipment tungsten filaments can be substituted by carbon nanotube filaments, light-emitting diodes or other light sources [9]. Figure 13 represent the distribution of end-users and corresponding substitutability assessment for tungsten [17] and substitutability of tungsten scoring included in the report on critical raw materials for the EU is presented in Table 1.4..

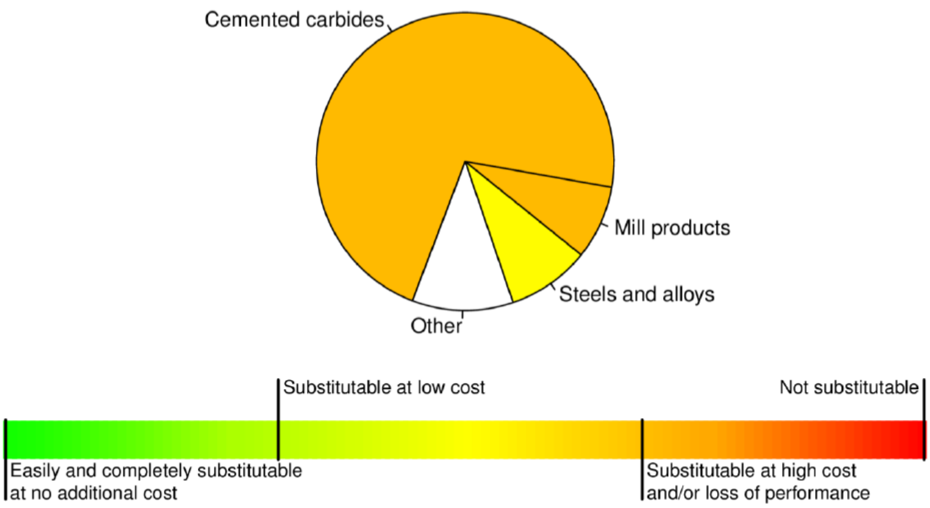


Figure 13. Distribution of end-uses and corresponding substitutability assessment for tungsten [17]

Table 1.4. Substitutability of tungsten scoring [9]

Use	Substitutability score
Tungsten alloys	0,7
Superalloys	1
Fabricated producs	1
Alloy steels (mainly tool steel, >80%)	0,7
Cemented carbides	0,7

1.3.2.2 POTENTIAL SUBSTITUTES

The next table gathers information about the potential substitutes for tungsten, their advantages and drawbacks for each application.

Table 1.5. Potential substitutes for tungsten, their advantages and drawbacks

Application	Potential substitute	Advantages	Drawbacks	Ref.
Cemented carbides	Tool Steel Ceramics Ceramic-metallic composites Molybdenum carbide Niobium Carbide Titanium carbide Titanium cabonitride in metallic binder phase (Ni and/or Co) possible with toughening additives	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 more lightweight Application area: tribotechnical and machining applications Ti lower risk of supply TiC hard metal grades shows a highest hardness, fracture toughness	Increase of cost Loss in product performance Molybdenum (RM) Nb (CRM)	[17], [19], [20], [21]
Tool/High speed	Molybdenum combined with alloying with chromium, vanadium	Better performance (addition of 5-10% of Mo increase the hardness	Molybdenum (RM) ASS (Overcoming	[17], [22]

Steels	and nickel ASS (Alumina, silicon nitride, sialon) (Cutting tool tips) AZS (Alumina, zirconia, silicon carbide) (seals, bearings, nozzles)	and toughness Cost-effective Mo combined with V prevents softening and embrittlement of steels at high temperature [ASS] can increase productivity [AZS] can improve wear and corrosion resistance	inadequate fracture toughness) AZS (No significant barriers)	
Super-alloys (corrosion resistance turbines blades, marine vehicles…)	Molybdenum Ceramic matrix composites (CMCs) made from a silicon carbide/nitride matrix toughened with a coating of silicon Tantalum fiber – reinforced superalloys (turbine blades)	Lower wight Strong, tough and can be mass produced CMC durability has been validated through significant testing in customer gas turbine engines accumulating almost 30,000 hours of operation (General Electric GE)		[17], [23]
Mill products	Carbon nanotube filaments Induction technology Light-emitting diodes		W replacement appears extremely difficult at the moment	[17]

For cemented carbides, different researches have been done in order to evaluate potential substitutes for tungsten. As an example, Lindroos et al., 2015 [20] evaluated the tungsten mechanical properties of TiC based hard metal compositions in Ni matrix compared to two medium carbide size grade WC-Co composites. The results are presented in Figure 14. Mechanical properties of different materials compositions. The results from the reseach concluded that TiC hard metals grades are potential candidates to substitute tradicional WC-Co in certain applications where high hardness and fracture toughness is needed.

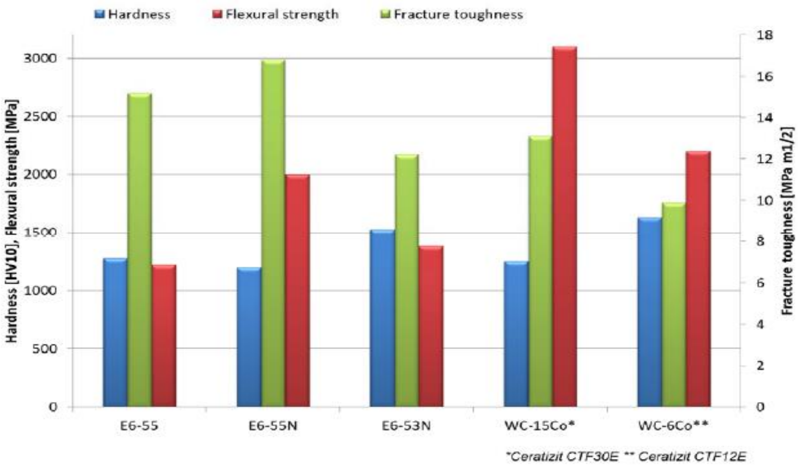


Figure 14. Mechanical properties of different materials compositions [20]

Ishida et al., 2011 [21] also compare cemented carbide and cermet (TiC) are properties comparison are presented in Figure 15. Comparison of propertis and micro structure of SEM for WC and TiCN. The solution proposed in the research was to develop a composite structure of cemented carbide and cermet that reduce tungsten used by 20%.

Properties		Cemented carbide	Cermet
Thermal conductivity	w/m • ˚C	105	33
Thermal expansion	$\times 10^{-6}$ / ˚C	4.5	7.5
Toughness	MPa • $m^{1/2}$	8	6.5
Young's modulus	GPa	620	420
Density	g / cm^3	15.0	6.1
Price	yen / cm^3	69	26

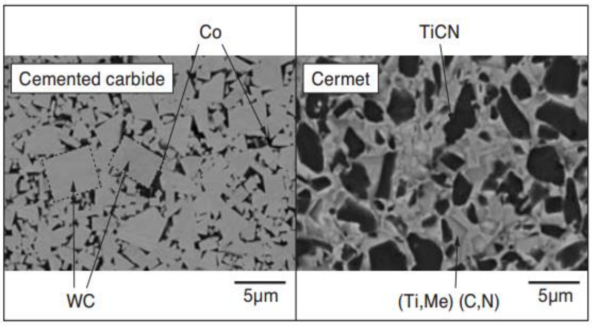


Figure 15. Comparison of propertis and micro structure of SEM for WC and TiCN [21]

As a summary, the consumption of W continues to increase as the amount of carbides tool production increases with the expansion of markets in developing countries. For Tungsten main application, WC-based cemented carbides, since to be difficult to substitute since the potential substitutes increase of cost and decrease the performance. Titanium carbides (TiC) and nitride (TiN) are potential substitute but the technology is not competitive at the moment. In steel products tungsten can be replace by other refractory metals as Nb (CRM) or Mo. In other application areas possible substitution of Tungsten is rationale, 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 is could be possible in 10 year since current TRLs are very low (TRL 3-4). There are some already substitution path in LEDs.

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CHAPTER 2. TANTALUM

2.1 TANTALUM PROPERTIES, APPLICATIONS AND PRODUCTION

2.1.1 TANTALUM PROPERTIES

Tantalum (Ta) is a dense, tough and ductile element with very high melting point 3 017°C. It is also highly corrosion-resistant to most acids below 150°C and in most cases chemically inert. It has good thermal and electrical conducting properties, and it is easy to machine. Some of the Tantalum main properties are gathered in **table 1** [1] .

Table 1.Tantalum main properties.

Property	Tantalum, Ta
Natural State	hard, blue-gray, lustrous transition metal, highly corrosion-resistant
Atomic Number	73
Atomic Mass	180.94788 amu
Crystal Structure	Body Centred Cubic (α-Ta), tetragonal (β-Ta)
Density	16.69 g/cm^3
Melting point	3017 °C
Boiling point	5458 °C
Coefficient of thermal expansion	6.3 µm/(m·K) (at 25 °C)
Thermal conductivity	57.5 W/(m·K)
Electrical conductivity	131 nΩ·m (at 20 °C)

Figure1. Tantalum metal[2].

2.1.2 APPLICATIONS OF TANTALUM

Excellent combination of tantalum properties implies a wide range of applications. The main use for tantalum derives from its high volumetric efficiency, which makes it a key material used in electronic capacitors. Major consumption is in electronics industry, mainly to produce capacitors from tantalum powder. Additionally, tantalum wire is consumed by the capacitor manufacturers as the anode lead. Tantalum metal is also used for sintering tray assemblies and shielding components for the anode sintering furnaces. Other non-capacitor uses in electronics create demand for tantalum mill products for sputtering targets and tantalum chemicals for audio and video components [1,3]. Tantalum properties and its main applications are gathered in **table 2**.

Table2. Tantalum properties and main applications.

Property	Parameters	Application as	Form of the element	Application in	Source
High capacitance (small size per microfarad rating/electrical storage capability); operation over a wide temperature range from -55 to +200°C; withstand severe vibrational forces		Capacitors	Powder or wire form	Electronic circuits in: - portable electronics e.g. laptop computers, cellular/mobile phones, video cameras, digital still cameras; - other equipment such as DVD players, flat screen TVs, games consoles, battery chargers, power rectifiers, cellular/mobile phone signal masts, oil well probes - medical appliances (e.g. hearing aids and pacemakers); - automotive components (e.g. ABS, airbag activation, engine management modules, GPS)	[4,5,6]
Increased high temperature deformation, thermal shock resistance, high temperature stability control of grain growth, hardness	HT oxidation, thermal shock resistance	Cemented carbides	Tantalum carbide	High-speed cutting and boring tools, other tools for environments with high levels of stress and temperatures (e.g. as teeth for excavator buckets, mining drills, high-performance bearings and cutting blades), refractory parts and coatings for furnaces and nuclear reactors	[5,6,7]
High melting point and resistance to corrosion	melting point 3290K, 3017 °C corrosion	Superalloys, typically nickel based	Tantalum fabricated sheets, plates, rods, wires	In aerospace and defence applications (e.g. missile parts), suitable for other turbine-type equipment (like gas turbines)	[5,6]
Oxidation resistance and shape memory properties		Ta-Ru alloy		Military	[5]
Superior corrosion resistance - equivalent in performance to glass		Alloys	Tantalum fabricated sheets and plates	- Chemical process equipment including lining, cladding, tanks, valves, heat exchangers - Cathodic protection systems for steel structures such as bridges, water tanks - Corrosion resistant fasteners, screws, nuts, bolts - Spinnerets in synthetic textile manufacture	[6]
Copper migration inhibitor		Sputtering targets	Tantalum ingot	Applications of thin coatings of tantalum, tantalum oxide or nitride coatings to semi-conductors	[6]
High temperature and corrosion resistance	melting point, corrosion	Alloys		Process equipment - heat exchangers, boilers, condensers, pressure reactors, distillation columns, crucibles, etc. where Ta is used as liner - dimensionally stable anodes in extreme environments (such as in the production of chlorine and	[4,5]

				soda in systems with ion exchange membranes) - Sintering tray assemblies and shielding components for the anode sintering furnaces	
High bio-compatibility		Tantalum fabricated sheets, plates, rods, wires		- Prosthetic devices for humans - hip joints, skull plates, mesh to repair bone removed after damage by cancer, suture clips, stents for blood vessels	[5]
High index of refraction	index of refraction	Tantalum oxide (Ta_2O_5)	Tantalum oxide (Ta_2O_5)	-lenses for spectacles, digital cameras and mobile phones - glass-coatings and in X-ray film/absorbers where yttrium tantalite reduces X-ray exposure and enhances image quality.	[4,6]
Electronic signal wave dampening			Lithium tantalate	Surface Acoustic Wave (SAW) filters in mobile phones, hi-fi stereos and televisions	[6]

Tantalum end uses in 2004 and in 2010 in different applications are presented in **figure 2**. Capacitor grade tantalum powder is responsible for major end use corresponding 42% of tantalum end uses in 2004 but its share has decreased to 24% in 2010. The shares of Tantalum metal products and metallurgical grade powder and metal have increased from 2004 to 2010.[8]

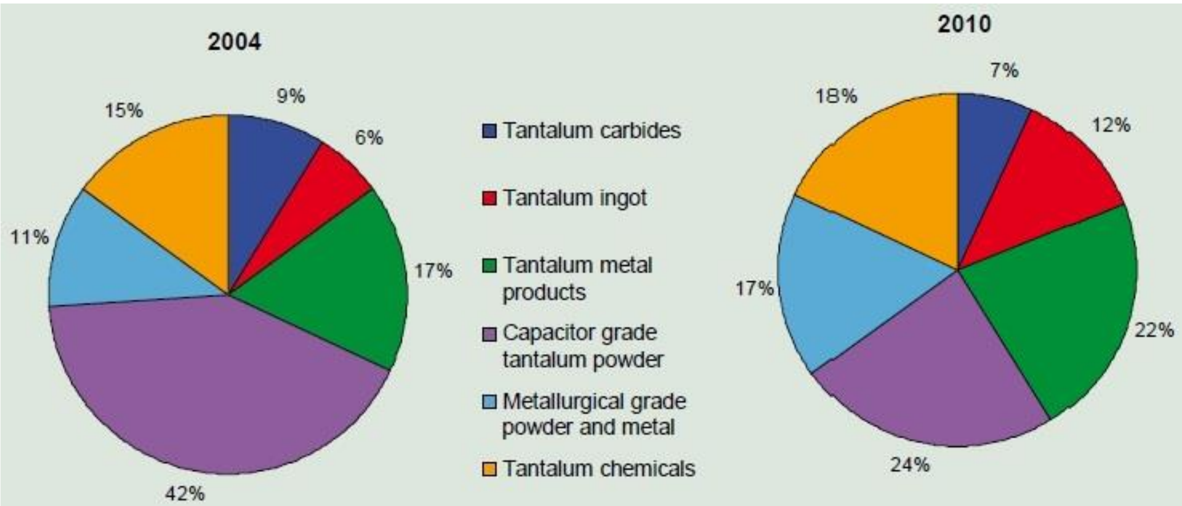

Figure2. Comparison of end use of tantalum: 2004 and 2010. [8]

2.2 THE SUPPLY CHAIN OF TANTALUM

2.2.1 PRODUCTION

Tantalum is 52nd most abundant element in the Earth's crust; its share is only 2.1 ppm (0.00021%). Economically important tantalum-containing minerals are tantalite, wodginite, microlite, and columbite. [9] **Figure 3** shows geographic distribution of the 2013 production of tantalum concentrates. There is no primary production of tantalum in Europe.

Figure3. Geographic distribution of the 2013 production of tantalum concentrates (percent of the total world production) and contribution from the European Union [10]

Tantalum is also produced as by-product during tin smelting from tin refinery slags. Globally, it has been estimated that 10-20 % of the global Ta supply is produced from tin slags and 20-30% from different types of manufacturing and End-of-Life scrap. The percentage of tin slag and srap recycling has increased in tantalum supply in recent years. **Table 3** shows tantalum global supply sources at 2008 and at 2012 [3].

Table 3. Global supply up until 2008 and as of 2012 [3].

Source	Percentage 2008 [%]	Percentage 2012 [%]
Primary concentrates	60	40
Secondary concentrates	10	10
Tin slag	10	20
Scrap recycling, synthetic concentrates	20	30

2.2.1 CONSUMPTION

Tantalum demand by application in 2012 is presented **in figure 4** and in **table 4** in year 2013. The greatest demand for tantalum is in powder or wire form in 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.

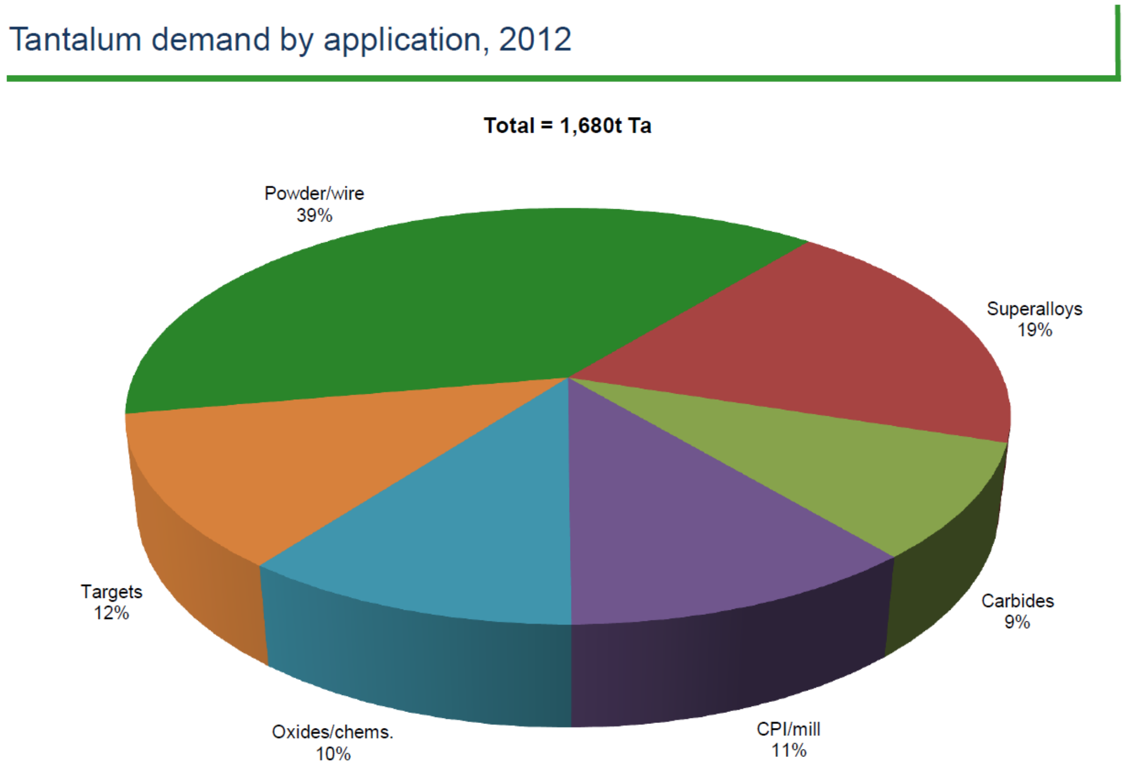

Figure 4. Tantalum demand by application in year 2012 [5].

Table 4. Tantalum end uses, shares and megasector assignment 2013. [7]

Material	Application	Share	Megasector
Tantalum	Capacitors	40%	Electronics
Tantalum	Superalloys	21%	Metals
Tantalum	Sputtering targets	12%	Electronics
Tantalum	Mill products	11%	MechEquip
Tantalum	Carbides	10%	MechEquip
Tantalum	Chemicals	6%	Chemicals

2.3 POTENTIAL SUBSTITUTES OF TANTALUM

2.3.1 TANTALUM SUBSTITUTABILITY SCORES

In **table 5** it is presented substitutability scores for tantalum presented by Oakdene Hollins and Fraunhofer ISI in report on Critical Raw Materials at EU Level at 2013. Score 0 represent easily substitutable with no additional cost or loss of performance and score 1 represents substitutable only with increase in cost and loss of performance.[11,5]

Table 5. Tantalum substitutability in different applications. [11]

Material	Application	Share	Megasector	Substitutability
Tantalum	Capacitors	40%	Electronics	**0.3**
Tantalum	Superalloys	21%	Metals	**0.7**
Tantalum	Sputtering targets	12%	Electronics	**1.0**
Tantalum	Mill products	11%	MechEquip	**0.7**
Tantalum	Carbides	10%	MechEquip	**0.3**
Tantalum	Chemicals	6%	Chemicals	**1.0**

Thus tantalum substitutability according to Table 5 scores is quite easy with low cost in capacitors and carbides. In superalloys and mill products the substitutability is possible with high cost and/or loss of performance. In sputtering targets and chemicals tantalum is still not substitutable. Thus, tantalum can be substituted by other materials but most substitutes have either higher costs or adverse properties. Distribution of end-uses and corresponding substitutability assessment for tantalum is presented in **figure 5**.

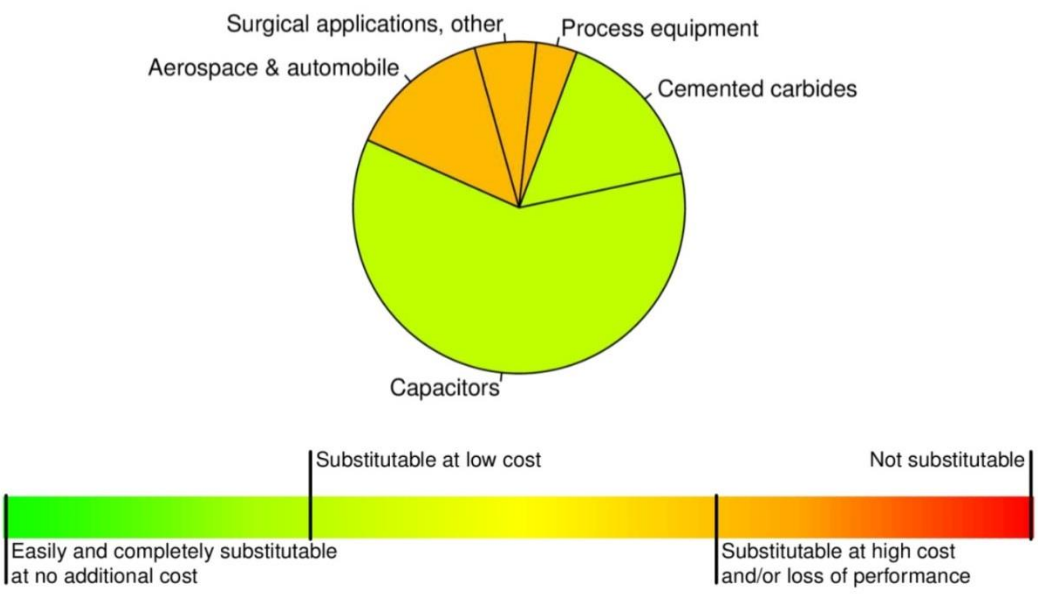

Figure 5. Substitutability of Tantalum in its major applications.

2.3.2 POTENTIAL SUBSTITUTES

Tantalum capacitors exploit the tendency of tantalum to form a protective oxide surface layer as the dielectric. For tantalum the dielectric layer can be very thin which results in that a high capacitance can be achieved in a small volume. In capacitors, aluminium and ceramic capacitors offer substitutes that are competative in cost and also in performance to tantalum. They also offer sustainable substitutes not utilizing critical raw materials. Ta capacitors are still used in applications which require high performance.

Murata Electronics first began to see industry acceptance of ceramic capacitors as substitutes for tantalum in the late 1990 century. By 2001, ceramics have proved they had enough advantages over tantalum to become permanent replacements. Most important benefit is that ceramic capacitors offer cost-effective solution to tantalum capacitors. The design modifications have led also to several advantages in ceramic capacitors, including ease of placement, low equivalent series resistance (ESR), non-polarization, and high voltage. [16] Aluminium capacitors offer lower cost and higher availability over tantalum capacitors. They also have shorter production lead times, low leakage current and higher voltage range. [14]

Due to the physical and chemical similarities of niobium and tantalum the two metals can be substituted for each other in number of application for example in cemented carbides, corrosion resistant coatings, optics and hard disc drives. Niobium is listed as critical raw material (CRM), so niobium is not offering a sustainable substitute for tantalum. Where strength at high temperatures is required in steels, metals such as molybdenum and vanadium could be used to substitute tantalum. In superalloys hafnium, iridium, molybdenum, niobium, rhenium and tungsten could substitute tantalum. Also these substitutes are not sustainable options and typically also have higher cost. In some electronic applications, like in SAW filters and SAW resonators, Lanthanum gallium silicate (La2Ga5SiO14) could substitute tantalum. But also lanthanum and gallium are listed as critical raw materials.

In **table 6** it is gathered potential substitutes for tantalum, their notable advantages and drawbacks.

Table 6. Potential substitutes for tantalum, their advantages and drawbacks [5,8,11,12,13,14,15,16].

Application	Potential substitute	Advantages	Drawbacks
Capacitors	Nb-oxide	Lower cost possible	Usually larger and have a shorter life-span, niobium listed as CRM
	Aluminium	Lower cost, higher availability, shorter production lead times, low leakage current, higher voltage range (up to 400 VDC)	More sensitive to harsh and hot operating conditions
	Ceramic	lower cost, smaller size, and/or reliability	
Cemented carbides	Niobium, tungsten		Niobium and tungsten both CRM
	titanium carbides (TiC) and titanium nitride (TiN)	Lower cost (price TaC~49.7-74,5EUR/kg, TiC~33.8-51.3EUR/kg) [12]	
Steel super-alloy applications where strength is required at high temperature	Vanadium or molybdenum		

Super-alloys for high-temperature applications	Hafnium, iridium, molybdenum, niobium, rhenium and tungsten		iridium, niobium and tungsten CRM
Process equipment, resistance to corrosion and high-temperature environment	Niobium	similar crystallographic properties	niobium CRM
Process equipment, corrosion-resistant	Glass, platinum, titanium and zirconium		platinum CRM
SAW filters and SAW resonators in electronic applications in cellphones, TV sets, video recording, etc	Lanthanum gallium silicate, La2Ga5SiO14		La and Ga both CRM
Orthopaedic applications	titanium and ceramics in some cases		
Surgical equipment	Chromium/nickel steel alloys		Lower durability of the oxide coating layer and a lower malleability,
Optics/lenses	Niobium in some cases		niobium CRM
Hard disk drives	Niobium		niobium CRM

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CHAPTER 3. MOLYBDENUM

3.1 MOLYBDENUM PROPERTIES AND APPLICATIONS

3.1.1 MOLYBDENUM PROPERTIES

Molybdenum is a shiny silvery metal moderately dense and moderately hard (5.5 Mohs hardness) with 6th highest melting point of all elements equal to 2623°C. Out of all engineering materials it has the lowest thermal expansion coefficient, and fairly high thermal conductivity. In nature it is most often found in molybdenite MoS_2 form [1,2]. In the table below some most important properties of molybdenum are outlined. Molybdenum properties make imply its use mostly as an alloying element in steels and other alloys, but is also used in catalytic applications and as a lubricant.

Table 3.1. Selected properties of molybdenum metal [1,2,3].

Property	
Natural State	Shiny silvery metal. Molybdenite (MoS_2)
Atomic Number	42
Atomic Mass	95.95 amu
Crystal Structure	Body-centered cubic, a= 3.1470 Å
Valence	0, 2, 3, 4, 5, 6
Oxidation State	From -2 to +6
Electron configuration	[Kr] $4d^5 5s^1$
Density	10.02 g/cm^3
Melting point	2623 °C
Boiling point	4639 °C
Coefficient of thermal expansion	4.8 x 10^{-6} / K at 25°C
Thermal conductivity	138 W/m K at 20°C (14th highest)
Electrical conductivity	20 MS/m at 20°C (11th highest)

3.1.2 OVERVIEW OF MAIN APPLICATIONS OF MOLYBDENUM

Molybdenum is mainly used as an alloying element in steels, stainless steels and alloys. The market share versus applications is shown in the figure below.

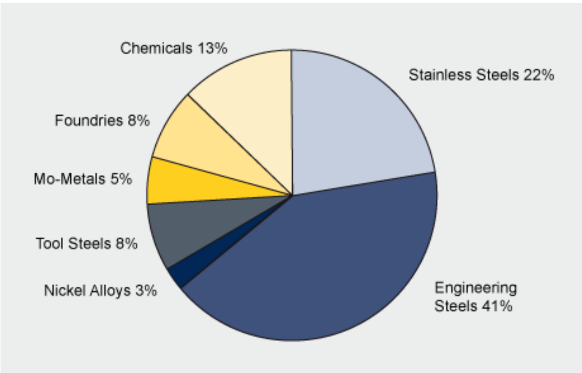


Fig. 1. First use of molybdenum, 2015 [4].

3.1.2.1 STAINLESS AND ALLOY STEELS

Stainless steels are main application of molybdenum in todays industry. Molybdenum in steel is an alloying element responsible for increase of corrosion resistance. Although molybdenum itself cannot provide corrosion resistance to steel, it can significantly improve it. On top of that molybdenum is necessary for significant resistance of steel to pitting corrosion and crevice corrosion in chloride-containing solutions. Stainless steels are high-alloy steels group that comprises of austenitic (ca. 75% market), ferritic (ca. 25 % market), duplex (ca. 1% market) and martensitic (ca. 1% market) steels.

Some of the most common stainless steel grades are given in table below with the content of chromium, molybdenum, nickel and nitrogen. The measure of pitting corrosion, PREN number, correlates well with molybdenum content.

Type 316 containing 2-3% Mo is the most widely used Mo-containing stainless steel. It is used in the tanks, piping and heat exchangers in food handling and processing and in the production of pharmaceuticals. The higher the molybdenum content the higher the resistance to wind-borne chlorides and so type 316 is chosen in marine and coastal environments for architecture applications.

The most corrosion resistant stainless steels contain 6 - 7.3% Mo. Such grades are found in power plant condensers, offshore piping, and critical components in nuclear power plants. The harshest operating environments that are found in power plant scrubbers, pulp and paper and chemical process equipment, require the use of alloys with even higher molybdenum contents. Examples are grades with 6 - 8% Mo and nickel base alloys with 10% and 16% Mo.

Table 3.2. Most common stainless steels parameters and their use [5-8].

N/ AISI/ UNS	Cr	Mo	Ni	N	PREN	Characteristics	Common applications
Ferritic grades – all not susceptible to chloride-induced stress corrosion cracking, Resistance to pitting and crevice corrosion is lower than that of austenitic chromium-nickel stainless grades [6]							
1.4512 / 409/ S40900	11.5				11.5	not susceptible to chloride induced stress corrosion cracking, particularly suitable for deep drawing	exhaust system parts, gas heaters and other elevated temperature applications (up to 600°C)
1.4016 / 430/ S43000	16.5				16.5	Good corrosion resistance in mildly corrosive environments combined with good formability good corrosion resistance in fresh water, steam, mild acids and bases, as well as in oxidizing acids (e.g. nitric acid)	- one of the most used non-hardenable ferritics, especially in indoor environments, Kitchen equipment, Household appliances, Sinks, Flanges and valves,
1.4113 /	16.5	**1**			19.8		Automotive trim fittings

434/ S43400							
1.4526 / 436/ S43600	17.5	**1.25**			21.6		Automotive exhaust systems & mufflers, Decorative trim in automotive applications
1.4521 / 444/ S44400	17.7	**2.1**			24.6		food processing, brewery and wine-making equipment, hot-water tanks, heat exchanger tubing and automotive exhaust components; where stress corrosion cracking needed; solar water heaters, tap water applications [7,8]
/ 446/ S4460 0	27	**3.7**	2		39.2	non-heat treatable stainless steel that provides good resistance to high temperature oxidation and corrosion;	Boiler baffles, furnace parts, X-ray tube bases, oil burner components, kiln linings, glass molds, annealing boxes and industrial muffler
Austenitic grades							
1.4301 / 304/ S30400	18.1		8.3		18.1	all-purpose product with good corrosion resistance and is suitable for a wide variety of applications that require good formability and weldability,	Building and Construction [IMOA], Household appliances and consumer goods, Kitchen equipment, Indoor and outdoor cladding, handrails, and window frames, Food and beverage industry equipment, Storage tanks, Flanges and valves
1.4401 / 316/ S31600	17.2	**2.1**	10.2		24.1		Building and Construction, 316 and 316L more resistant to chloride salts (coastal and deicing) and to pollution related corrosion, Heat exchangers, Flanges and valves
1.4438 / 317L/ S31703	18.2	**3.1**	13.7		28.4		chemical processing industry - Chemical tankers, Pulp and Paper equipment, Condenser tubes and heat exchanger tubes, Equipment for the petrochemical industry, Flue-gas desulfurization equipment
1.4439 / 317LM	17.8	**4.1**	12.7	0.14	33.6	excellent resistance to chloride pitting and crevice corrosion	in the bodies, structural members, and internals for scrubbers for flue gas

N/ S31726							desulfurization, chemical processing applications
1.4539 / 904L/ N08904	20	**4.3**	25		34.2	very high resistance to corrosion. Commonly used in chemical and petrochemical industry for handling medium concentrated sulphuric acid,	Process equipment in chemical industry, Petrochemical industry, Bleaching equipment in the pulp and paper industry, Flue gas cleaning, Desalination, Seawater handling, Hydrometallurgy, Food and beverage, Pharmaceuticals, Heat exchangers
/ 254 SMO (6%Mo)/	20	**6.1**	18-24	0.2	43.3	extremely high resistance to both uniform and localized corrosion, developed especially for oil and gas offshore platforms and the pulp and paper industry,	Applications requiring resistance to chlorinated seawater, Flue gas cleaning, Maritime exhaust gas cleaning (EGC), Bleaching equipment in the pulp and paper industry, Flanges and valves
Duplex grades							
1.4362 / 2304/ S32304	23	**0.3**	4.8	0.1	25.6	good resistance to localized corrosion and stress corrosion cracking in combination with high mechanical strength,	Desalination plants, Firewalls and blast walls on offshore platforms, Bridges Components for structural design, Storage tanks, Pressure vessels, Heat exchangers, Water heaters, Rotors, impellers and shafts
1.4462 / 2205/ S32205	22	**3.1**	5.7	0.17	35.0	very good resistance to uniform and localized corrosion and stress corrosion cracking in combination with high mechanical strength,	Tanks in chemical tankers, Pulp and paper industry applications such as digesters and process tanks, Oil and gas industry applications such as flanges, valves, tubes, and pipes, Structural components in bridges
1.4410 / 2507/ S32750	25	**4**	7	0.27	42.5	corrosion resistance and mechanical strength,	Desalination plants, Industrial piping, Scrubbers, Tubes for oil and gas applications, Deep-sea pipelines, Flanges and valves

In steel production all Mo metal, ferromolybdenum or roasted Mo concentrate as well as steel scrap are used in the production process during melting. Table below shows the form of molybdenum used for certain steel and alloy applications.

Table 3.3. Form of molybdenum used as alloying element in stainless steels and other alloys [5,9,10]

Form of the element	Application in
Molybdenum oxide (reduced to Mo)	- water distribution systems, food handling and chemical processing equipment; at home, hospital and laboratory devices - automotive parts, construction equipment, and gas transmission pipes - superstrong steel in heavy construction (skyscrapers and bridges) – cheaper with Mo and the same - steels - in parts of engines, heating elements, drills and saw blades
Mo metal	Ti alloys
	Alloying element added to molten metal in steel and alloy production
	CoCrMo alloys for implants
Pure MoO_3	Al/Ti alloys
ferromolybdenum	Full alloy steel, stainless and heat-resisting steels, welding, Al/Ti alloys, High Speed Steels and Tool Steels, Low Alloys, Special Alloys, Stainless & Special Steels
Mo metal	in solid and powder forms - high speed steels, tool steels, dual phase steels, stainless and special steels, tool steels
Pure MoO_3	Steel alloy production
Roasted Mo concentrate	Al/Ti alloys, High Speed Steel and Tool Steel production, Low Alloys, special alloys, Tool steels and applications production, Stainless & Special steels, dual phase steels
Sodium molybdate	Al/Ti alloys

3.1.2.2 SUPERALLOYS

Molybdenum is also a component in high performance nickel-based superalloys that can be divided to:

- Corrosion-resistant alloys
- High temperature alloys – comprising of solid-solution strengthened and age-hardenable alloys.

Table 3.4. properties and appplicatins of molybdenum in different superalloys.

Application as	Property	Application in	Source
Alloying element in corrosion-resistant superalloys	- resistance to nonoxidizing environments (HCl, HBr, HF, H_2SO_4) - resistance (together only with Cr) to crevice and pitting corrosion - high melting point	highly corrosive environments in chemical processing, pharmaceutical, oil&gas, petrochemical and pollution control industries	[5]
high-temperature alloys solid-solution stregthened	- HT creep resistance due to slow diffusion of Mo in Ni which reduces creep rate - high melting point - reduce diffusivity of other elements, e.g. Ti and Cr in Ni22Cr2.8Ti3.1Al at 900°C – this influences stability of carbides and γ' phase	- as turbine engines for components such as turbine disks, combustors, transition ducts, turbine cases, seal rings, afterburners parts, and thrust reversers. They are also used in applications involving industrial heating, heat treating, mineral processing, heat exchangers, and waste incineration - seal rings in gas turbine engines (S	[5,11]

		alloy)	
high-temperature alloys age-hardenable	- HT creep resistance due to strengthening of matrix and reducing lattice mismatch between matrix and γ′ precipitate phase, preventing its coarsening or carbide formation [18] - Reduce thermal expansion coefficient - formation of ordered strengthening Ni2(Mo,Cr) phase with minor loss of ductility (in 242®™) - high melting point	- as turbine engines for components such as turbine disks, combustors, transition ducts, turbine cases, seal rings, afterburners parts, and thrust reversers. They are also used in applications involving industrial heating, heat treating, mineral processing, heat exchangers, and waste incineration - seal rings in gas turbine engines (242®™)	[5,12]

3.1.2.3 CHEMICAL APPLICATIONS

Molybdenum owes its application in chemical industries to the versatile properties such as:

- Wide range of oxidation states from (−II) to (VI);
- coordination numbers from 4 to 8;
- varied stereochemistry;
- the ability to form compounds with most inorganic and organic ligands, particularly with a preference for oxygen, sulfur, fluorine and chlorine donor atoms;
- forms bi- and polynuclear compounds containing bridging oxide or chloride ligands or molybdenum-molybdenum bonds.

Chemical applications – catalysts

Molybdenum-based catalysts belong to group of heterogeneous catalysts which in total account for 80 % of the global catalysts market [13]. The most of the molybdenum use in catalytic applications is in hydrotreatment reactions of petroleum, petrochemicals and coal-derived liquids. Hydrotretment reactions include hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO), hydrodemetalization (HDM) and are the earliest refining stages in processing of crude oil to remove poisonous sulfur, nitrogen, oxygen and particulate metals, respectively. The most important is the HDS reaction by which the emission of acid-rain precursor SO_2 during fuel combustion is reduced and also sulfur-poisoning of PtRe catalysts is avoided. The active catalyst is Mo disulfide promoted by Ni or Co and supported on γ-alumina. The catalyst precursor is most often γ-alumina impregnated with molybdenum oxide, ammonium heptamolybdate or ammonium dimolybdate and nickel or cobalt(II) nitrate as a promoter procursor [5,9,10,13].

Other molybdenum-based compounds are important catalysts in selective oxidation reactions of methanol, propene or acrolein.

Property/ reaction	**Application for/as**	**Form of the element**	**Application in**	**Source**
Remove sulfur	Hydrotreating	sulfided/used CoO(2–	Oil and petroleum	[5,9,10,

from crude petroleum		5%)MoO_3(10–20%)P(0–2%)/Al_2O_3; NiO(2–6%)MoO_3(6–20%)P(0–2%)/Al_2O_3, Ammonium Di- and heptamolybdate Co-Mo or Ni-Mo on alumina	refining	13]
-	Catalyst production	Iron molybdate, MoO_2, Pure MoO_3,	Catalyst production	[9]
-		sodium molybdate	catalysts for the petroleum industry	[9]
-		Roasted Mo concentrates	Catalyst production	[9]
-		Sodium molybdate	Catalyst production	[9]
Synthesis acrolein, acrylonitrile	Propene selective oxidation, ammoxiation	Bi-Mo oxides: $Bi_2(MoO_4)_3$ [Bi_2MoO_6 + Support(e.g., SiO_2) + Promoters(e.g., Me(II)8=Ni, Co, Mn, or Mg; Me(III)3=Fe, Cr, or Al)]	Making polymers and plastics	[5,9,10, 13]
Synthesis acrylic acid	Acrolein oxidation	Mo-V oxides	Making polymers and plastics	[5,9,10]
Synthesis formaldehyde	Methanol oxidation	Fe-Mo oxides $Fe_2(MoO_4)_3$	Making formalin, polymers, resins	[5,9,10]
Propene to ethene and butene	Olefin metathesis	Mo oxide on alumina,	Olefin synthesis	[5,9,10]
Olefin to epoxide	Epoxidation	Mo complexes	Polyether synthesis	[5,9,10]
Propene to alcohol	Propene hydration	Heteropolyacids-phosphomolybdate	Alcohols synthesis	[5,9,10]

Chemical applications – lubricants

Form of the element	Application in	Source
MoS_2	lubricant additive for ball and roller bearings, automotive, metalworking, extrusion, cold working, gears; aircraft, automotive and rail brake pads,linings	[5,9,10]
Ammonium dimolybdate	Industrial formulation of lubricant additives, lubricants and greases General use of lubricants and greases in vehicles or machinery. Includes filling and draining of containers and enclosed machinery (including engines). Application of lubricant to open work pieces or equipment by dipping, brushing or spraying (without exposure to heat), e.g. mould releases, corrosion protection, slideways & chains.	[5,9,10]

Chemical applications – pigments

Molybdenum is used as a pigment for the red-yellow to bright reddish-orange color in paints, inks, plastics and rubber materials but also as anticorrosion pigment. The element is used in the form of roasted molybdenum concentrate, sodium molybdate, molybdenum dioxide, MoO_3, ammonium octamolybdate, Ammonium dimolybdate [14].

Chemical applications – corrosion inhibitor

Mo metal, roasted Mo concentrate, ammonium dimolybdate and sodium molybdate are used in the production processes for corrosion inhibitors in lighting, electronics, and specialty steel alloys, but also in aerospace Industry for forging dies, propulsion nozzles.

Chemical applications – smoke suppressants and flame retardants

Flame supressant production requires molubdenum in the form of pure MoO_3, roasted Mo concentrate, ammonium hepta- and octamolybdate.

3.1.2.4 OTHER APPLICATIONS

Other applications include nutrients in fertilizers and in feed additives, surface treatment products for metal surfaces and detergents. Molybdenum is used there as ammonium dimolybdate, ammonium heptamolybdate, sodium molybdate, MoO_3 [9].

3.2 THE SUPPLY CHAIN OF MOLYBDENUM

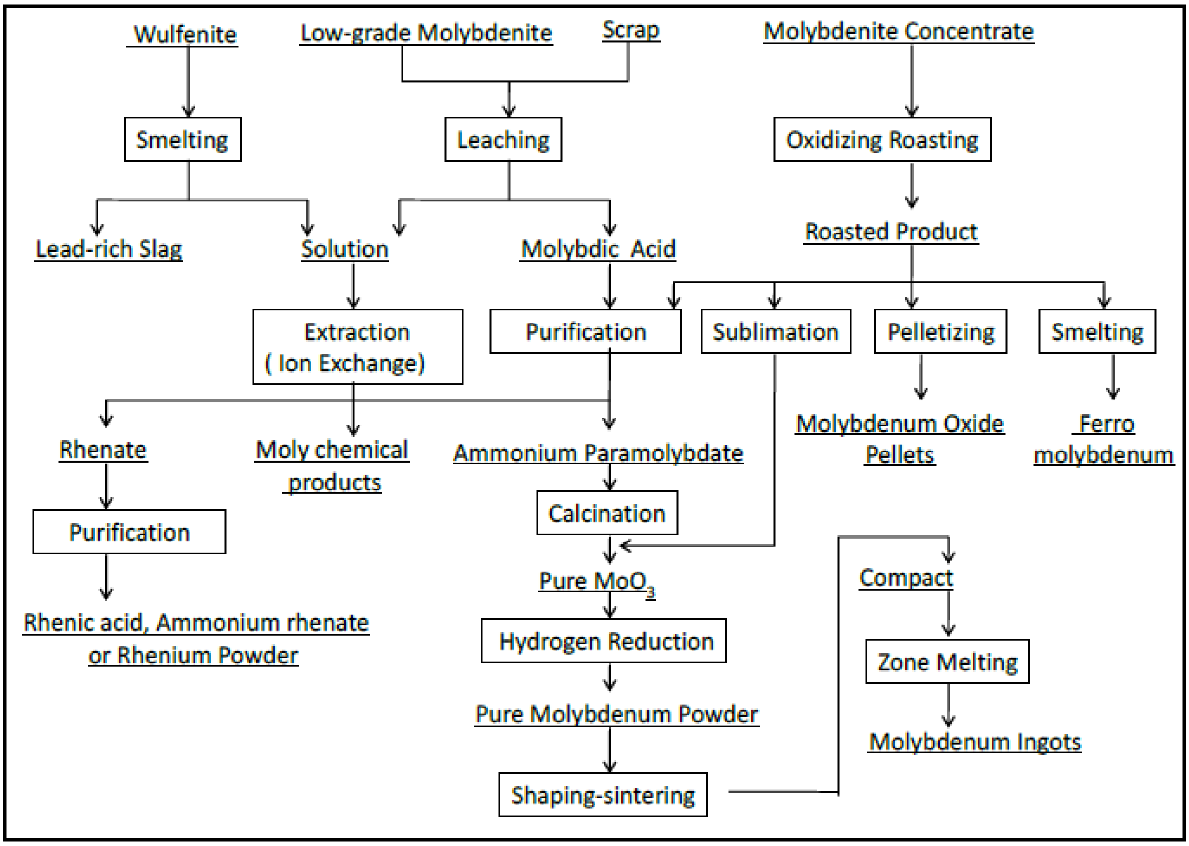


Fig. 2. Molybdenum flowchart [15]

3.2.1 THE SUPPLY CHAIN

World production of molybdenum is mostly occurring in China and USA. There are two minor European (partially) producers of molybdenum – Norway and Turkey, however the total production there is well below 1 % per year.

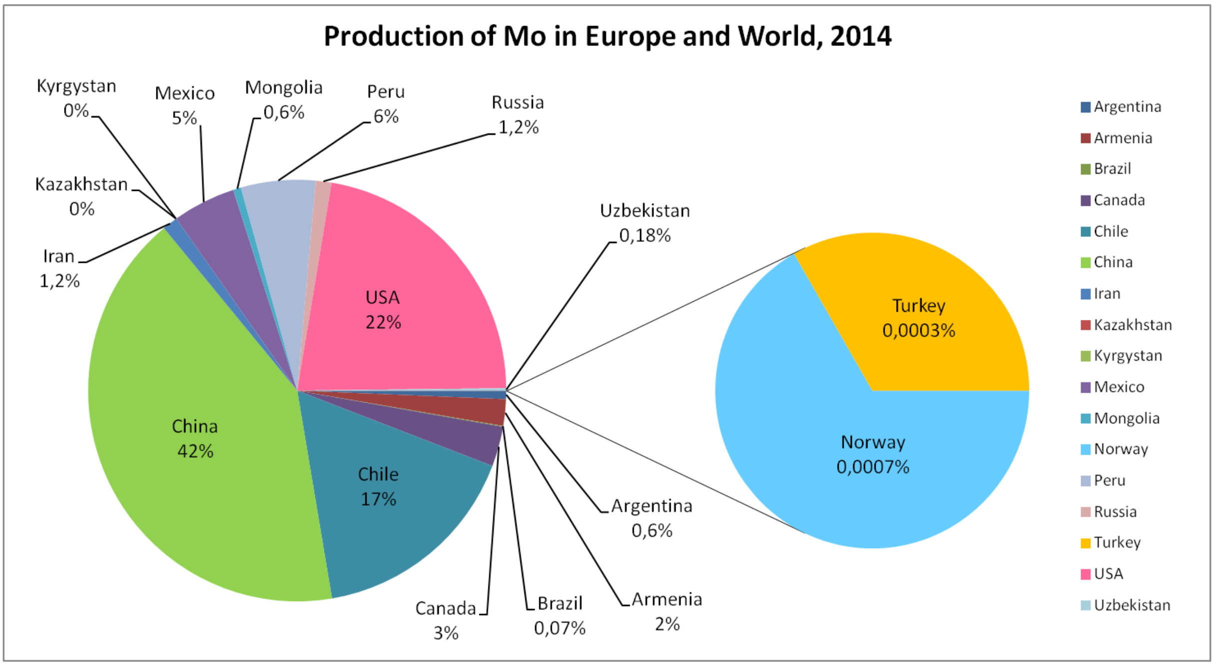


Fig. 3. Production of molybdenum in 2014. In addition to the countries listed, Australia, Georgia, India, Democratic P.R. of Korea, Romania, Tajikistan and Uzbekistan are believed to produce molybdenum (1992 Onwards) [16,17]

Data indicates that an increase in molybdenum production has occured since 2004. This is related to industrial growth in China.

Fig. 4. Mo mine production between 2004-2014 in tons [16,17].

However in last three years the molybdenum production is stabilizing, with a slowdown rather than small increase. Simultaneously the molybdenum world consumption has lowered in 2015 with respect to 2014 and recent years.

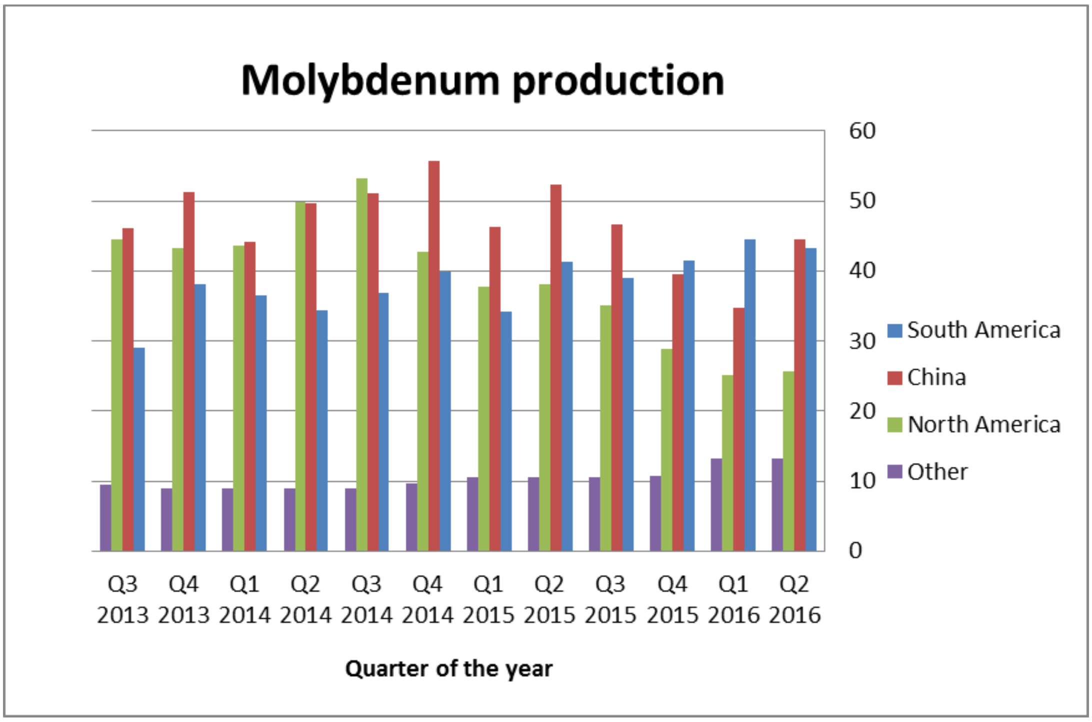


Fig. 5. Molybdenum production in different regions, in million lbs [18].

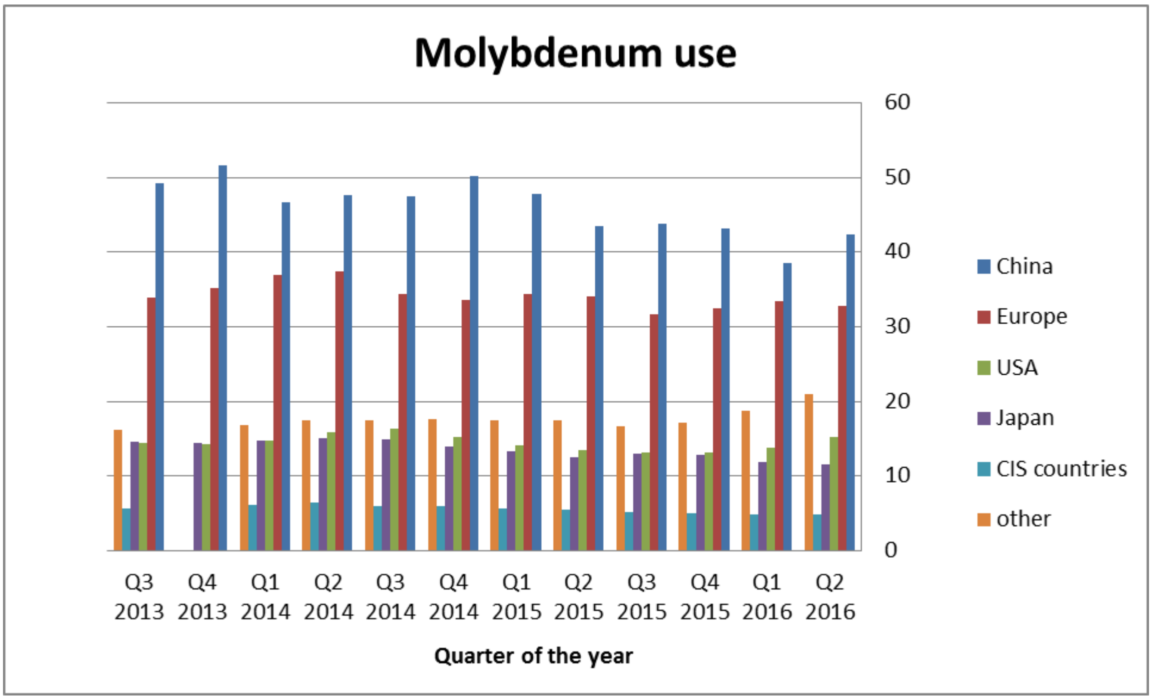


Fig. 6. Molybdenum total use in different regions [18].

3.3 POTENTIAL SUBSTITUTES OF MOLYBDENUM

3.3.1 STEELS, SUPERALLOYS & OTHER ALLOYS

3.3.1.1 STAINLESS STEELS

Main beneficial molybdenum function in stainless steels is enhancing the corrosion resistance resulting from chromium alloying element. The passivating chromium-based layer is strengthened by molybdenum and easily reforemed in chloride environment.

In steels several corrosion types influence largely the choice of certain grade. The most characteristic in stainless steels are localized corrosion such as pitting and crevice corrosion, environmental cracking – stress corrosion cracking (SCC), high temperature corrosion. Molybdenum imparts higher corrosion resistance in many harsh environments including

Molybdenum content lowers pitting and crevice corrosion in a most effective and economic way. A measure of this resistance, given by the PRE number, is a rough estimation of the behaviour of a certain grade, without consideration of specific environment. Many steel grades are equivalent in terms of PREN for different chemical composition (different Mo content). This is illustrated by the graph below for PREN typically calulated as follows PREN = %Cr + 3.3*%Mo + 16*%N [5].

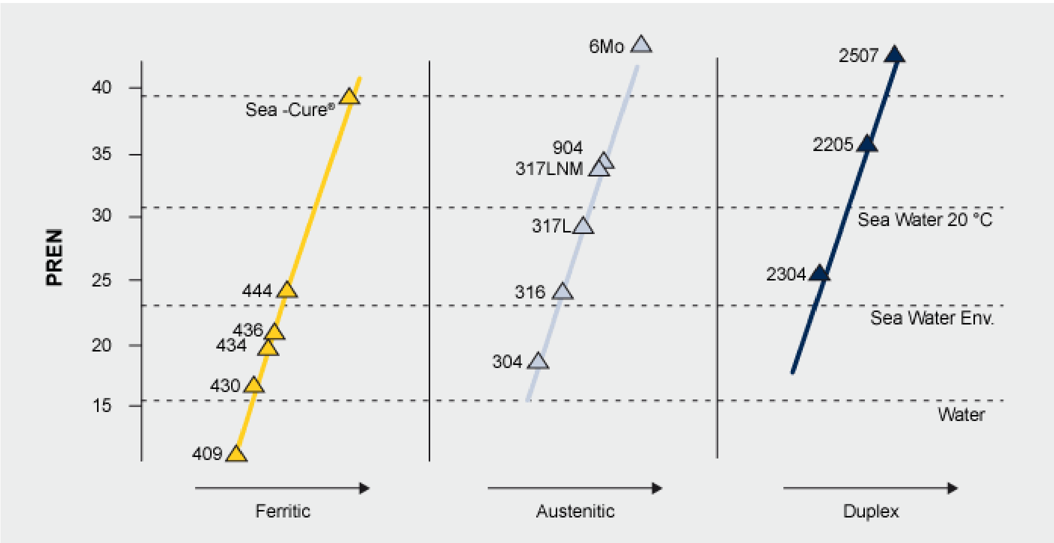


Fig. 7. PREN in various stainless steel grades [6].

The graph indicates (in comparison with table 3.2) that for a certain corrosion resistance one can choose between many steel grades. Of course the pitting corrosion may differ in environments of different harshness (sulfide, sulphate, chloride). The substitution potential of molybdenum in steels is related mainly to switching between hundreds of different steel grades.

A list of potential substitution for molybdenum in steels and alloys is given in the table below.

Table 4. Potential substitutes for molybdenum in steel and alloy applications, their advantages and drawbacks [10,11,19-22].

Application	Potential substitute	Type	Advantages	Drawbacks
Stainless steel grade 316	Grade 445M2 (higher Cr content)	Product by product	No Ni addition, smaller, decrease from 2.2 to 1.2 % Mo, better pitting corrosion resistance	Higher use of Cr
Alloy steels	B, Cr, Nb, V	-	-	-
Tool Steels	W	-	-	-
refractory materials in high-temperature electric furnaces	graphite, Ta, W	-	-	W (CRM)
refractory properties	Nb	-	-	Nb (CRM)
material strengthening	Nb	-	- Lower and stable prices - Nb is the lightest of the refractory metals - Nb is unique in that it can be worked through annealing to achieve a wide range of strength and elasticity	Nb (CRM)
Superalloys	W-alloyed Ni- and Co-based super-alloys	-	HT strength and creep strength, high thermal fatigue resistance, good oxidation resistance, excellent hot corrosion resistance, air melting capability, air or argon re-melting capability and good welding properties	W (like Mo) can form detrimental carbides and tcp phases, density increase [11]

3.3.2 CHEMICAL APPLICATIONS

3.3.2.1 CATALYSTS

UAODS – sulphur from thiophenes is oxidized to sulfoxides and sulfones.Instead of hydrogenating agent (H2) in HDS, and oxidizing agent H_2O_2 is used in UAODS. The polar products can be then separated by decantation or extraction. The same process – patented BHUT – Barbell Horn Ultrasonic Technology.

3.3.2.2 PIGMENTS

In pigments a possible substitution by harmful toxis substances based on chromium and cadmium are questionable alternative.

Table 3.5. Potential substitutes for molybdenum in chemical applications, their advantages and drawbacks [19-21,23-27].

Application	Potential substitute	Type	Advantages	Drawbacks
Catalysts in HDS	Depending on application for HDS	product by	-	-

	and nature of the feed– Ru, Ni, Co and W	product		
Catalysts in HDS [10, 11]	NEBULA (Ni-Mo-W-based trimetallic catalyst) Mo in ammmonium nickel tungsten molybdate form	-	higher activity than known hydrotreating catalysts	-
Catalysts in HDS [12-16]	alternative process UAODS (Ultrasonically Assisted Oxidative Desulfurization), BHUT	process by process	process conducted at lower temperature and pressure, H2 not required, lower costs, time-saving, scalable	suitable for small or medium-sized refineries, alone may not be sufficient for desulfurization
Catalysts in HDS [17]	Palladium nanoparticle complexes from [(PEt3)2PdCl2], [(PPh3)2PdCl2], [(dippe)PdCl2], [(dppe)PdCl2] +MeMgBr in toluene	process by process	-	under study
Pigments	Cadmium -red, chrome-orange, and organic -orange pigments for molybdenum orange	-	-	Cadmium – toxic, chrome - toxic

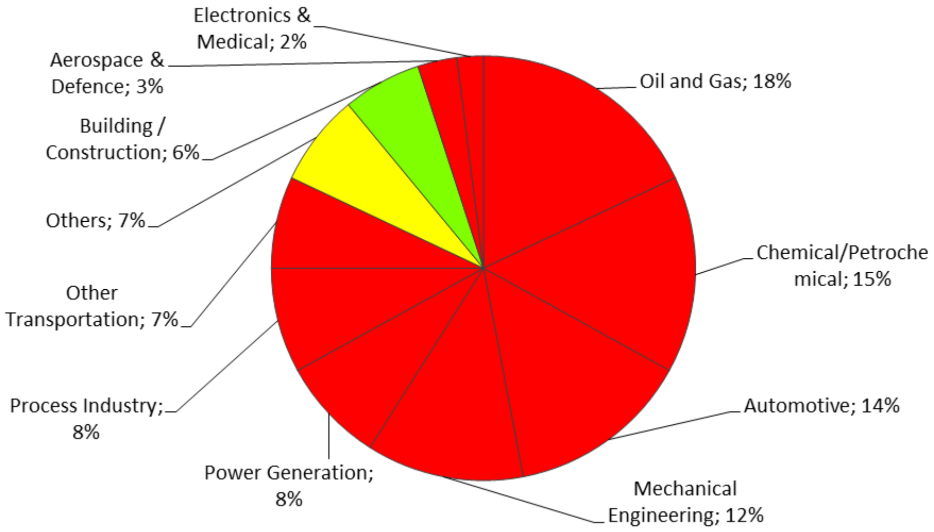
3.3.3 EVALUATION OF SUBSTITUTION POTENTIAL OF MOLYBDENUM

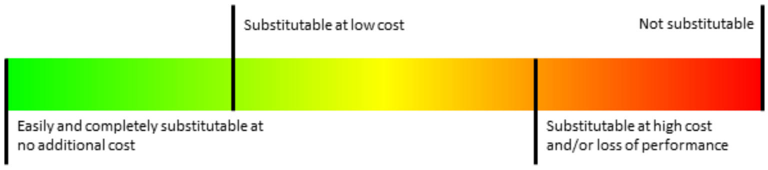
The substitutability of molybdenum in present applications is rather low, with a high substitutability index. The reason for it may be that most of the alternative applications are closely related with a loss of performance, increase of cost and harmfulness of possible substitute.

Table 3.6. Substitutability of molydbenym given by appplication [28].

Application	Share	Megasector	Substitutability index
Oil and Gas	18%	Oil	1.0
Chemical/Petrochemical	15%	Chemicals	1.0
Automotive	14%	Transport-Road	1.0
Mechanical Engineering	12%	MechEquip	1.0
Power Generation	8%	Electrical	1.0
Process Industry	8%	MechEquip	1.0
Other Transportation	7%	Transport-Other	1.0
Others	7%	Other	0.5
Building / Construction	6%	Construction	0.3
Aerospace & Defence	3%	Transport-Other	1.0
Electronics & Medical	2%	Electronics	1.0

The data is visualized in the following graph.





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CHAPTER 4. NIOBIUM

4.1 NIOBIUM: PROPERTIES, APPLICATIONS & PRODUCTION

4.1.1 PROPERTIES OF NIOBIUM

Niobium is a soft greyish-silvery metal that resembles fresh-cut steel. It neither tarnishes nor oxidize 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. [1]

Figure 1 : Niobium metal[2]

Niobium is used in the industry in a variety of forms. Even though niobium metal and its powder version are sometimes used, they are mostly used in other forms depending upon the application. Some of the important forms of niobium are:

- Niobium pentoxide (Nb_2O_5) – This is a colourless and unreactive solid. Different varieties of high purity (>99%) are produced. They are usually used as the starting point for production of other niobium compounds like niobium chloride ($NbCl_5$), niobium carbide (NbC) and lithium niobate ($LiNbO_3$).
- Niobium carbide (NbC) – It is a heavy, brown-grey metallic powder containing around 87% niobium.
- Ferro-niobium (FeNb) - This is an alloy of iron and niobium with about 60-70% of niobium. It is one of the most significants forms of niobium is involved in the steel industry. [3]

Other alloyed version of niobium, with aluminium and tin are used in the field of superconductors. Table 2 gives a comprehensive list of the various forms of niobium, along with their unique properties and applications.

4.1.2 APPLICATIONS OF NIOBIUM

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. To further explain the applications of niobium, this section would be divided into two. They are:

- Use of niobium in HSLA steel in automobile, energy and construction industries.
- Use of niobium and its compounds/alloys in superconductors and other industries.

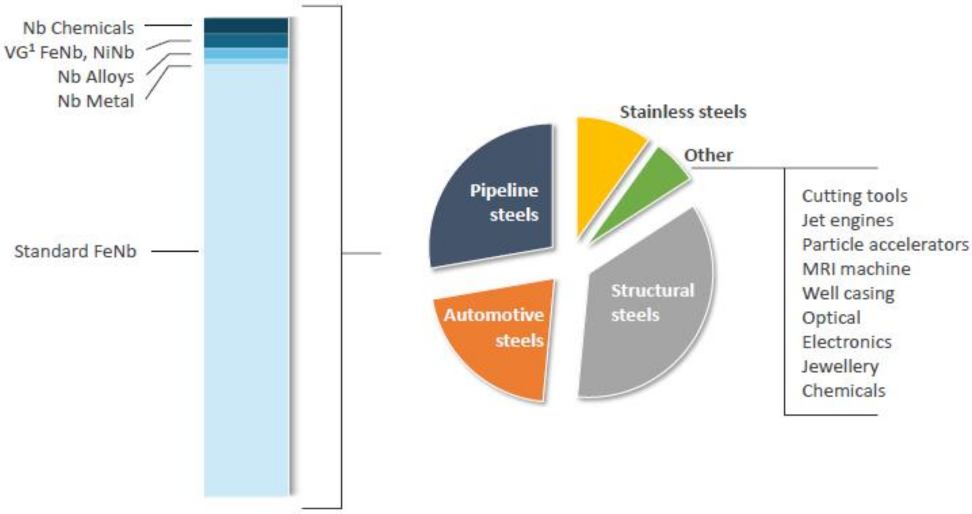

Figure 2 : Niobium Products & Uses (1 = Vacuum Grade)[4]

The earliest information about the use of niobium dates to 1925 when it was used to replace tungsten in tool steel production. [5] Niobium was first applied as a material in the industry in 1933 to stabilize stainless steels against inter-granular corrosion. In early 1960s, researches showed that niobium contains micro-alloying properties that promote significant improvements in corrosion resistance of steels. To summarise, niobium, a grain refiner and precipitation hardener, enhances the steels' mechanical strength, toughness, high-temperature strength, and corrosion resistance. [6] This makes niobium pivotal to the automotive, construction and energy industries.

- **<u>Automotive industry</u>**: Increased employment of niobium has led to a series of innovations in the manufacturing of parts requiring several types of steels, for example, HSLA steels. The manufacture of parts from use of HSLA steels help to reduce fuel consumption, reduce CO_2 emissions and increase passenger safety. 30 to 40% of the steel mass of a modern car consists of HSLA steels, the aim of which is to reduce the total mass using the higher strength of HSLA steels in comparison to niobium-free mild steels [7]. CBMM (Companhia Brasileira de Metalurgia e Mineração, Brazil) estimates that a mere 300 grams of niobium in the steel of a mid-size car reduces its weight by 200 kilograms, which results in fuel economy of one litre per 200 kilometres and therefore much lower emissions [8]. Therefore, in view the increased production of cars worldwide, the demand for niobium in the automotive industry is expected to grow significantly in the coming years. [9]

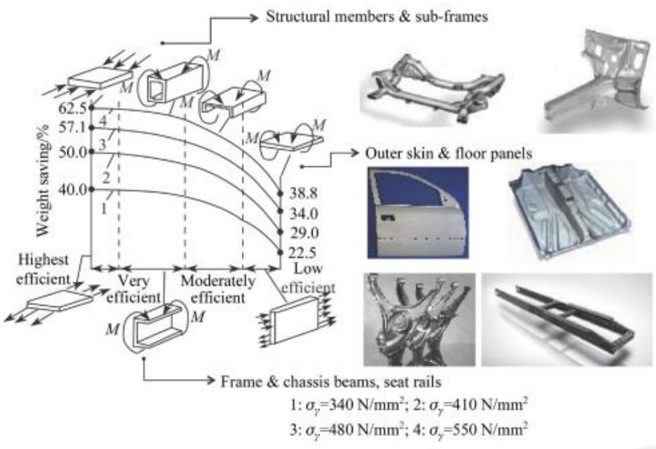

Figure 3 : Weight saving potential by substituting 200 MPa steel with high strength steels[10]

- **Construction industry**: Niobium micro-alloying increases steel strength and toughness simultaneously, which is the key to meeting the challenges of modern construction, especially regarding seismic requirements and fire resistance. For example, niobium is used alone or in combination with other micro-alloying elements in the production of numerous structural steel grades such as ASTM A992 beam, ASTM A572 high strength construction plate steels and ASTM 706 high strength reinforcing bars. Two such examples involve low carbon high strength niobium structural beams with superior toughness replacing V-bearing high carbon steels and the developing application of seismic and fire resistant steel varieties. Leaner structures are environmentally friendly structures since they consume fewer resources [11]. In addition to strength and toughness, excellent weldability and formability are additional characteristics of niobium steels that make them ideal for other structural applications like wind towers, ship building, train rails and wheels, energy transmission towers, construction beams and offshore drilling platforms. Niobium steels have better performance under mechanical fatigue, as required in these structures. On the other hand, the demand of the construction industry will continue to be increasingly growing due to urbanization, population growth and replacement of very old infrastructure, so the need for lighter structures result in greater use of high quality steel containing niobium. [9] [12]

- **Energy industry**: In the energy sector, there is a forecast for strong growth in production and consumption of natural gas (NG) by the year 2035. For example, an increase around 20% in OECD countries (The Organisation for Economic Co-operation and Development) and up to 68% in non-OECD countries according to the information from the EIA (US Energy Information Administration). The usage of niobium in the energy sector can be divided into two:
    - Carbon-based non-renewable sources of energy
    - Renewable or unconventional sources of energy

  For the non-renewable sources of energy, the increase in production of niobium will be directly linked to the growth in demand for HSLA steel, depending on the need of transporting over long distances at high pressure, which would require steel tubes with increased mechanical strength and with this will increase the use of niobium in energy production. In the petroleum industry, the use of HSLA steel is higher, especially in offshore drilling platforms which need to withstand the harshest conditions. In short, niobium steels increase pipeline performance and project safety, all at reduced costs. While there is no pipeline steel with less than 0.035% niobium in its composition, the most modern and efficient pipelines are built with stronger steels containing up to 0.11% niobium. [9] [13]

  In the realm of renewable sources of energy, the steel industry has an important role to play. Wind energy is a good example. Wind turbines depend on iron and steel heavily. Like in other market sectors such as automotive, oil and gas pipeline systems, the use of higher strength steels (>355MPa Yield Strength) can lead to several advantages resulting in significant cost savings. The higher strength of the steel would allow a reduction in the tower shell thickness, leading directly to lower material, fabrication and welding costs, as well as reduced transportation costs. Recent studies have investigated the use of high strength steels (> 690MPa YS) for the tower application and found that such steels can be applied to wind towers, and for the lower section of the tower. This could lead to a reduction of nearly 65% of the original shell thickness. However, it should be noted that while the use of higher strength steels for the lower tower section is feasible, construction of the entire tower with S690 steels would also lead to a reduction in the dead weight of the tower and consequently the Eigen frequency of the tower (i.e., the normal modes at which the tower will vibrate). Those plates produced via the TMCP (thermo-mechanically controlled process) route afford excellent weldability, low temperature toughness produced via a cost-effective steel chemistry design and process route. In developing nations, such as India with the potential of an additional 14,000 wind tower units alone, the opportunity to use higher strength S460 Nb-microalloyed steel plates would lead to a 20% reduction in plate thickness and result in significant savings in the total tower construction weight and cost. Further savings could also be made by small additions of Nb to develop higher strength rebar (>450MPa YS) possessing good bendability and weldability for use in the tower foundation structure. [14]

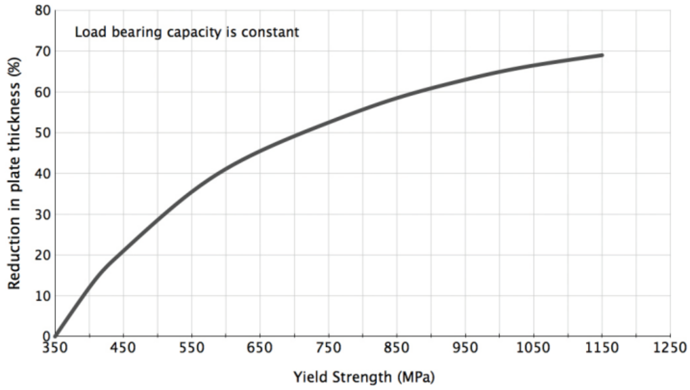

Figure 4 : Weight savings when moving to higher strength steel [14]

Solar energy is another renewable source of energy that has been gathering interest over the past decade. Niobium as a micro-alloying element can play a role in solar thermal energy. Solar water heaters are an effective way of utilizing the energy we receive from the sun. The tanks used to store the water heated by solar radiation, especially its inner part, demands high corrosion resistance. The ferritic stainless steel (304 SS) traditionally used for this purpose suffers from vulnerability to corrosion. It is susceptible to local corrosion, stress corrosion, pitting corrosion and inter-granular corrosion depending on the environment. The mjor culprits among these are the inter-granular corrosion and pitting corrosion. Steels alloyed with Nb, Ti or similar elements show a decreased sensitivity to these modes of corrosion. Addition of Nb and Ti can realise complete stabilization and prevent the harmful influence of single stabilization. The specially developed Nb-alloyed 445 variety of stainless steel is an example used for this purpose. It also boasts of increased pitting corrosion resistance. [15]

Steel-making is the world's most carbon-intensive industry, emitting 2.5 Gigatonnes of carbon dioxide annually. The above-mentioned advantages offered by niobium micro-alloying can also decrease steel production which would lead to a decrease in carbon dioxide emission. [16]

Stainless steel that has been combined with niobium is less likely to break down under very high temperatures. Hence, it is used in the production of **superalloys** which are used at high temperatures, for example in the aerospace use that are present in the manufacture of turbine components. There are different varieties of superalloys used in a variety of high temperature or corrosive environments, the single most important member being Inconel 718. This is a nickel-based alloy containing 5.3-5.5 wt % niobium. Alloy 718 was initially developed as a disk material for aircraft gas turbines but its uses have expanded over the years to include other engine parts such as bolts, fasteners and rotor shafts. Further uses for this remarkable alloy have also been found in other industries such as nuclear, cryogenics and petrochemicals. They also find use in land based turbines [17]. Other industrially important nickel-based alloys containing niobium are Inconel 706 (3 wt.-% Nb) and Inconel 625 (3.5 wt.-% Nb). The most common jet engine in service today, the CFM56 made by the GE/Snecma joint venture, contains about 300 kilos of niobium. [18]

IN718 –type alloys	Niobium composition (Wt %)
IN718 - 1	5.26
IN718 – 4	5.28
IN718 – 9	4.32
IN718 – 10	4.91
IN718 – 11	5.42
IN718 – 12	5.72
IN718 – 13	5.38
IN718 - 14	5.66

Table 1 : Niobium composition of the IN718-type alloys [19]

High purity niobium oxide is being used in the manufacture of **fine ceramics**. These materials have functional and structural (engineering) applications. The former category includes ceramic capacitors for electronics and optical lenses. The latter group consists of heat resistant and abrasion resistant materials, tools, engine parts and other structural articles. [18]

Niobium can ensure very cold temperatures, which improves its ability to conduct electricity. This characteristic makes it a suitable metal for low temperature electrical **superconductors**. Niobium alloyed with germanium becomes a superconductor of electricity that does not lose its superconductivity at 23.2K as large amounts of electrical current pass through it, as do some other superconductive alloys. In the pure metallic state, niobium wires are also superconductors when the temperatures are reduced to near absolute zero (–273°C). [10] Since the 1960s, Nb–Ti (superconducting transition temperature T_c = 9 K) and Nb_3Sn (T_c = 18 K) have been the materials of choice for most superconducting magnets and they have opened the field for research into High temperature superconducting materials. The market has for years consisted of magnetic resonance imaging (MRI) and nuclear magnetic resonance (NMR), and magnets for high-energy physics accelerators and plasma fusion devices, together with smaller niches for research magnets [20]. In the medical field, the use of niobium is growing and evolving, like in **magnetic resonance imaging** (MRI), which is a diagnostic tool, whose use has increased significantly over the past three decades. In addition, niobium alloys are physiologically inert and thus hypoallergenic. Thus, they are used in **orthopaedic implants** [21] and **pacemakers** [22] by the addition of other bio compatibles metals.

There are other developing niche uses of niobium. Niobium can be electrically heated and anodized, which can lead to the incorporation of a wide array of colours using reactive metal anodizing. This is useful in making **jewellery**[23]. Niobium also finds use in **coin minting industry**. It is used as a precious metal in commemorative coins, with silver or gold [24]. In the field of electronics and nanotechnology, niobium and tantalum in powders are used in industry as **nanostructured materials**, due to its characteristic of high purity, as small amounts of contaminants oxygen and metals low density. For example, they find use in microelectronic and plasmo-chemical applications. [9] [25] Niobium can also play a role in the advent of **quantum computing**. In 2007, the Canadian company D-Wave showed the Orion computer based on a silicon chip, which is formed by portion of niobium, surrounded by a coil. When the coil is electrically stimulated, it generates a magnetic field that causes changes in the state of niobium atoms. These state changes are captured and processed by the circuits and transformed into data. For all this to work, the quantum chip needs to be frozen to 4mK. This is done by means of a cooling system with liquid helium and becomes low temperature superconducting niobium [10]. Lithium niobate, which is a ferroelectric, is used extensively in mobile telephones and optical modulators, and for the manufacture of surface acoustic wave devices [26]. The following table describes the different forms of niobium and its end uses.

Niobium Forms	Principal Properties	Applications	Market Share
Oxide	High index of refraction High dielectric constant Increase light transmittance	Camera lenses, Glass coating for computer screens, Ceramic capacitors	8%
Carbide	High temperature deformation and controls grain growth	Cutting tools, Railway tracks and ship hulls	
Nitride	Superconductivity	Superconducting magnets for MRIs etc.	
Powder	High dielectric constant, stability of oxide dielectric	Nb capacitors for electronic circuits	
Metal	Corrosion resistance	Chemical processing Equipment	5%
Alloys (with Ti and Sn)	Zero electrical resistance of alloy wire at low temperature	Superconducting magnetic coils in MRI, NMR, particle accelerators and magnetic levitation transport system	
Alloys (with Zirconium) 1. 1% 2. 2.5%	1. Corrosion and embrittlement resistance, fixation of oxygen 2. Permits thinner wall sections for neutron absorption	1. High – intensity sodium vapour lamps 2. Heavy water nuclear reactors	
Vacuum grade FerroNiobium and Nickel-niobium (Inconel family) superalloys	Increased high temperature, corrosion, oxidation, creep and erosion resistance.	Aircraft gas turbine engines, rocket thruster nozzles, turbines for electricity generation	
FerroNiobium (60% Nb)	Weight reduction Increased strength and toughness due to grain refining	Additive to HSLA & stainless steel	HSLA steels: • Construction: 29% • Automotive: 24% • Energy: 24% Stainless Steel – 10%
Niobium in cast iron	Good wear resistance Formation of very hard carbides	Automobile components	
Niobium in steel castings	High strength and toughness	Ingot moulds, Slag pots, Nodes for off-shore platforms	
Lithium niobate	Optical, pyroelectric and piezoelectric properties	Electronic components like Surface Acoustic Wave (SAW) filters and capacitors used in mobile phones, motion detectors and touch screen technologies	
Niobium mill products	Increased resistance towards corrosion, high temperature, oxidation and creep	Sputtering targets, Cathode protection, Chemical processing equipment	

Table 2 : Forms of niobium and its end uses[9][3][27][18]

Niobium may also be used in carbon sequestration, geothermal energy, nuclear fission and advanced fossil fuel power. Niobium micro-alloyed steels with its superior properties are used for structural and other purposes.

Carbon capture and storage (CCS) technologies can be applied to energy production wherever carbon dioxide (CO_2) is produced in large quantities, including during power generation. By implementing CCS, electricity could be made from fossil fuels with near zero emissions. CCS can capture at least 90% of CO_2 emissions from power plants and heavy industry before transporting it by pipeline or ship and storing it. The three distinct stages of CCS are:

- Capture and isolation of CO_2 emitted from fossil fuel combustion.
- Transport of the captured CO_2 from the plant to long term storage.
- Long term storage of CO_2

The materials used include high specification steel alloys to upgrade existing generators and for the construction of the pipelines. However, metals demand is not directly related to capacity, as it also depends upon the length of pipeline constructed. As discussed above, niobium directly features in the production of steels with higher strength and durability and hence it can help CCS implementation. Nuclear and geothermal energy sectors involve harsh operating conditions and steels with higher mechanical strength and high temperature durability are required in reactor vessels to resist irradiation and temperature embrittlement, thermal ageing and corrosion. Thus, these energy sectors could also benefit from steels micro-alloyed with niobium. [28]

Cumulative steel demand arising from CCS Pipeline

	Demo Plants	Pipeline (km)	Commercial Plants	Pipeline (km)	Total Pipeline (km)	Steel (tonnes)
2020	12	3,600	18	9,000	12,600	4,939,200
2030	12	3,600	89	44,500	48,100	18,855,200

EC JRC/SETIS (2011), Critical Metals in Strategic Energy Technologies

Predicted steel grades used in CCS implementation

Composition	C	Mn	P	S	Si	Cr	Ni	Cu	V	Nb	Mo	Co
API X65	0.07	1.5	0.009	0.004	0.093	0.13	0.16	0.11	0.04	0.04	0.003	0.003
API X100	0.07	1.9	0.008	0.005	0.1	0	0.5	0.3	0	0	0	0

EC JRC/SETIS (2011), Critical Metals in Strategic Energy Technologies

Table 3 : Steel demand and Steel grade information for CCS[29]

Another interesting indirect use of niobium in the energy sector involves solid niobic acid that catalyses the conversion of palm oil to bio-diesel fuel [30]. It paves the path for research into **heterogeneous catalysts**.

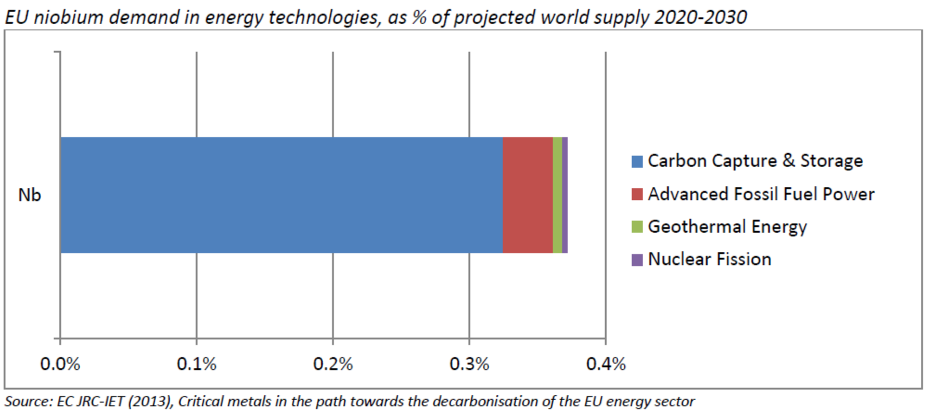

Figure 5 : Niobium demand in decarbonization of EU

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4.2 THE SUPPLY CHAIN OF NIOBIUM

4.2.1 PRODUCTION OF NIOBIUM

Niobium is the 33rd most abundant element in the Earth's crust. It does not exist as a free elemental metal in nature. There are 49 isotopes of niobium, ranging from Nb-81 to Nb-113. Except niobium-93, which is stable and makes up all the element's natural existence in the Earth's crust, all the other isotopes are radioactive. The abundance of niobium in the Earth's average continental crust is 8 ppm [1][2]. Some sources also mention the abundance as 24 ppm [3]. It is found primarily in several mineral ores known as columbite (Fe, Mn, Mg, and Nb with Ta) and pyrochlore [$(Ca, Na)_2Nb_2O_6$ (O, OH, F)]. These ores are found in Brazil and Canada (accounting for 90 % and 7.5% of the global supply respectively). Niobium and tantalum [$(Fe, Mn)(Ta, Nb)_2O_6$] are also products from tin mines in Malaysia and Nigeria.

Brazil is the world's largest supplier of niobium. The largest currently worked niobium deposit is owned and operated by Companhia Brasileira de Metalurgia e Mineração(CBMM) at Araxá, Brazil. A second major deposit is operated by Anglo American plc at Catalão. Pyrochlore is the main niobium ore mineral in both these deposits. The largest active niobium outside Brazil is the Niobec mine in Quebec, Canada, which is operated by the Iamgold Corporation. This is the only underground niobium mine in the world. As in Brazil, Pyrochlore is the main niobium mineral ore. There are other niobium deposits around the world like the Tomtor deposit in Siberia, Russia and the Morro dos Seis Lagos deposit in Brazil. These are not currently being exploited. The Morro dos Seis Lagos deposit is poorly known and is thought to represent the largest single niobium deposit in the world with 2897 million tonnes of niobium. Other smaller deposits include Lueshe (Democratic Republic of Congo), Oka (Quebec, Canada) and Sokli, Finland. The Bayan Obo rare earth element deposit in China is also enriched in niobium ore. The Motzfeldt deposit in Greenland is also an area of interest. The figure below shows the major niobium and tantalum mines, deposits and occurrences [1].

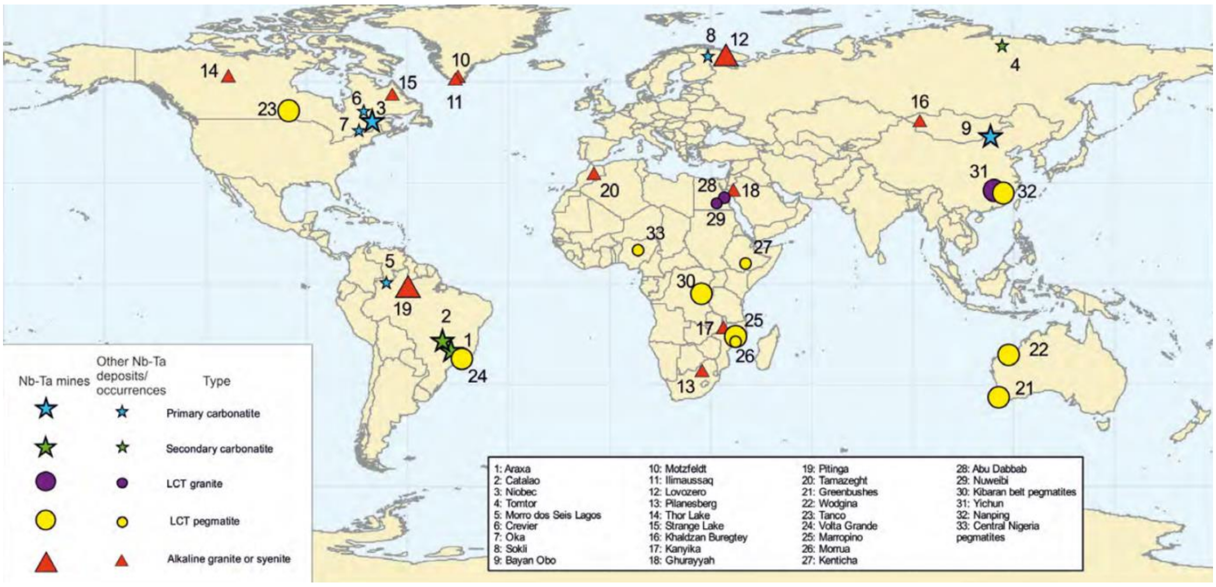


Figure 1 : The global reserve map for niobium and tantalum[1]

Brazil has the world's largest reserves of Nb (98.53%), followed by Canada (1.01%) and Australia (0.46%). Niobium principally was imported in the form of ferroniobium and niobium unwrought metal, alloy, and powder. Brazil was the world's leading niobium producer with 90% of global production, followed by Canada with 9% [4]. Brazil exported about 5,000 to 7,000 tons of ferroniobium per month, distributed among China, Europe, and the United States per 2016 Niobium Statistics and Information by the U.S Geological Survey. [5]

Country/Region	Production 2014	Production 2015
Brazil	50000	50000
Canada	5480	5000
Others	420	1000
World total (rounded)	55900	56000

Table 1 : World mine production of niobium in tonnes[5]

Country	Reserves (10^3 tonnes)
Brazil	4133
Canada	61
Others Countries	21
Total	4215

Table 2 : Profile of the mineable reserves of niobium by countries[4]

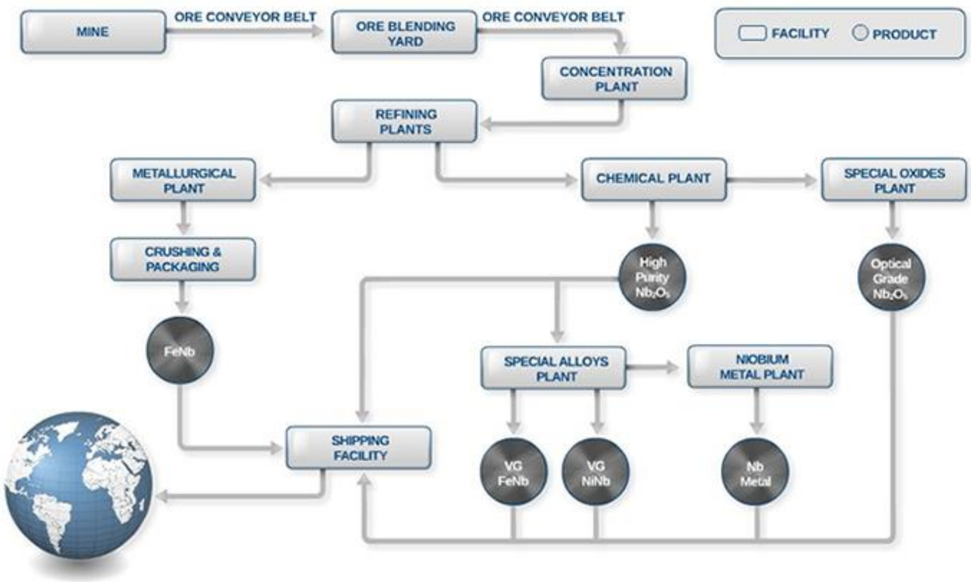


Figure 2 : Niobium manufacturing flow-chart[6]

The above figure shows niobium manufacturing flow chart from the CBMM website.

4.2.2 CONSUMPTION OF NIOBIUM

The demand of niobium in steel has been increasing for two main reasons:

- **The global economic growth** – The fast-paced growth of the world economy has sparked a need for advanced high strength materials in industries like construction, energy and aerospace, which has necessitated a higher involvement of niobium in the market. For example, in the aerospace industry, the demand of superalloys has grown over the years.
- **Increased usage of niobium in steel** – The largest consumer of niobium is steel and hence, the need for high strength steel grades has resulted in an increase in the consumption of niobium. Conventional carbon-manganese or mild steel grades are being replaced with higher HSLA grades (niobium-containing steel), requiring less steel for the same application.

FeNb demand growth picked up, with over 7% year-on-year growth. The demand almost reached the 2007 historic high of 84,000 t. Over the last 10 years it has grown on average by 6.2% per annum whereas steel output has grown on average by 4.7% [8].

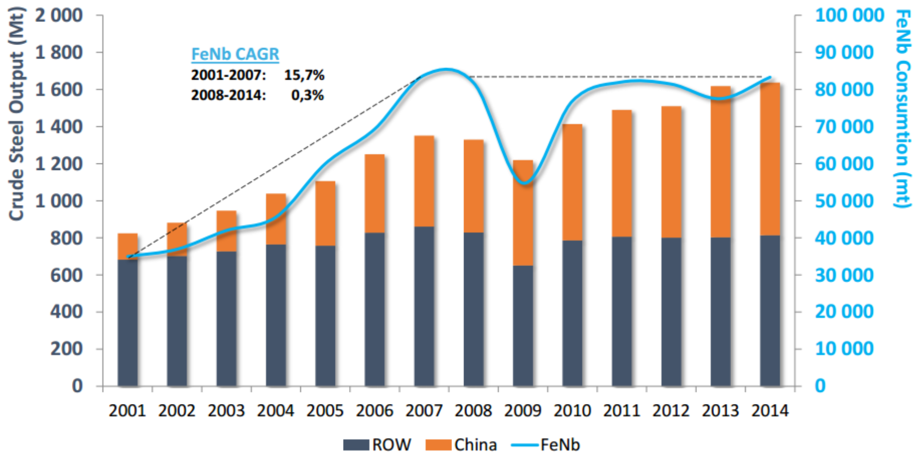


Figure 1 : Yearly crude steel output & FeNb consumption (ROW – Rest of World)[8]

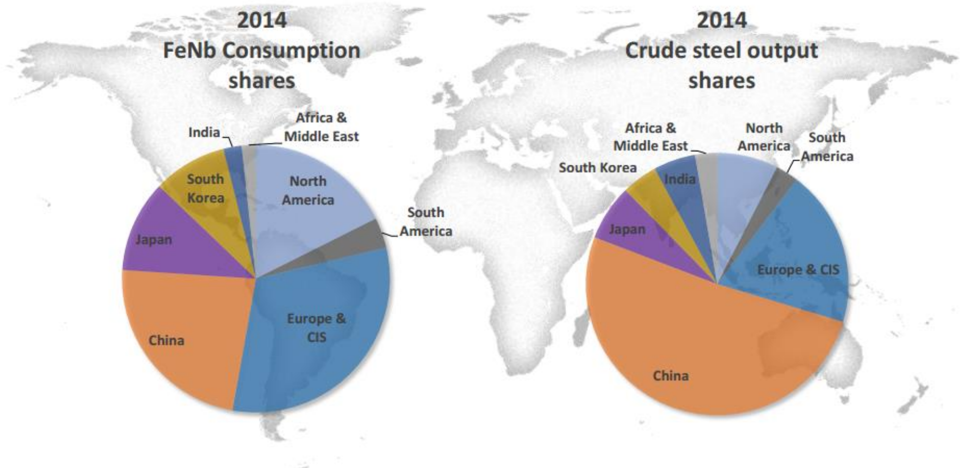


Figure 2 : Global country-wise niobium consumption(CIS – Commonwealth of Independent States)[8]

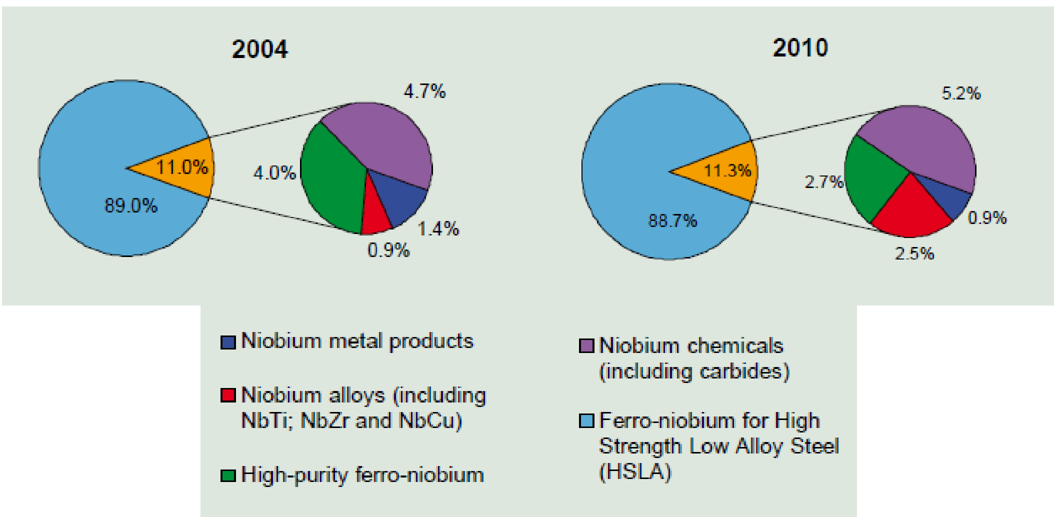
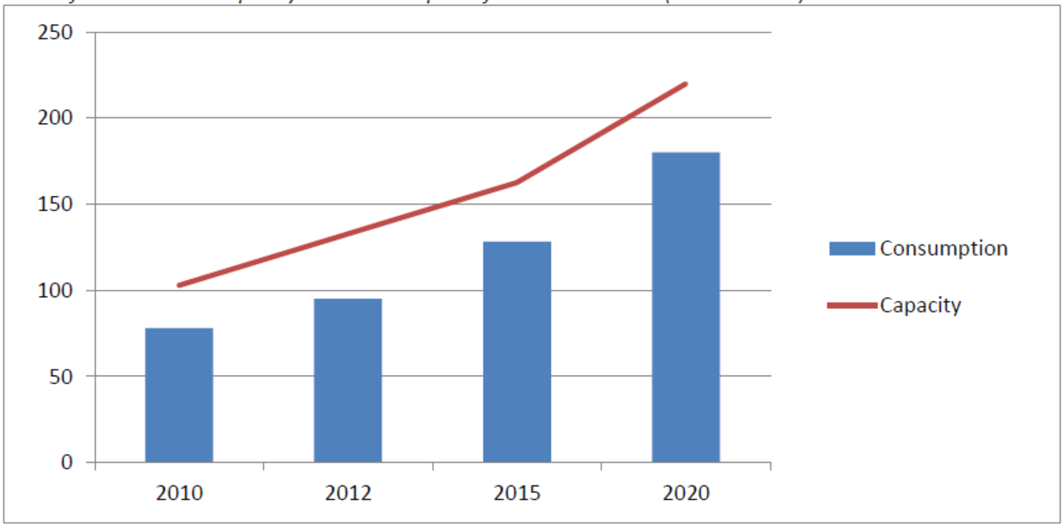


Figure 3 : Comparison of end uses of niobium in 2004 & 2010[1]

As we can see, the consumption of niobium is directly linked to the steel production. China which leads the world in steel production is a major consumer of niobium. However, other countries like that of the EU, South Korea, India, Japan and the countries of North America are also significant consumers. Coupled to the fact that niobium deposits are concentrated in some regions, it may lead to geo-political tensions. EU consumption of niobium is estimated to represent 24% of global niobium consumption. Since there is no primary niobium production in Europe, scrap is the only available intra-European raw material source. It is directly processed in steel production. Ores and concentrates, oxides and niobium metal must be imported. [8]

World ferro-niobium capacity and consumption forecasts to 2020 ('000s tonnes)



Source: Niobec (March 2012), Niobium 101

Figure 4 : World FeNb capacity and consumption forecasts

References:

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4.3 REDUCTION POTENTIAL OF NIOBIUM

4.3.1 POTENTIAL SUBSTITUTES

Niobium was listed as one of the 21 critical raw materials for EU in the December 2015 study by Oakdene Hollins Research & Consulting and Frauhofer ISI. It is interesting to note that more than 90% of niobium is produced in Brazil. The table below shows the split up of applications of niobium with their respective substitutability.

Application	Share	Megasector	Value (GVA)	Substitutability
Steel: Structural	31	Construction	104.4	0.7
Steel: Automotive	28	Transport – Road	147.4	0.7
Steel: Pipeline	24	Oil	50.0	0.7
Superalloys	8	Metals	164.6	0.7
Others	6	Other	63.3	0.5
Steel: Chemical	3	Mechanical Eqpt.	182.4	0.7

Table 1 : End uses, megasector assignment and substitution values. Reproduced from [1]

The substitution of Niobium is possible depending on the applications it is used for. The following table describes the various possibilities.

Application	Substitutes
HSLA Steels	Titanium, Vanadium, Molybdenum
Stainless steels	Titanium, Tantalum, High Nitrogen steels
Superalloys	Ceramic Matrix Composites
Superconductors	Vanadium - Gallium alloys, BSSCO alloys

Table 2 : Possible substitutes of Niobium [1][2]

The figure below shows the distribution of the uses of niobium and their substitutability. The manner and scaling of the assessment is compatible with the work of the Ad-hoc Working Group on Defining Critical Raw Materials (2010) [3].

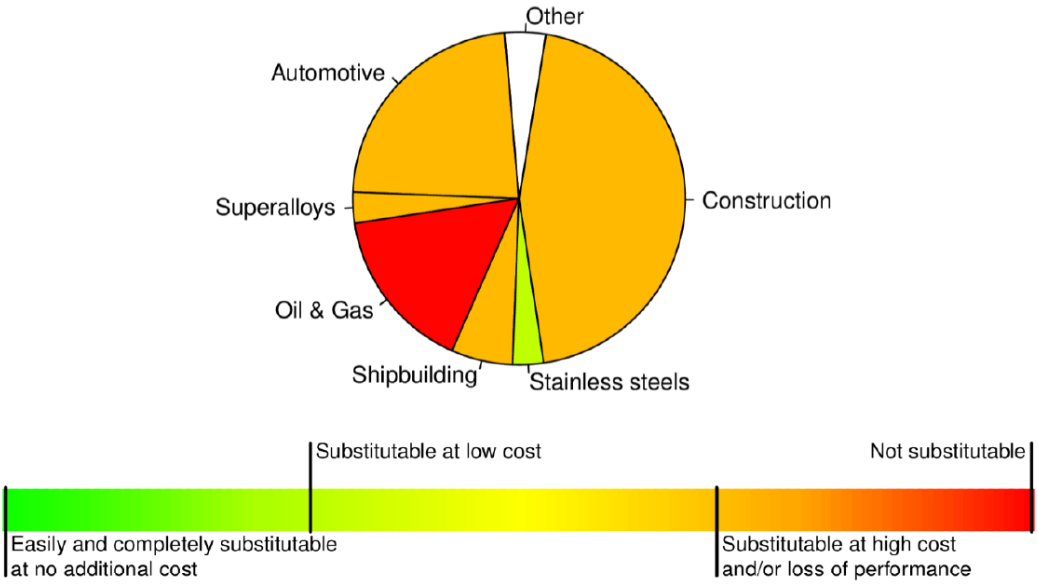

Figure 1 : Distribution of end-uses and corresponding substitutability assessment for niobium [2]

References :

[1] Chapman, A., et al. "Study on Critical Raw Materials at EU Level." *Oakdene Hollins: Buckinghamshire, UK* (2013).

[2] CRM_InnoNet: Substitution of Critical Raw Materials. "*Critical Raw Materials Substitution Profiles*". September 2013. Revised May 2015. Accessed Online: October 2016. Link: http://www.criticalrawmaterials.eu/wp-content/uploads/D3.3-Raw-Materials-Profiles-final-submitted-document.pdf

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CHAPTER 5. RHENIUM

5.1 PROPERTIES, APPLICATIONS AND PRODUCTION

5.1.1 PROPERTIES OF RHENIUM

According to 2010 and 2014 reports on critical raw materials for EU rhenium is an element important for european economy however it is not critical due to low supply risk even in conjunction with moderately high economic importance [1][2]. Rhenium is economically interesting due to its its outstanding properties [3]:
- second highest melting point,
- 3rd highest Young's modulus,
- 4th highest density,
- outstanding wear properties due to - very high strain hardening exponents, low friction coefficient,
- high hardness, tensile strength and creep-rupture strength over a temperature range up to 2000°C,
- corrosion resistance in seawater and hydrochloric and sulfuric acids,
- inertness to most combustion gases apart from oxygen.

Due to the metal's hexagonal close-packed structure, it does not undergo ductile-to-brittle transition and is applicable at low temperatues [3].

5.1.2 APPLICATIONS OF RHENIUM

Those properties make rhenium and important element in number of applications. The main applications include nickel-based superalloys where its addition is about 3 % and platinum bimetallic catalysts for reforming process with a 0.3 % addition. The total industry demand of those appliciations sums up to over 90 % of total rhenium market demand with superalloys being the dominant use. Table 5.1 presents the applications of rhenium by its form.

Table 5.1. Applications of rhenium by its form [3]

Metal-form	Application	Sub-application
Alloying element	Superalloys	single-crystal, HT, turbine blades in aircraft engines and land-based turbine applications Additive to Ni-based superalloys in single crystal gas turbine engine blades to increase high temperature creep strength of superalloys - can increase temperature of γ' phase solvus and its volume fraction ->increased HT strength and creep resistance

	W-Re alloys	To enhance the tensile strength and RT ductility of refractory metals and their alloys- e.g. - W-Re alloys in electrode materials for HT thermionic energy converters in space-power applications
	Mo-Re alloys	To enhance the tensile strength and RT ductility of refractory metals and their alloys- e.g. - Mo-Re alloys show superior corrosion resistance against liquid lithium (Li) and good mechanical properties - potential for use as structural materials in advanced nuclear reactors
	catalysts	reforming process for production of high-octane, lead-free gasoline (Pt-Re/Al_2O_3)
Re coating	-	Face seal rotors, in air turbine starter components for gas turbine engines, a diffusion barrier (e.g. on top of graphite)
Re metal	-	Filaments in photoflash lamps, ion gauges, mass spectrometers – improve stability
Re radioactive isotopes	-	Liver and pancreatic cancer treatment

Superalloys are Ni-Co-Fe-based alloys to withstand extreme heat, wear and corrosive conditions. Primarily the term described applications of over 800°C however it is being applied for lower temperatures as well where the wear and corrisive conditions remain difficult. Superalloys also should show high endurance towards stretching, thermal ad shock strain and oxidation.

Rhenium is included in the superalloy matrix and its role is to increase its temperature resistance. First Re-containing alloys included 3 % of rhenium which increased late 1990 up to 6 %. Further increase of rhenium content has not shown any positive affect and in the fourth generation of these superalloys Re content was decresed to 4.5 % due to ruthenium supplementation [4].

Table 5.2. Composition of typical monocrystalline nickel-based superalloys, % mass. [4]

Generation		Cr	Co	Mo	**Re**	W	Al	Ti	Ta	Nb	Hf	Other
I	SRR99	8.0	5.0	-	-	10.0	5.5	2.2	3.0	-	-	-
	RR2000	10.0	15.0	3.0	-	-	5.5	4.0	-	-	-	V
	AM1	7.8	6.5	2.0	-	5.7	5.2	1.1	7.9	-	-	-
II	CMSX4[1]	6.5	9.0	0.6	3.0	6.0	5.6	1.0	6.5	-	0.1	-
	PWA1484	5.0	10.0	2.0	3.0	6.0	5.6	-	8.7	-	0.1	-
III	CMX10[1]	2.0	3.0	0.4	6.0	5.0	5.7	0.2	8.0	0.1	0.03	-
	TMS75	3	12.0	2.0	5.0	6.0	6.0	-	6.0	-	0.1	-
IV	MC-NG	4.0	<0.2	1.0	4.5	5.0	6.0	0.5	5.0	-	0.1	Ru

Source: „The Use of Minor Metals in Cast Nickel Base Superalloys and Market Considerations" (presented by L. La Braca, Ross and Catherall Ltd., at Minor Metals 2003)

[1] alloys patented by Cannon- Muskegon Corporation

5.2 THE SUPPLY CHAIN OF RHENIUM

5.2.1 PRODUCTION

Rhenium production is highly concentrated, Fig 8.

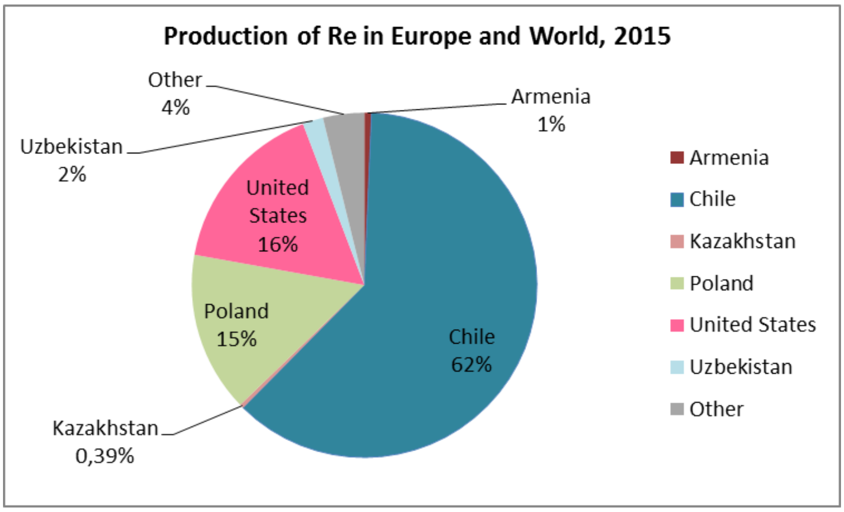


Fig. 8. Total world production of rhenium by country in 2015 (Polyak, January 2016).

5.2.2 CONSUMPTION

Rhenium consumption is mostly based on superalloy applications, most of which are designed for aerospace industry. The market share of most important application is given in the figure below.

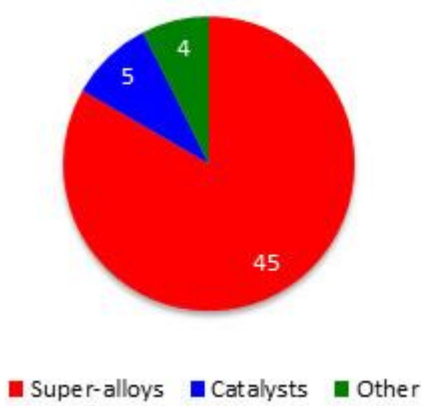


Fig. 9.Rhenium demand by application in 2012, in metric tons [5].

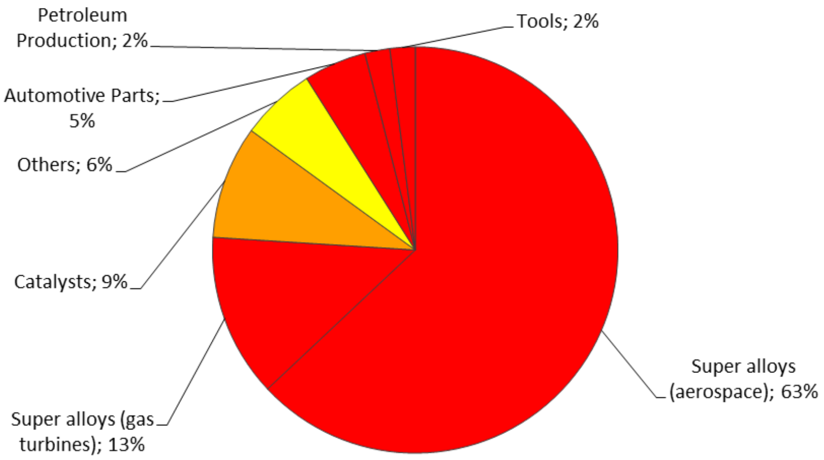
5.3 POTENTIAL SUBSTITUTES OF RHENIUM

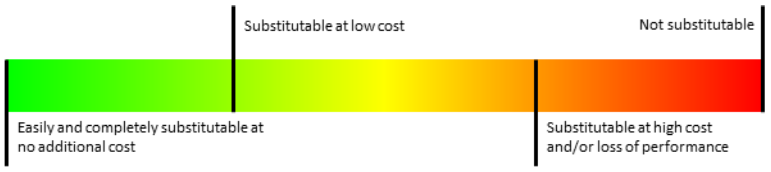
5.3.1 POTENTIAL SUBSTITUTES

The substitutability index of rhenium is given in the table below and visualized in a subsequent graph.

Table 5.3. Substitutability of rhenium given by application [6].

Application	Share	Megasector	Substitutability index
Super alloys (aerospace)	63%	Transport-Other	1.0
Super alloys (gas turbines)	13%	MechEquip	1.0
Catalysts	9%	Chemicals	0.7
Others	6%	Other	0.5
Automotive Parts	5%	Transport-Road	1.0
Petroleum Production	2%	Refining	1.0
Tools	2%	MechEquip	1.0





Substitutability in superalloys

Rhenium advantage in superalloys is that rhenium addition can be designed with closer tolerances, operating at higher temperatures, with prolonged engine life and increased engine performance and operating efficiency. Rhenium is hard to substitute although in 2008, General Electric announced that they will aim to reduce rhenium content in production of jet engines in favour of ceramic matrix composites (CMC).

Substitutability in catalysts

Platinum-rhenium on a silica or silica-alumina base are used for reforming process of low-octane petroleum refinery naphtas into high-octane liquids for high-octane gasoline.

References:

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