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**Report on refractory metal increase potential ? substitutes nonrefractory metals**

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### Summary

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# REPORT ON REFRACTORY METAL INCREASE POTENTIAL-SUBSTITUTES NON-REFRACTORY METALS

## MSP-REFRAM D5.2

December 2016

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## CHAPTER 1 TUNGSTEN

### 1 TUNGSTEN SUMMARY OF EU INDUSTRIAL PANORAMA

#### 1.1 MAIN 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 [1]. 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 [2]. 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 1 for the year 2015 [2].

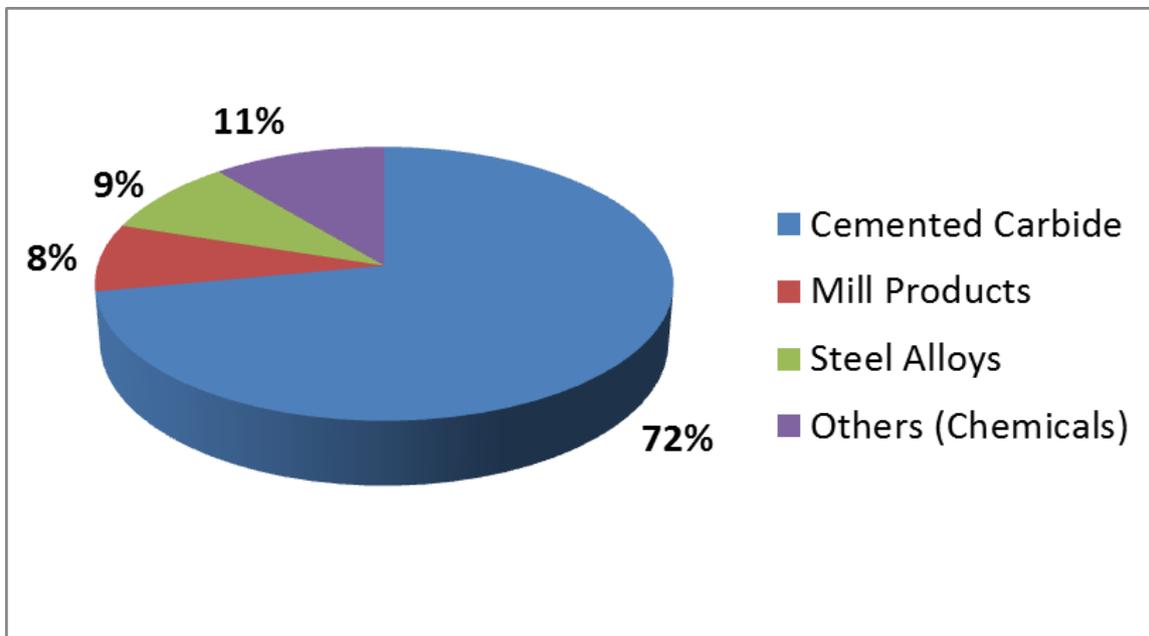


Figure 1. Figure of tungsten applications: Primary use of tungsten in Europe for the year 2015. [2]

#### 1.2 THE SUPPLY CHAIN IN EU

The tungsten supply chain is presented in Figure 2.

## EU TUNGSTEN SUPPLY CHAIN

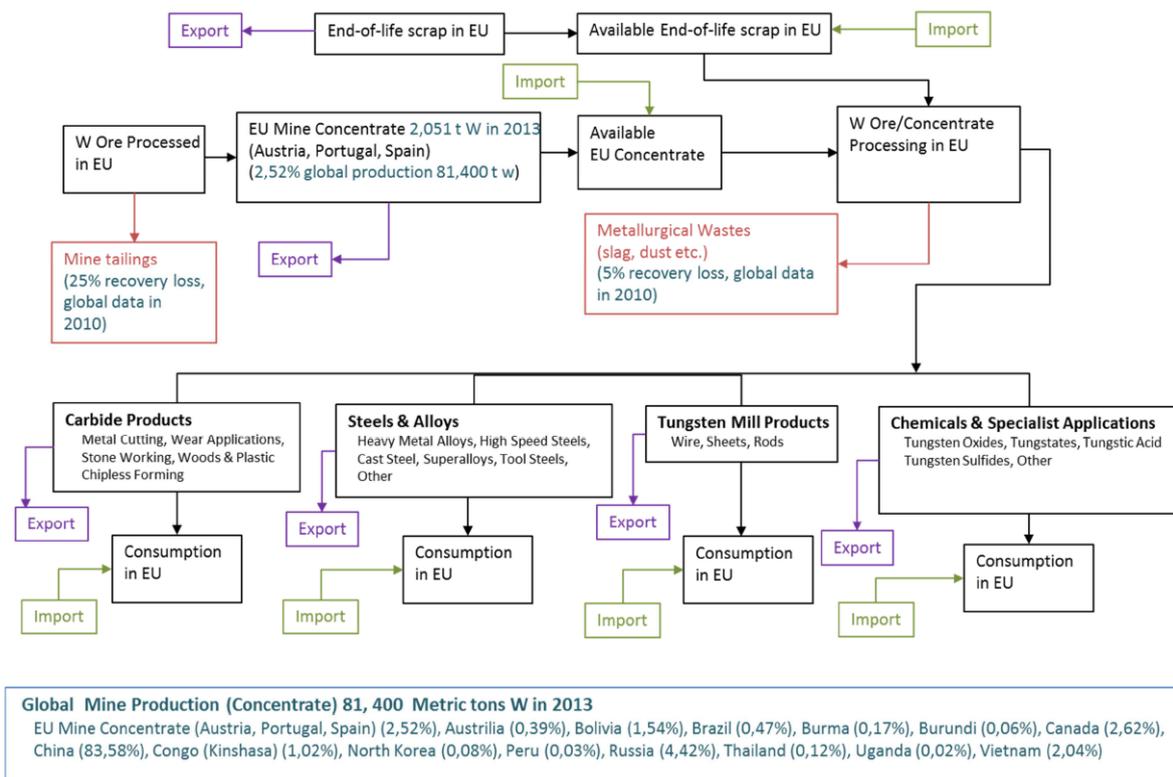


Figure 2. Figure of tungsten EU supply chain.

### References:

[1] Tungsten profile. Keyworth, UK: British Geological Survey.

[2] International Tungsten Industry Association <http://www.itia.info/>

## 2 EVALUATION OF SUBSTITUTION POTENTIAL

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 [5]. Figure 3 represent the distribution of end-users and corresponding substitutability assessment for tungsten [6] and substitutability of tungsten scoring included in the report on critical raw materials for the EU is presented in Table 1.

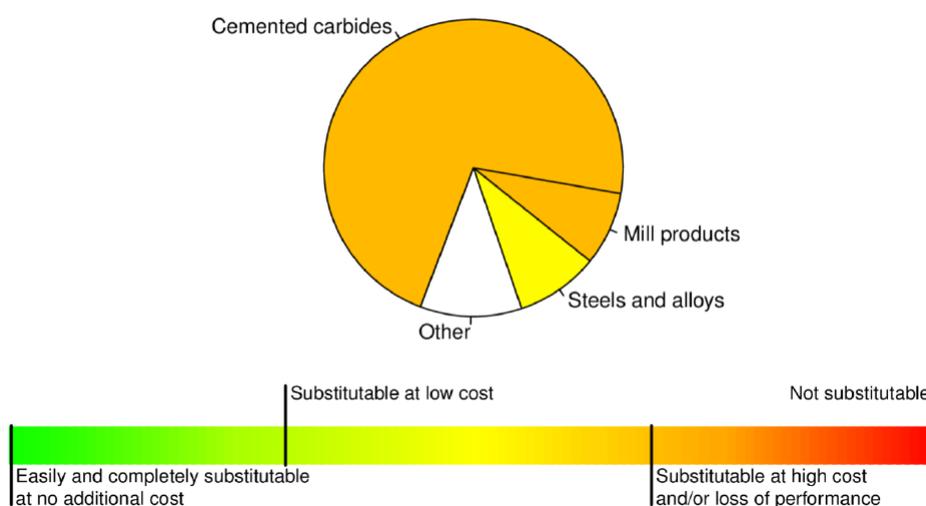
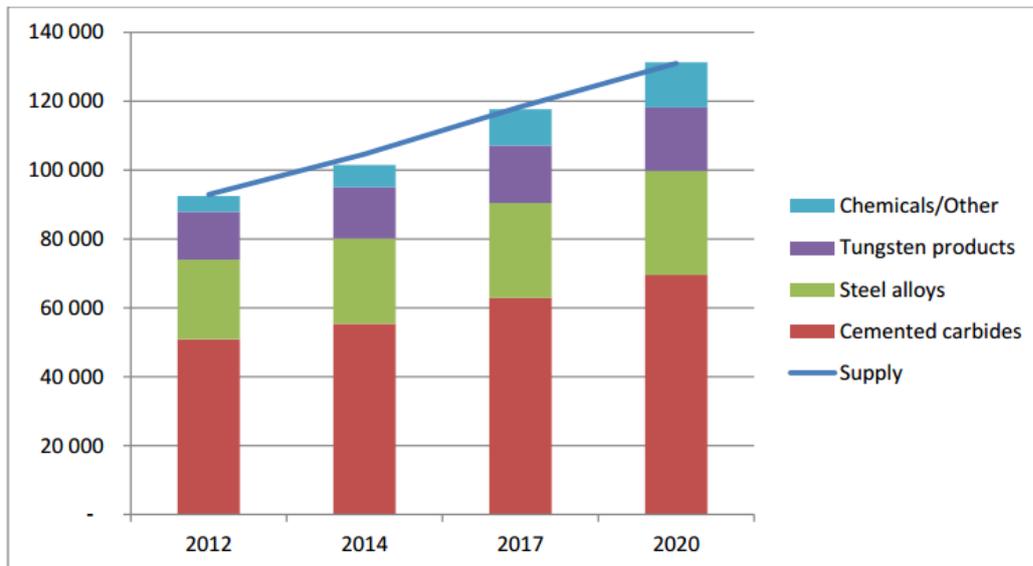


Figure 3. Distribution of end-uses and corresponding substitutability assessment for tungsten [2]

Table 1. Substitutability of tungsten scoring [13]

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

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%) [3]. Following the report on critical raw materials from the EU, 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 4.



Source: Roskill Information Services for 2013 CRM study

Figure 4. Data from Roskill information Service for 2013 CRM study for tungsten demand

## 2.1 ALTERNATIVE MATERIAL. REPLACE ONE MATERIAL FOR ANOTHER WITHOUT LOSS OF FUNCTIONALITY

### 2.1.1. TECHNICAL REVIEW

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

Table 2. Potential substitutes for tungsten, their advantages and drawbacks

Application	Potential substitute	Advantages	Drawbacks	Ref.
<b>Cemented carbides</b>	Tool Steel	TiC microstructure that contains a complex carbide phase (K-phase)	Increase of cost	[2],
	Ceramics	forming a frame around each carbonitride particle core and providing a strong bond between these hard phase particles and ductile binder metal.	Loss in product performance	[4],
	Ceramic-metallic composites	TiC more lightweight	Molybdenum (RM)	[5],
	Molybdenum carbide	Application area: tribotechnical and machining applications	Nb (CRM)	[6]
	Niobium Carbide	Ti lower risk of supply		
	Titanium carbide	TiC hard metal grades shows a highest hardness, fracture toughness		
<b>Tool/High speed Steels</b>	Titanium carbonitride in metallic binder phase (Ni and/or Co) possible with toughening additives	Better performance (addition of 5-10% of Mo increase the hardness and toughness)	Molybdenum (RM)	[2],
	ASS (Alumina, silicon nitride, sialon)	Cost-effective	ASS ( Overcoming inadequate fracture toughness)	[7]
	(Cutting tool tips)	Mo combined with V prevents softening and embrittlement of steels at high temperature	AZS (No significant barriers)	
	AZS (Alumina, zirconia, silicon carbide) (seals, bearings, nozzles)	[ASS] can increase productivity [AZS] can improve wear and		

corrosion resistance

<b>Super-alloys (corrosion resistance turbines blades, marine vehicles...)</b>	Molybdenum	Lower wight	[2],
	Ceramic matrix composites (CMCs) made from a silicon carbide/nitride matrix toughened with a coating of silicon	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)	[8]
<b>Mill products</b>	Carbon nanotube filaments Induction technology Light-emitting diodes		W replacement appears extremely difficult at the moment [2]

For cemented carbides, different researches have been done in order to evaluate potential substitutes for tungsten. As an example, Lindroos et al., 2015 [9] 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 of mechanical properties of different materials compositions are presented in Figure5. Mechanical properties of different materials compositionsThe 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.

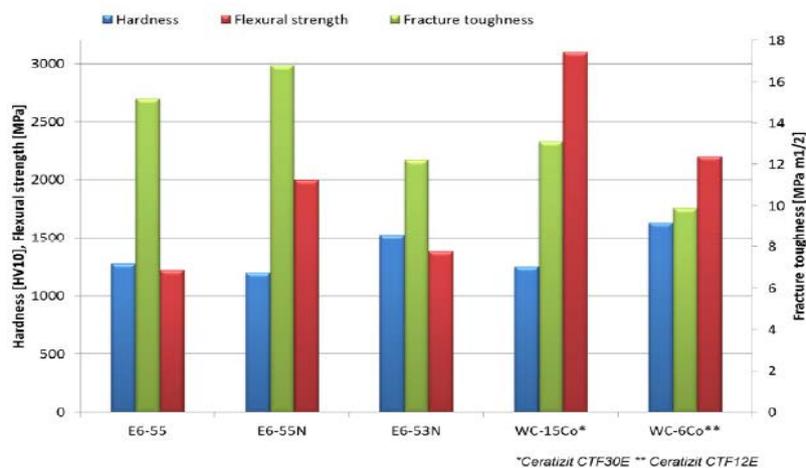


Figure5. Mechanical properties of different materials compositions [20]

Ishida et al., 2011 [6] also compared cemented carbide and cermet (TiC) properties, the comparisons of properties and micro structure of SEM for WC and TiCN are presented in Figure 6. 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	×10 <sup>-6</sup> / °C	4.5	7.5
Toughness	MPa • m <sup>1/2</sup>	8	6.5
Young's modulus	GPa	620	420
Density	g / cm <sup>3</sup>	15.0	6.1
Price	yen / cm <sup>3</sup>	69	26

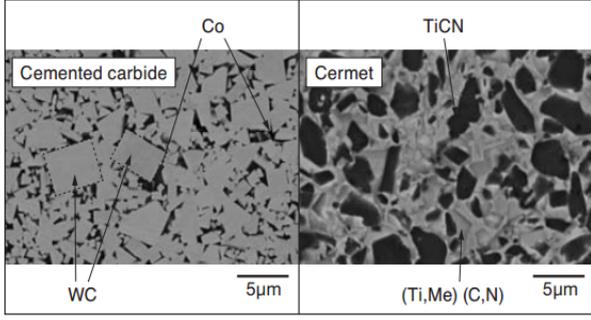
  


Figure 6. Comparison of properties and micro structure of SEM for WC and TiCN [21]

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. Tungsten in main application WC-based cemented carbides, is 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, also any substitute lack the extensive user experience that tungsten carbide cobalt base cemented carbides have. In steel products tungsten can be replaced 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 nc-alloys could be possible in 10 year since current TRLs are very low (TRL 3-4). There are some already substitution path in LEDs.

## 2.2 ALTERNATIVE SYSTEM. REPLACE ONE/SEVERAL COMPONENT WITHIN THE SAME PRODUCT

The industrial use of Tungsten is linked directly with its special capacities to harden and strengthen composite materials. Hardmetals are used to make wear-resistant abrasives and cutters for drills, circular saws, milling and turning used by the metalworking, woodworking, mining, petroleum, and construction industries [6].

The special needs of these tools and the high performance of tungsten carbides with cobalt binder for this purpose lead to a lack of substitutes for these products currently in the market. The simplicity of the tools (with no mechanisms or systems for its commissioning) leads to believe that the substitution must rely on the composition of the material itself instead of looking for alternatives for the system.

Any recent literature about hardmetal machinery substitution was not found.

## 2.3 ALTERNATIVE PRODUCT. REPLACE EXISTING TECHNOLOGY WITH DIFFERENT PRODUCTS AND/OR SERVICES

Evolution of lighting and heating industry in the latest years has led to the development of new devices and products that may evolve to a drastic reduction and even total substitution of tungsten in lighting and heating technology. Nevertheless this is a challenge and replacement is extremely difficult at the moment. This review includes the latest technologies in the market that may become future alternative to tungsten products.

Application	Potential substitute	Drawbacks	Ref.
Mill products	Carbon nanotube filaments Induction technology Light-emitting diodes	W replacement appears extremely difficult at the moment	[2]

### 2.3.1. TECHNICAL ANALYSIS

#### CARBON NANOTUBE FILAMENTS

Tungsten filaments is used in different applications, most of them, used for lighting equipment, such as lamps and household light bulbs. The more common examples are:

- The halogen lamp is similar to an inert gas-filled lamp, except it contains a small quantity of an active halogen gas such as Bromine. The inert gas suppresses the evaporation of the tungsten filament, while the halogen gas acts to reduce the amount of tungsten that plates the interior wall of the lamp. The halogen gas reacts with the tungsten that has evaporated, migrated outward, and been deposited on the lamp wall. When the lamp wall temperature is sufficient, the halogen reacts with the tungsten to form tungsten bromide, which is freed from the wall of the lamp and migrates back to the filament. The tungsten bromide compound reacts the filament of the lamp and deposits the tungsten on the filament and is freed to repeat the cycle again.
- The tungsten filaments of a vacuum incandescent lamp is heated to temperatures where visible light is emitted by resistance heating. The filament acts as an electrical resistor, which dissipates power proportional to the voltage applied, times the current through the filament. When that power level is sufficient to raise the temperature to above 1000 degrees Kelvin, visible light is produced. As the power dissipated is increased, the amount of light increases and the peak wavelength of the light shifts to the blue.
- Tungsten light bulb uses tungsten filament in incandescent light bulbs. A filament is a thin metal wire that glows when electricity is passed. In a tungsten light bulb the light is generated by heating a filament with electricity until it becomes white hot and glows. Tungsten filaments are used due to its high melting point. Because of this high melting point tungsten filaments are very opt to be used in the electric bulbs.
- Gas filled lamps produce light from an incandescent filament operated in an inert gas atmosphere. The addition of the inert gas suppresses the evaporation of the tungsten filament, which increases the lifetime of the lamp or allows higher temperature operation for the same life. The normal gases used are Nitrogen, Argon, Krypton and Xenon. The cost rises dramatically as the rarer gases are used, particularly for Xenon, due to their very low natural abundance. The advantage of the higher atomic weight gases is they suppress the evaporation of the tungsten filament more effectively than the lower weight gases. This allows the filament of gas filled lamps to be run at temperatures up to 3,200

degrees Kelvin and achieve reasonable life times. The light from these lamps has a high blue content giving the light a pure white appearance. [1]

**Substitution technology (alternative product):**

Single-walled carbon nanotube (SWNT) and double-walled carbon nanotube (DWNT) used as bulb filaments: Carbon nanotubes (CNTs) are expected to be one of the most promising candidates in future electronic industry. Household light bulbs made from macroscopic single-walled and double-walled carbon nanotube filaments were fabricated and tested. The nanotube bulbs are found to possess several interesting features when compared to a conventional tungsten filament in safelight. The carbon bulb filaments were very fragile and the bulbs darkened rapidly as a result of the deposition of carbon on the glass envelop and suffered easily from premature burnout. SWNT and DWNT are prepared using an improved chemical vapor deposition method, making them more resistant. The experimental results of microscopy, micro-Raman and small angle x-ray diffraction techniques show that the strands are large collections of well-aligned nanotube bundles, which consist of single-walled nanotubes in two-dimensional triangular lattice. [2]

**Benefits / Drawbacks**

- Household light bulbs made from macroscopic single-walled and double-walled carbon nanotube filaments possess lower threshold voltage for light emission and higher brightness at high voltages, compared with conventional tungsten filament.
- Nanotube filaments showed a lower threshold voltage for operation and higher brightness at high voltages when compared to tungsten filaments.
- The lifetime and stability of the nanotube filament bulbs is higher. They can be turned on and off for more than 5000 times and could continue functioning well.
- The irradiance intensity of the nanotube filament is stronger than that of the tungsten. The nanotube filaments can emit more visible light than tungsten at the same applied voltage.
- At high voltages of operation, the emissive power of the carbon nanotube bulbs is much higher than that of the tungsten bulb, indicating a higher efficiency in electrical power consumption of the nanotube bulbs when compared to the tungsten bulb. [2]

**INDUCTION TECHNOLOGIES**

Tungsten filaments are commonly use to made heaters due to its properties of high temperature resistance, high corrosion resistance, and lower thermal expansion. Tungsten filament can have a better effect in producing heat.

Tungsten heating elements have an upper temperature operating range of 3,000°C (3,273°K) in an inert atmosphere. Tungsten has a very high vapor pressure, which allows for this high-temperature operation.

The tungsten mesh heating element operates in the same manner as an incandescent light bulb. A 100-watt light bulb runs at about 2,200°C. The partial-pressure argon gas in the light bulb protects the element from oxygen and dissipates the heat. The distance from the element to the glass bulb protects the glass (the glass would melt before reaching 2,200°C). Incandescent lights produce more heat than light; this is why alternative lighting technologies are being increasingly used today.

**Substitution technology (alternative product):**

Electromagnetic induction is a method of heating electrically conductive material such as metals.

Induction pre-heating is a process where materials or workpieces are heated by induction prior to further processing. The reasons for pre-heating vary. In the cable and wire industry, cable cores are pre-heated before insulation extrusion. Steels strips are pre-heated prior to pickling and zinc coating. Induction pre-heating also softens metals before bending, and prepares tubes and pipes for welding. Mobile pre-heating solutions facilitate onsite repairs of bearing assemblies.

Induction post-heating refers to any process where induction is used to heat workpieces or materials that have already undergone significant processing. Metal components and welds, for example, must often be post-heated to relieve internal stresses caused by a previous process. Induction post-heating is also used to heat cable cores following extrusion. [3]

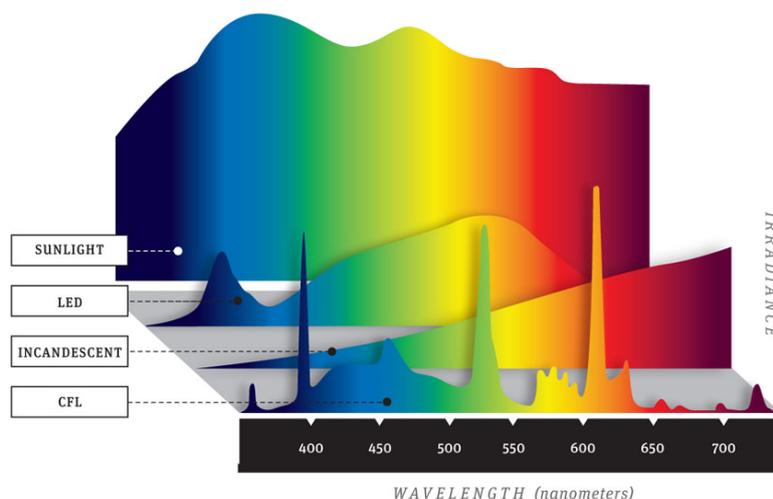
### **Benefits / Drawbacks**

- Quick heating. Development of heat within the workpiece by induction provides much higher heater rates than tungsten heaters.
- Energy savings. The induction power supply can be turned off because restarting is so quick.
- Less scale loss. Rapid heating significantly reduces material loss due to scaling relative to slow gas-fired furnace processes.
- Fast start-up. Tungsten heaters must be heated during start-up, resulting a large thermal inertia. The internal heating of induction process eliminates this problem and allows much quicker start-up.
- High production rates. Because heating times are short, induction heating often allows increased production and reduced labor cost.

### **LED**

Tungsten involving technology in lightning:

Tungsten lighting devices (incandescent or tungsten-halogen lamps, its evolution) were appreciated in house lighting and photography due to its calid color temperature, around 3.200°K. They still offer the best color redering for photography and video. But they have some drawbacks related to a high energy consumption, short useful life and the fact that they warm-up quickly (risk of fire), so they are being substituted by other options in non-professional activities.



**Figure 7: Color renders comparison between different lighting products**

### **Substitution technology (alternative product):**

A light-emitting diode (LED) is a two-lead semiconductor light source. It is a p–n junction diode, which emits light when activated [13]. When a suitable voltage is applied to the leads, electrons are able to recombine with electron holes within the device, releasing energy in the form of photons. This effect is called electroluminescence, and the color of the light (corresponding to the energy of the photon) is determined by the energy band gap of the semiconductor.

**Benefits / Drawbacks**

The benefits of LED technology regarding the use of W are clear as they completely dispose this element. Substitution of incandescent / fluorescent bulbs with more advanced light-emitting diode (LED) technology also decrease the demand for europium, tungsten and yttrium, though, demand for gallium and indium will increase [14]. Nevertheless, the new OLED offers new possibilities to substitution as it relies in one Critical Raw Material only, Indium.

Possible megatrends in lighting applications are illustrated in following Figure 8 [15]:

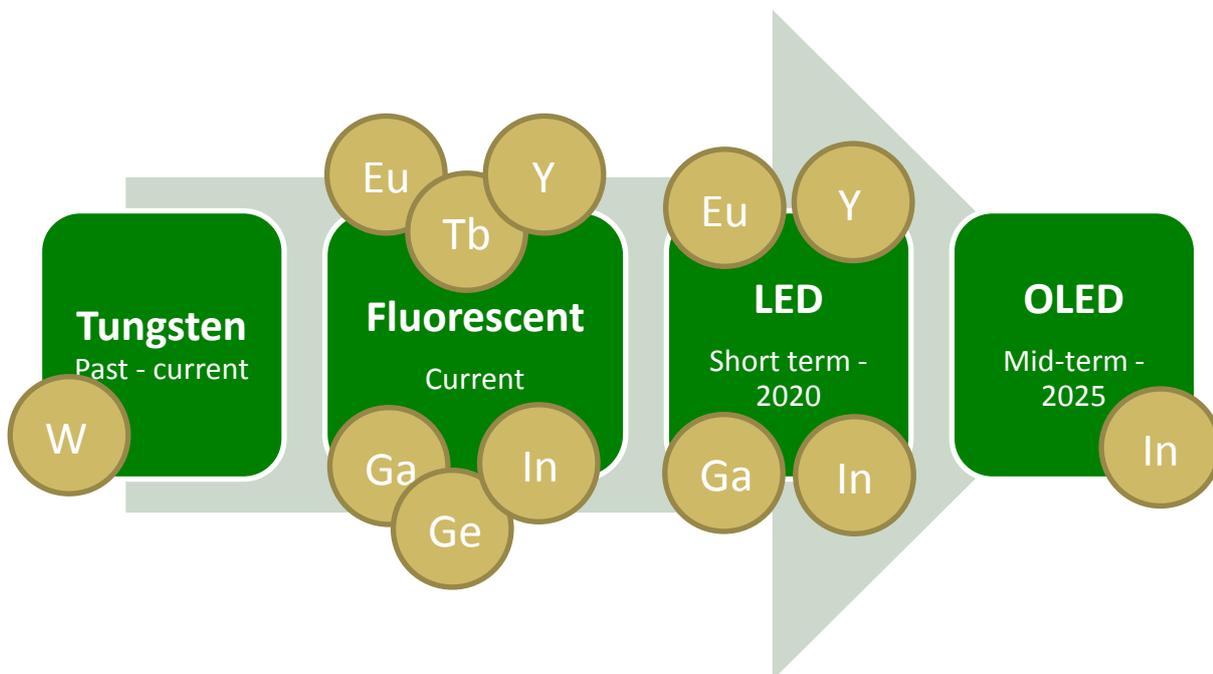


Figure 8. Possible megatrends in lighting applications. [10]

Additionally, this technology has been tested from the safety point of view and it’s found to be as safer as the technology it’s substituting. Also SSL technology is not expected to have more direct negative impacts on human health with respect to non-visual effects than other lighting technologies. For electromagnetic fields, human exposure emitted by SSL products does not appear to be a critical issue as their magnitude is generally much smaller than those corresponding to discharge lamps or certain household appliances [15].

**2.4 REFRACTORY METALS SUBSTITUTE OTHER ELEMENTS. IMPROVED FUNCTIONALITY**

**2.4.1. TECHNICAL REVIEW**

Current uses of tungsten are wide (In the Second World War, the allies were estimated to have more than 15,000 uses for tungsten, including armour plate and armour-piercing ammunition [16]). Material science is evolving around its use, giving it a role as a key component for materials exposed to extreme conditions. In this regard, ongoing research projects in the frame of H2020 are developing high specialized solutions where tungsten may play a significant role for its singular characteristics. Other research projects are oriented to improve OLED properties for the new lighting generation. Below, different new uses for tungsten are identified:

#### **Refractory ceramics for aerospace**

Transition metal borides and carbides with melting temperatures exceeding 2700°C are commonly referred to as ultra-high-temperature ceramics (UHTCs). Of these materials, hafnium diboride ( $\text{HfB}_2$ ) has shown the highest oxidation resistance. This material has found to be a leading candidate for extreme environment thermal protection systems to deal with hypersonic vehicles needs. However, oxide formed on the surface of this material allows future oxygen penetration. Silicon carbides additions (5-30% volume) have been used from the '60s followed by  $\text{SiO}_2$  glass (improving oxidation resistance at moderate temperatures (<1700°C), but still not enough to prevent from the extreme conditions of hypersonic cruises (including temperatures higher than 1723°C). Most recently, *Zhang et al.* [17] have prepared  $\text{ZrB}_2$ -based UHTCs with additions of WC to promote liquid-phase sintering in the oxide scale. It was shown that the sample containing WC had a denser  $\text{ZrO}_2$  scale and the weight gain during oxidation was reduced at temperatures of 1600°C and below.

Further researches are focused addition of tungsten (W) to an  $\text{HfB}_2$ -based UHTC to promote improved oxidation resistance at temperatures >1600°C [18].

#### **Wear resistant alloys with coatings**

The erosive wear of materials caused by the impingement of solid particles is a well-known industrial problem, for instance, in the case of compressor blades used in gas turbine engines in aeronautics. The deposition of W/W—C coatings can be accomplished by reactive magnetron sputtering which provides very highly erosion resistant coatings. Compared with Ti-based alloys, the erosion resistance is at least improved by two orders of magnitude. This very good behavior seems related to the achievement by physical vapour deposition PVD of very hard W—C solid solution layers that can be closely combined with pure W layers. The mechanical properties of the substrate were found to be unaffected by the coating treatment [19]. In general the use of tungsten carbide cobalt system is very reliable route of improving wear performance of the less wear resistant alloys and coatings. Tungsten carbide cobalt system (with different volume fractions of Co) includes wide usage experience and relative extensive possibilities to adjust wear performance including toughness versus hardness property tailoring.

#### **Nanostructured stable alloys (ICARUS)**

Aerospace, engineering, energy industry among others requires new materials able to resist coarsening, radiation, wear and high temperature. Nanocrystalline alloys are very promising materials, but none of them resists to even modest temperature rises. European projects as ICARUS (FETOPEN-RIA-2014-2015, GA-713514) – coordinated by ICCRAM - UBU are conceived to face this drawback identifying thermodynamically stable nc metal alloys resistant to coarsening, enabling its design and fabrication, which can result in new families of materials with unprecedented properties and performances, paving the way to applications from structural engineering to catalysis and energy generation.

Within this project, one of the approaches is to obtain Mo, Nb, W based alloys, which are identified as suitable materials to achieve radiation-resistant metal alloys for radiation-shielding space applications. ICARUS tasks will be developed during the next 4 years through a systematic thermodynamic exploration of the phase space for

a precise selection of families of alloys and high-throughput screening (HTS). The most promising and theoretically stable alloys will be then selected, which will culminate in a new future improved functionality for these elements.

Based on literature review refractory metals may substitute other elements in forefront materials improving functionality.

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## CHAPTER 2 TANTALUM

### 1 TANTALUM SUMMARY OF EU INDUSTRIAL PANORAMA

#### 1.1 MAIN APPLICATIONS OF TANTALUM

Tantalum's applicability for capacitors and its superior corrosion-resistance have led to its economic importance. Tantalum main end-uses are presented in Figure 1. About 60% of tantalum total consumption is in electric devices. Most of this is used in the form of metal powder in capacitors manufacturing. Tantalum is also used as an alloying element for nickel and cobalt base super-alloys in high-temperature applications like aircraft engines. Another main application area for tantalum is in corrosion resistant equipment. Tantalum has outstanding corrosion-resistance because of thin oxide film which coats tantalum in air. This passive oxide layer enables tantalum use in chemical and process industry for manufacturing of corrosion-and heat-resistant equipment like heat exchangers, condensers, thermowells and lined vessels. In sputtering targets tantalum ingots are used in applications of thin coatings of tantalum, tantalum oxide or nitride coatings to semi-conductors to prevent copper migration. Tantalum carbide is used in fabrication of cemented carbides e.g. in cutting tools. Tantalum is also used in some medicine applications because of its non-toxicity in human tissue. It is also completely bio-inert in the body because of its passive oxide layer. Tantalum oxide is used for manufacturing of special glasses and it is also used in optical industry as tantalum compounds (like tantalum pentoxide) in special glasses like for heat-reflecting, high refractive index and low optical scattering. [1,2,3,4]

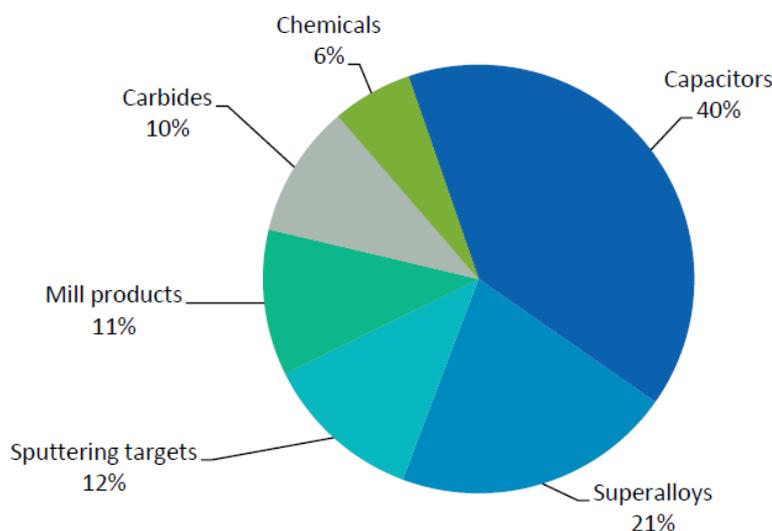


Figure 1: Main end-use global markets for tantalum in 2011.[1]

#### 1.2 THE SUPPLY CHAIN IN EU

World Tantalum supply chain (Figure 2) presents the volumes and forms of tantalum used in different application areas.

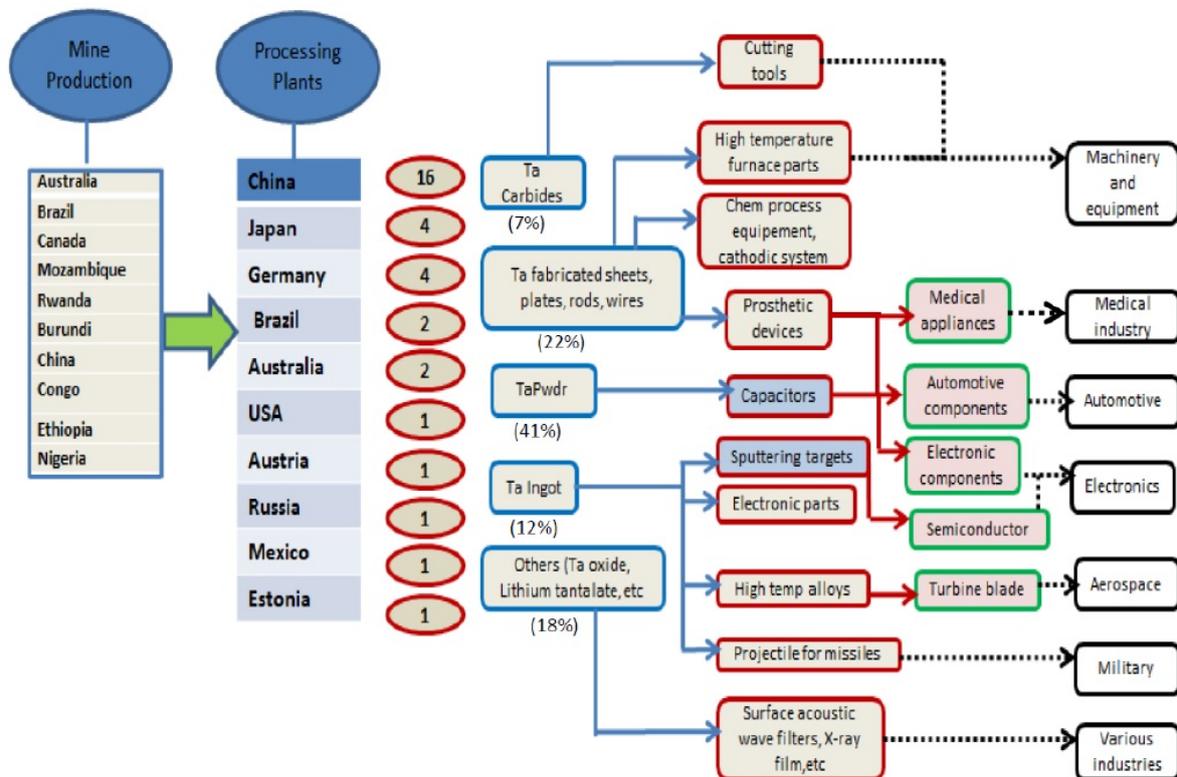


Figure 2: World Tantalum supply chain.[5]

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## 2 EVALUATION OF SUBSTITUTION POTENTIAL

Tantalum worldwide demand in 2012 is approximately 1,680t [1]. In Table 1 it is presented how tantalum demand is divided between different applications and the substitutability index for each application area.

Table 1. Tantalum end uses, shares and megasector assignment 2013. [2]

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

Roskill [3] forecasts this year that total new supply of tantalum will increase by 22% between 2016 and 2020. Roskill expects overall demand to grow at 4.7% py until 2020 but growth rates for individual end-use markets will vary. In capacitor which is the main application area of tantalum the demand growth is projected to be below average. This results from miniaturisation and material substitution which exist. The second-largest markets are in superalloys which have the highest rate of growth because of the positive outlook for the commercial aerospace industry. Demand in sputtering targets, tantalum chemicals and mill products will also show above-average growth because they have a wide range of final applications and this diversity provides a measure of protection from swings in individual end-use markets. The use of tantalum in carbides will decline slowly. Tantalum demand forecast in 2013 to 2016 in different application areas is presented in Figure 3.

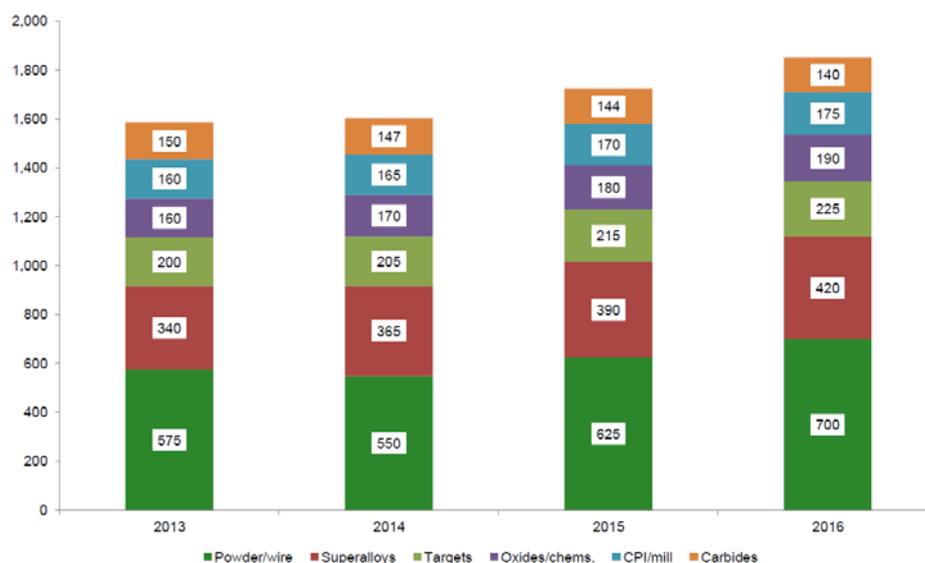


Figure 3: Tantalum demand forecast.[1]

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## 2.1 ALTERNATIVE MATERIAL. REPLACE ONE MATERIAL FOR ANOTHER WITHOUT LOSS OF FUNCTIONALITY

When the possibility of reducing the tantalum containing materials is evaluated, the following design scenarios could be evaluated:

- development of alloys by element by element(s) substitution
- developing bi-metallic structures with additive production technologies, limiting the tantalum containing metal alloy on the exposed surface area.
- coatings with sufficient thickness, limiting the use of tantalum on the exposed surfaces
- developing hybride structrus or composites for reducing need for metallic high temperature alloys, and substituting metals with ceramic and glass materials in the high temperature use.

### 2.1.1. TECHNICAL REVIEW

#### **Substitutability in process equipment (corrosion-resistant, high temperature)**

Because of tantalum's excellent corrosion-resistant properties, strength and high thermal conductivity determine its use as and fabricated products in equipment for the chemical industry (i.e., heat exchangers, heating elements, evaporators, condensers, pumps, reactors, and in prepared components such as thermal screens of furnaces and crucibles). [1,2,4]

Glass, niobium, platinum, titanium, and zirconium could replace tantalum in corrosion-resistant equipment. Hafnium, iridium, molybdenum, niobium, rhenium, and tungsten can be used for high-temperature applications.[3]

#### **Substitutability in superalloys**

Because of Tantalum high melting point (about 3 000°C), good strength at elevated temperatures, and good corrosion resistance, it is combined with cobalt, iron, and nickel to produce superalloys that are used in aerospace structures and jet engine components. In superalloys hafnium, iridium, molybdenum, niobium, rhenium and tungsten could substitute tantalum.[3] In the study [6] it was evaluatde the total replacement of tantalum by niobium atoms in MAR-M247 superalloy (10.2 Co, 10.2 W, 8.5Cr, 5.6 Al, 1.6 Nb, 1.4 Hf, 1.1 Ti, 0.7 Mo,0.15 C, 0.06 Zr, 0.015 B, Ni balance—wt.%).

These high end materials need years of development and acceptance, the type strategy can be classified as substitution of element by element(s) in superalloys, typically called alloy development (leading for specific performance).

#### **Substitutability in carbides**

Adding tantalum carbide into the material for the fabrication of cutting tools increases the resistance to the thermal shock and lowers high-temperature oxidation. Tantalum carbide is used mostly in mixtures with carbides of such metals as niobium, titanium and tungsten. Tantalum carbides are used in cemented-carbide cutting tools, wear resistant parts, farm tools, and turning and boring tools.Possible substitutes for tantalum in carbides are niobium and partial substitution of titanium carbides. [3,4].

Any recent literature about tantalum substitution in carbides was not found. Some earlier publications are found e.g. substitution of Ta for Nb in Ta-containing hard alloys was studied in [5]. There is also some literature found where tantalum carbide is used to substitute other carbides. E.g. in [7] it is determined that the introduction of tantalum (as a carbide) into TiCN–Ni–Mo and TiCN–Ni–Mo–WC hard alloys increases their bending strength, which was evaluated in the milling of steel.

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## 2.2 ALTERNATIVE PRODUCT. REPLACE EXISTING TECHNOLOGY WITH DIFFERENT PRODUCTS AND/OR SERVICES

### 2.2.1. TECHNICAL ANALYSIS

Capacitors are made from two metallic electrodes placed in mutual opposition with an insulating material (dielectric) between the electrodes for accumulating an electrical charge. Capacitors are available in a wide range of types, materials, structures, sizes, rated characteristics, loss ratings, and applications. Of the various types of electrolytic capacitors, there are several types which use an electrolyte: aluminum electrolytic capacitors, tantalum electrolytic capacitors, niobium electrolytic capacitors and electric double-layer capacitors.

Capacitors are divided into two mechanical groups: Fixed capacitors with fixed capacitance values and variable capacitors with variable (trimmer) or adjustable (tunable) capacitance values. The most important group is the fixed capacitors. Many got their names from the dielectric. For a systematic classification these characteristics can't be used, because one of the oldest, the electrolytic capacitor, is named instead by its cathode construction. So the most-used names are simply historical.

The most common kinds of capacitors are:

- **Ceramic capacitors** have a ceramic dielectric.
- **Film** and **paper capacitors** are named for their dielectrics.
- **Aluminum, tantalum** and **niobium electrolytic capacitors** are named after the material used as the anode and the construction of the cathode (electrolyte)
- **Polymer capacitors** are aluminum, tantalum or niobium electrolytic capacitors with conductive polymer as electrolyte
- **Supercapacitor** is the family name for:
  - **Double-layer capacitors** were named for the physical phenomenon of the Helmholtz double-layer
  - **Pseudocapacitors** were named for their ability to store electric energy electro-chemically with reversible faradaic charge-transfer
  - **Hybrid capacitors** combine double-layer and pseudocapacitors to increase power density
- **Silver mica, glass, silicon, air-gap and vacuum capacitors** are named for their dielectric.

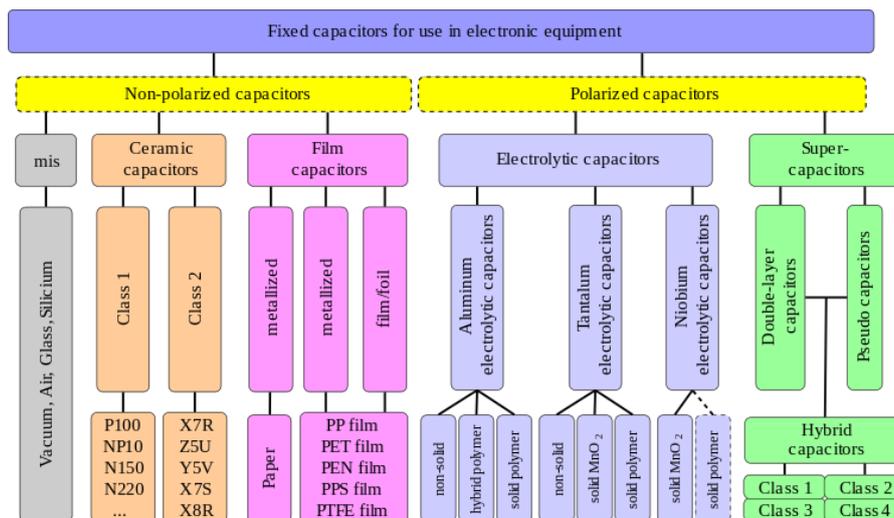


Figure 4: Capacitors are divided into two mechanical groups: Fixed capacitors with fixed capacitance values and variable capacitors with variable (trimmer) or adjustable (tunable) capacitance values. /Wikipedia/

There are three types of tantalum electrolytic capacitors on the market: wet electrolytic capacitors which use sulfuric acid as the electrolyte and solid electrolytic capacitors which use MnO or polymer, as the solid electrolyte.[1]

The tantalum in capacitors is used as a fine powder. The production of a solid tantalum capacitor involves making a porous tantalum pellet by pressing and sintering tantalum powder. These porous tantalum anodes have high surface area which increasing the capacitance value. The pellet, with an attached tantalum lead wire, is electrochemically oxidized to grow a thin layer of insulating tantalum oxide on the surface of the tantalum. In the case of tantalum, an amorphous Ta<sub>2</sub>O<sub>5</sub> dielectric is then electrochemically grown on this high-surface-area porous tantalum anode. This dielectric layer could be very thin which results higher capacitance value per volume, superior frequency characteristics and excellent stability over time. Then the anodized pellet is then impregnated with manganese nitrate which is then thermally decomposed to leave or deposit semiconducting

manganese dioxide on the tantalum oxide. At finally, the unit is encapsulated usually in the chip configuration.(Figure 5) [2,3,4,5,6,7]

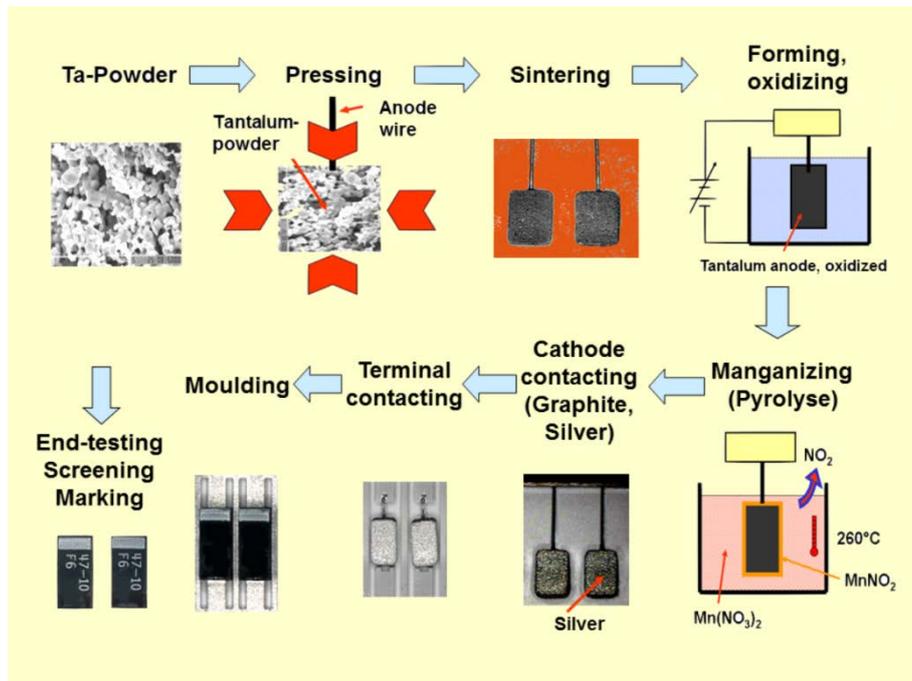


Figure 5: Tantalum capacitors production flow [2]

Miniaturization of electronic devices demands higher and higher capacitance in a smaller volume. Tantalum capacitors exhibits reliable performance in a broad range of temperatures combined to compactness (small volume) and high efficiency (capacity). Solid tantalum capacitors are chosen in applications that require any combination of volumetric efficiency, long-term stability, high-temperature exposure, low noise generation and self-healing capabilities. This includes applications in computers, wireless handsets, automotive safety solutions, smartphones, test and measurement equipment, oil and gas systems, medical implants and defense electronics. New tantalum capacitors with enhanced capabilities, such as lower ESR, lower profiles, higher temperature handling capabilities and advanced packaging will be enabling technology for emerging markets in wearable electronics; as well as for the extension and growth of a variety of new end products currently being designed in computers, communications, automotive, medical, defense and aerospace platforms for future deployment worldwide (Figure 6).[3,4,5,6,8]

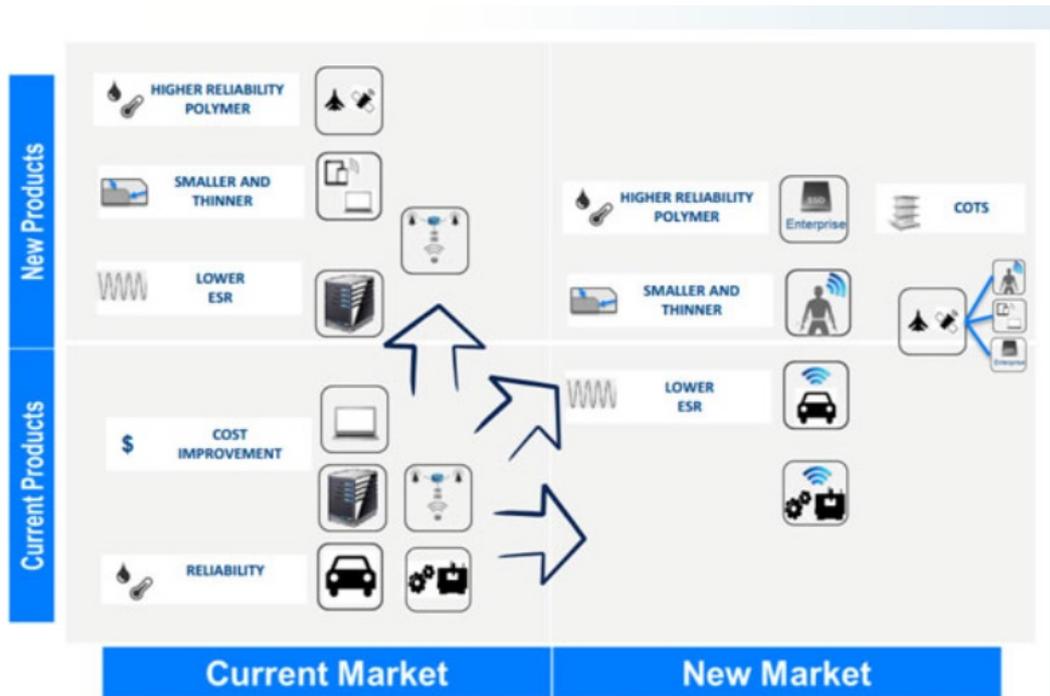


Figure 6: Tantalum capacitors current products for current markets and new products for new markets.[8]

### Substitutability in capacitors

In the last 40 years it has been the goal of various researchers to find a substitute for tantalum in electrolytic capacitors. The logical substitute for tantalum is niobium because of the similarity of its chemical properties and some of the physical properties. However, niobium exhibits higher oxygen solubility than tantalum, and it is not so easy to produce a thermally stable oxide film. In addition in some cases the chemical purity of niobium powder was not as good as that of tantalum powder, which contributed to poor dielectric properties. Several capacitor manufacturers offer niobium capacitors (with niobium metal or NbO as the anode material) with almost the same quality as tantalum capacitors for some applications. The major advantages of niobium metal and NbO capacitors over tantalum capacitors are stable supply, lower price (half the density), and potentially equal quality. [9,10] In capacitors, aluminium and ceramic capacitors offer also substitutes for tantalum. Aluminium capacitors offer lower cost and higher availability over tantalum capacitors. Aluminium electrolytic capacitors are however larger in size than tantalum capacitors of the same capacitance. Tantalum an equivalent series resistance (ESR) is ten times smaller than the ESR of aluminium electrolytic capacitors which enables larger currents to pass through the capacitor with less heat generation in tantalum capacitors compared to aluminium ones. Tantalum capacitors also offer more stability and unchangeable capacity over time compared to aluminium electrolytic capacitors. Ceramic capacitors started to substitute for tantalum capacitors in the late 1990 century. 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. [3,4,5,12]

In recent study [11] discussion on multilayer ceramic capacitors (MLCC) replacement for tantalum capacitors was presented. Tantalum capacitors have advantages used in condition of low voltage and the temperature below 60 °C for higher capacitance than MLCC. Until now a totally replacement of MLCC for tantalum capacitors is unrealistic. The future in tantalum capacitors lies in improving the quality of tantalum powder and the volumetric efficiency, so as to place more capacitance in the standard case sizes. Although from cost point of view, tantalum has difficulties in competing with MLC's and aluminium with their very large volume of

production, but it could be mitigated by the continued exploitation of high CV/g powders, taking full advantage of the higher CVs achievable at lower voltages.

Capacitance ranges from picofarad to more than hundreds of farad. Voltage ratings can reach 100 kilovolts. In general, capacitance and voltage correlates with physical size and cost.

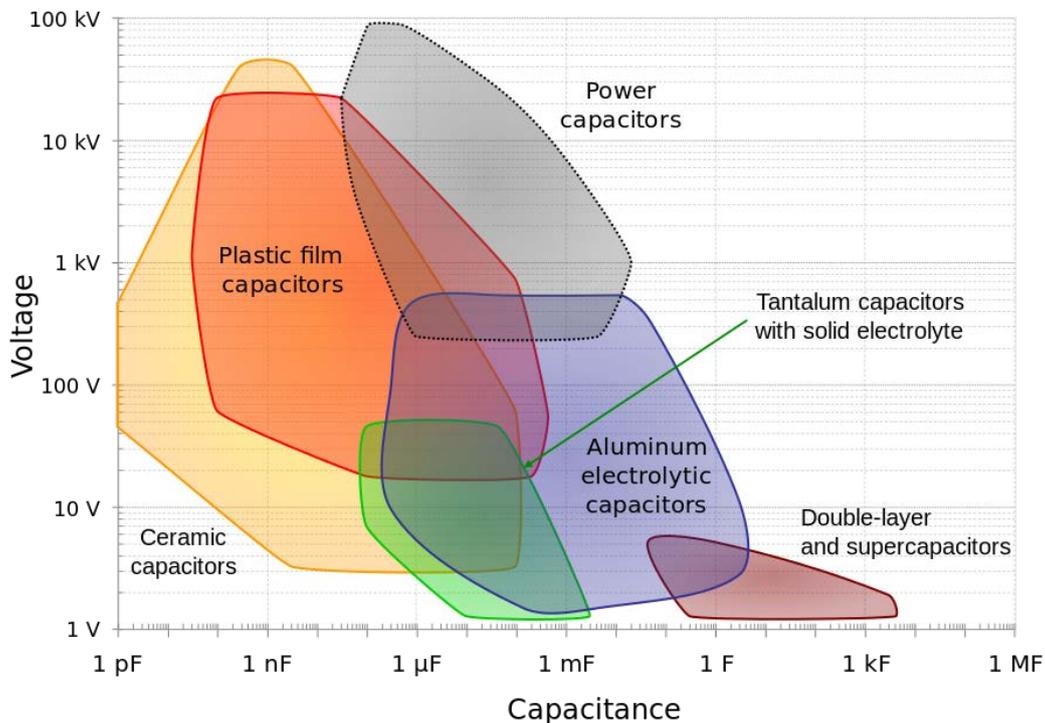


Figure 7: Capacitance and voltage ranges of different capacitor groups. /Wikipedia/

Integrated passives are widely available as arrays or networks, usually fabricated on IC-sized Si using basic front-end technologies that can be surface mounted onto ceramic or organic boards using the same sort of infrastructure used to install discretes.

To date, integrated passives have not been utilized as embedded structures in organic substrates to a significant degree, particularly with FR4, which makes up the vast majority of boards sold today.

Methodology from the ceramic side is difficult to use with organics because these processes typically require much higher processing temperatures than can be tolerated by organic board materials and can only be applied if processed separately and laminated onto the board afterwards. [14]

The general consensus in integral passives today is that resistor technology is viable, capacitors need further research and development work, and inductors are beneficial only for relatively low values (\*100 nH). Currently, discretes are recommended for high value resistors, capacitors and inductors.[13]

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#### References:

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## CHAPTER 3 MOLYBDENUM

### 1 MOLYBDENUM SUMMARY OF EU INDUSTRIAL PANORAMA

#### 1.1 MAIN APPLICATIONS OF MOLYBDENUM

Main applications of molybdenum include alloying elements in various steels and chemical – lubricants and pigments. The market share of the applications is shown in the figure.

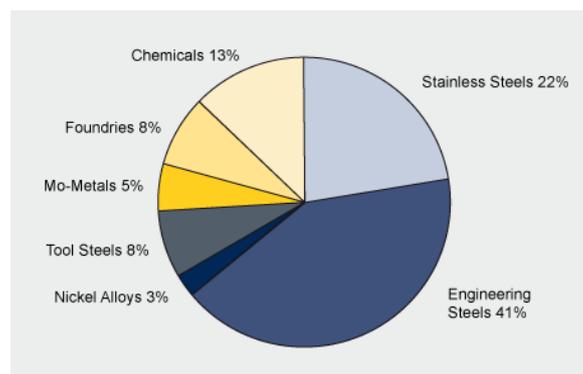


Fig. 1. First use of molybdenum, 2015 [0].

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<sub>2</sub> 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.

Stainless steels are main application of molybdenum in today's industry. Molybdenum in steel is an alloying element responsible for significant increase of corrosion resistance. It is necessary for steel to sustain resistance to pitting and crevice corrosion in chloride-containing solutions. One of the most popular stainless steels is 316L with about 2.1 wt. % of molybdenum, used mainly in building&construction industry. In harsher environments where chlorinated seawater is a corrosive agent, grades with 6 or even 28 % of molybdenum are used in steels or nickel-base superalloys, respectively.

In chemical application large share of molybdenum use is in catalysts and lubricants industries. Molybdenum in the form of oxide supported on  $\gamma$ -alumina is the precursor of Mo silfide active catalyst used mostly in hydrotreatment of petroleum. Molybdenum-based catalysts belong to group of heterogeneous catalysts which in total account for 80 % of the global catalysts market [13].

MoS<sub>2</sub> is a lubricant additive in ball and roller bearings, automotive, metalworking, extrusion, cold working, gears as well as in aircraft industry [5,9,10].

These applications account for about 90 % of total molybdenum use.

## 1.2 THE SUPPLY CHAIN IN EU

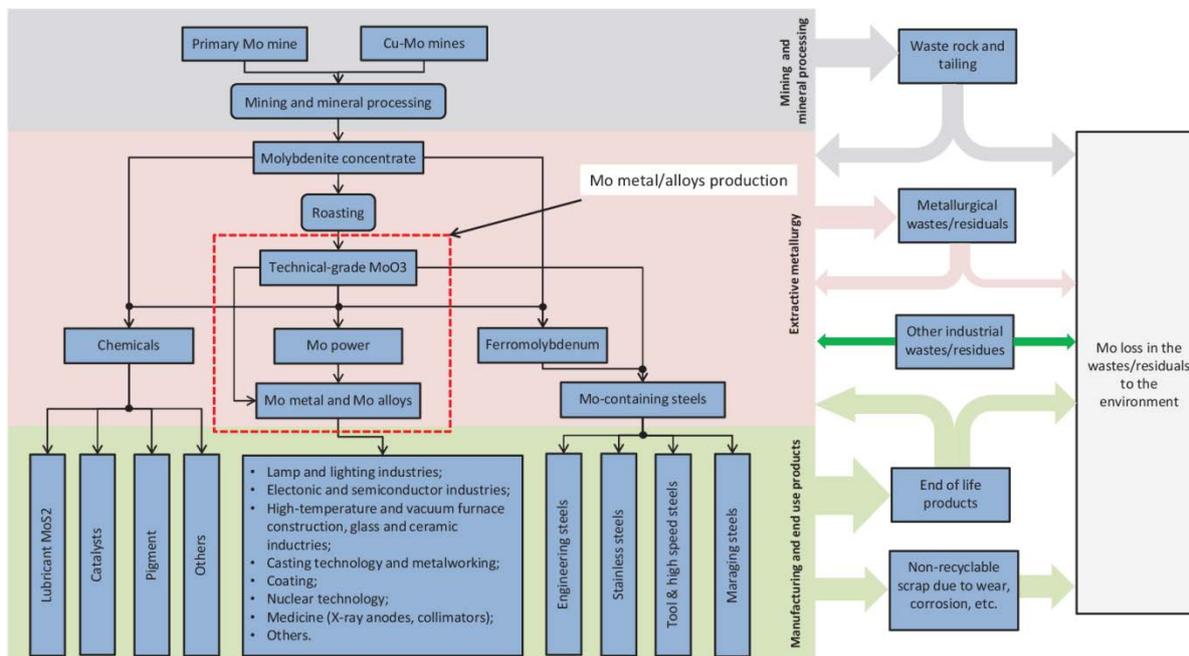


Fig. 2. Molybdenum industrial value chains of EU. [D1.2]

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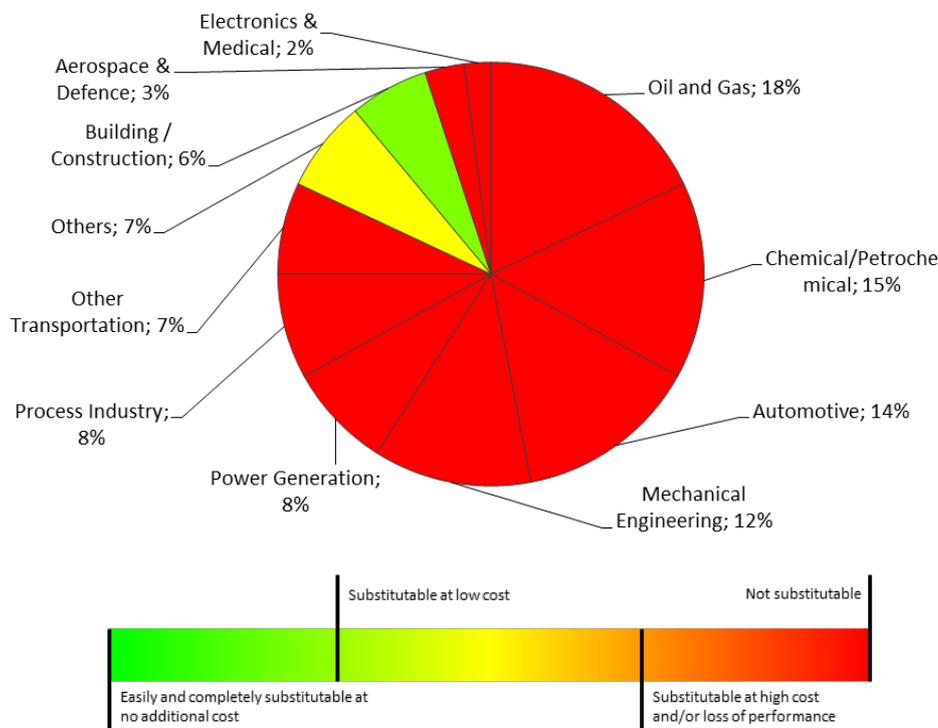
## 2 EVALUATION OF SUBSTITUTION POTENTIAL

In order to substitute one material for another ideally one should be vested in a material that has exactly the same properties as the one to be substituted, or better. In general, it is not the case. Some materials have shortcomings that either rule them out from a group of possible substitutes or their use needs to be reframed with a possibility of developing a different product or component. Therefore, in view of inevitable costs related with substitute implementation, the substitution is allowed almost only when the estimated benefits are to be substantial.

Table 3.1. Substitutability of molybdenum by application [1].

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.



### 2.1 ALTERNATIVE MATERIAL. REPLACE ONE MATERIAL FOR ANOTHER WITHOUT LOSS OF FUNCTIONALITY

### 2.1.1. TECHNICAL REVIEW

#### Wear-resistant hard materials - Cemented carbides

Cemented carbides are said to be one of the most reliable engineering materials. It is because of their high wear resistance in many applications. A proper combination of hardness and toughness is needed in applications such as wear parts, metal cutting tools, in oil & gas industry. Those properties depend strongly on the amount of the binder phase and on the grain size of hard phase material. Figure below presents the applications of cemented carbides of various hardness. In these materials cobalt and tungsten are the elements to be substituted.

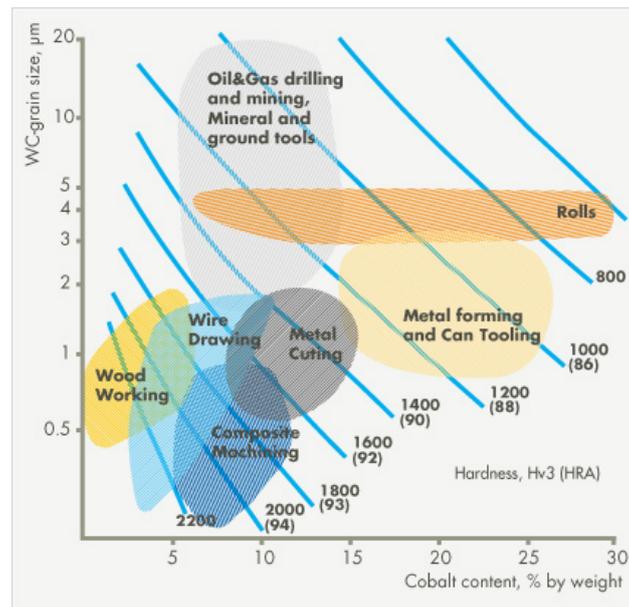


Fig. 3. The range of applications of straight grade cemented carbides [2].

In comparison with cemented carbides, the ternary borides have equivalent hardness and flexural strength, but superior fracture toughness and thermal expansion coefficient. Ternary borides with molybdenum such as  $\text{Mo}_2\text{FeB}_2$  or  $\text{Mo}_2\text{NiB}_2$  immersed in a metal matrix have already proven useful in injection moulding or die casting machine parts, extruding dies [3,4]. For example  $\text{Mo}_2\text{NiB}_2$  hard particles bound by nickel in addition to their high hardness, show also very good corrosion resistance. The increase of molybdenum content up to  $\text{Mo}/\text{B} = 1.2$  ratio results in higher transverse rupture strength (TRS) up to 3.2 GPa and higher hardness [4].

While the ternary borides have themselves beneficial properties, a further doping of  $\text{Mo}_2\text{NiB}_2$  with chromium up to 15 wt. % Cr provides even higher hardness and high elastic modulus in comparison with WC and TiC [5,6]. Therefore it is a potential substitute for the hard phases in cemented carbides. However competitive techniques of improving the hardness and lifetime of cemented carbides exist that might seem more justified even despite their shortcomings. For example, the technique of boriding/boronizing is used to improve the properties of cemented carbides by formation of harder boride phases, such as  $\text{WCoB}$ ,  $\text{CoB}$ ,  $\text{W}_2\text{CoB}_2$  and others, however it may produce some surface porosity [7]. Other solutions in surface protection include brazed cladding, welding and thermal spraying. The techniques may improve the properties of surface, but may not be sufficient to improve the material for use in extreme conditions for which the core WC phase may appear too brittle.

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### Cermet coatings

The ternary borides have their temperature expansion coefficient (CET) close to values for steels and that makes them a good option for protective coating for steel materials. The  $\text{Mo}_2\text{NiB}_2$  was already used in a laser-cladded coating for 304 stainless steel protection [8, 9]. The phase was a reinforcement of  $\gamma$ -(Fe,Ni) metallic matrix. Some trouble with the coating itself were observed as galvanic corrosion triggered selective removal of  $\text{Mo}_2\text{NiB}_2$  particles from the coating. However such metal matrix composite coating was found to increase the wear resistance several times as well as lower corrosion rate and prevent pitting corrosion.

### Ceramic Matrix Composites

Used in applications that require high strength and wear resistance, up to high temperatures, combine the high-temperature beneficial properties of ceramics with strength and toughness imposed by its construction. Depending on the form of strengthening phase, the CMCs may show improved resistance to catastrophic failure (continuous, fiber-like reinforcement) or cracks (whiskers reinforcement). However any crack propagation will end in catastrophic failure.

Despite their extreme properties, CMCs still have some limitations. The manufacturing process is not simple and is somewhat hazardous due to handling thin fibers. On top of that, the risk of cracking is not completely overcome. Therefore research on ceramic-matrix composites with ductile particle reinforcement is ongoing and at the moment might be seen as a 'scientific curiosity' and needing more theoretical approach [10, 11]. However they have important advantages. The first one is the relative simplicity of production when compared to production of CMCs. Metallic powder is mixed with ceramic matrix powder and sintered in a suitable temperature. Such materials have already proven to have improved properties over pure ceramic. For example molybdenum reinforced aluminium nitride present higher bending strength and fracture toughness than not only pure AlN but also other ceramics such as SiC,  $\text{Al}_2\text{O}_3$ , TiC [12,13]. The value depends on molybdenum volume content in the matrix phase.

Other composites based on alumina were also investigated. Synthesis of  $\text{Al}_2\text{O}_3$  composites with immersed molybdenum particles have yielded the increase of toughness with Mo increase of over 30 % and strength 26 % higher when compared to pure alumina [14,15]. Somewhat mirror composites proposed for high-temperature applications include molybdenum matrix composites reinforced with  $\text{Al}_2\text{O}_3$  possibly with the addition of rhenium [16, 17]. Composites are produced by the powder metallurgy route using a planetary ball mill. Molybdenum matrix composites strengthened with alumina are very promising materials offering enhanced strength and wear resistance at high temperature in comparison with molybdenum alloys.

The linear coefficient of thermal expansion (CTE) of molybdenum is equal to  $5.35 \cdot 10^{-6} \text{ K}^{-1}$  and is close to that of alumina ceramic ( $5.5 \cdot 10^{-6} \text{ K}^{-1}$ ), which may be beneficial from the point of view of the residual stress state induced in the composite materials with metal or polymer matrix. Due to its good dielectric, ferroelectric, piezoelectric and thermal shock properties it finds an application in the electronics industry. The linear CTE of rhenium ( $6.6 \cdot 10^{-6} \text{ K}^{-1}$ ) is similar to both molybdenum and alumina, therefore the low residual stress could be generated during the processing and exploitation of the composite.

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## 2.2 ALTERNATIVE SYSTEM. REPLACE ONE/SEVERAL COMPONENT WITHIN THE SAME PRODUCT

### 2.2.1. TECHNICAL REVIEW

### Glass industry applications

Molybdenum coatings improve the underlying materials' properties and decrease their wear. They are resistant to high temperatures up to 1600 °C and abrasion as well as high corrosion [1–3]. Also high modulus of elasticity, good resistance to rapid temperature changes (due to low thermal expansion coefficient and high thermal conductivity), low specific heat, high resistance to corrosion and good wettability by molten glass as well as chemical inertness towards glass that helps avoid unfavourable glass colouring, favour its use in glass industry [4]. Molybdenum can either be used as an individual component or as a composite element [5] imparting increased wear resistance of refractory components of a furnace. It is resistant to thermal shock and chemically compatible with a wide range of glass compositions [6].

Molybdenum alloyed with rhenium is an alternative to present solution that utilizes molybdenum metal sheets on top of metallic elements to increase the erosion and corrosion resistance towards molten glass [6,7]. Rhenium compounds and alloys show significant chemical resistance and are suitable for protection of surface of other metals against acids, bases, sulphur compounds, sea water and operation in other environments [8]. Rhenium improves strength, ductility, weldability, while lowering the ductile to- brittle transition temperature and removal of the brittleness occurring after recrystallization. This is the so called “rhenium effect” – observed when group VI metals are alloyed with group VII and VIII metals [9–13].

### High-temperature applications

Nickel-based turbine blades used in gas turbines in power plants work in extreme, high-temperature conditions and require cooling in order to function. In order to lower the fuel consumption and decrease CO<sub>2</sub> emissions an alternative is needed. Recently developed molybdenum silicide binary composite synthesized by directional solidification was proposed [14]. With this method MoSi<sub>2</sub>/Mo<sub>5</sub>Si<sub>3</sub> composites were developed that show properties superior to modern superalloys such as the melting temperature of well above 1000 °C. However one of the most prominent is the yield stress value which was shown to be higher than Ni-base superalloys like CMSX-4 and of recently developed ultrahigh-temperature structural materials - ULMAT Mo-Si-B alloys and Nb silicide-based DS alloys.

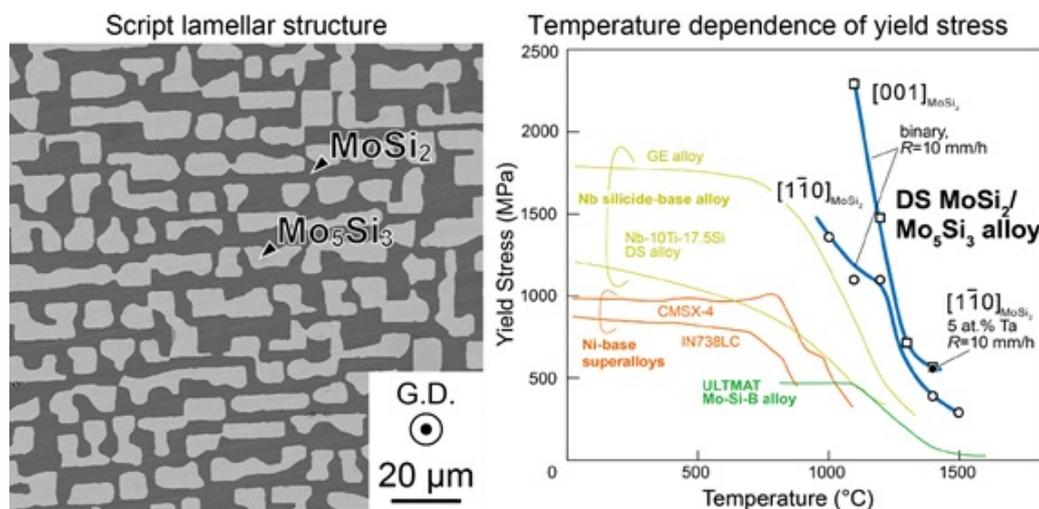


Fig. 4. Directionally solidified molybdenum silicide binary composite (left). Yield stress versus temperature for the MoSi<sub>2</sub>/Mo<sub>5</sub>Si<sub>3</sub> composite and comparison with some high-temperature materials (after[14]).

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## 2.3 ALTERNATIVE PRODUCT. REPLACE EXISTING TECHNOLOGY WITH DIFFERENT PRODUCTS AND/OR SERVICES

### 2.3.1. TECHNICAL ANALYSIS

#### Space-reactor applications

Despite the beneficial properties of molybdenum such as high melting point, thermal behaviour and excellent high temperature strength, molybdenum is still often not used in high-temperature reactors due to

troubles with fabrication, insufficient ductility at low temperatures and radiation-induced embrittlement. Possible candidates for applications as fuel cladding and structural components include molybdenum-rhenium alloys, whose beneficial properties were described in previous section.

However studies of Mo–41Re and Mo–47.5Re alloys still did not prove their feasibility for these applications [1]. The neutron irradiation induces strengthening, loss of ductility, intergranular failures at fracture surfaces. Depending on the treatment conditions, the samples showed either ductile fracture or intergranular embrittlement. The effects of neutron irradiation were also tested for alloys with decreased rhenium content such as Mo–16Re and Mo–21Re alloys [2]. The rhenium content does not significantly influence the fracture toughness. The differences are mainly related to the irradiation temperature – at low temperatures the intergranular fracture is more prominent and while the temperature increases it gradually changes to transgranular fracture.

Further research concerns molybdenum alloyed with a fraction of silicon and indicates an increase ductility, especially at room temperature for only 0.3 atomic percent of silicon addition [3]. The alloy shows 60 % tensile elongation at room temperature and superior fatigue strength as compared to pure molybdenum or Mo-27 at.% Re alloy [4]. However irradiation tests are lacking.

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## 2.4 REFRACTORY METALS SUBSTITUTE OTHER ELEMENTS. IMPROVED FUNCTIONALITY

### 2.4.1. TECHNICAL REVIEW

#### Stainless steels

In the 1980' the U.S. Congress has already seen the need for dealing with possible vulnerability in import of strategic materials [1]. One of them was 18% chromium-8% nickel stainless steel used in reactor vessels, heat exchangers, and tubing in power plants, due to high chromium content. The possible substitution was seen in modified 9% chromium-1% molybdenum steel with a fully developed technology.

In stainless steels the selection of proper material is bound to evaluation of four features, i.e. - in the order of importance: corrosion resistance, cost performance, fabricability, mechanical properties. Corrosion resistance is the most basic feature that justify the use of stainless steel. Substitution in these applications is most often compromised by the conditions of use, price, estimated lifetime. Chromium and molybdenum alloying additions to stainless steel yield more corrosion resistant materials for harsher environments.

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Assuming an extended access to molybdenum, combined with a favourable price could trigger an interest in more resistant stainless steel grades.

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## CHAPTER 4 NIOBIUM

### 1 NIOBIUM SUMMARY OF EU INDUSTRIAL PANORAMA

#### 1.1 MAIN APPLICATIONS OF NIOBIUM

Almost 90% of the niobium is produced as Ferroniobium (40-70% Nb), which is an alloy on iron and niobium. Automobile, construction and energy (pipeline) industry form the major portion of the end-user. Niobium is also used as an alloying element in superalloys in the aviation, nuclear and structural industries which require the construction material to withstand demanding conductions. Niobium alloys are also used to manufacture superconductors. Niobium is also used in small quantities in many other applications such as magnets, superconductors, jewellery, thermometers, capacitors or catalysts. However, considering the amount of usage, the relevant areas of use are steel, superalloys and superconductors.

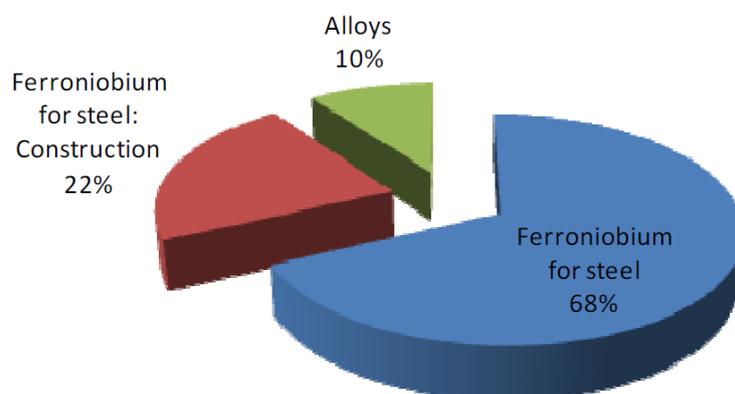


Figure 2 : Main end-use global markets for niobium, Source: Report of the Ad-hoc Working Group on defining critical raw materials by EU. [1]

#### 1.2 THE SUPPLY CHAIN IN EU

##### ***EU trade flows and consumption***

Trade statistics are shown are for imports and exports from the EU of ferro-niobium. Data for niobium ores and metal are not available; however, ferro-niobium is the leading commercial niobium-containing material and contains on average 60% niobium. The EU is a net importer of ferro-niobium, importing around 19,000 tonnes per year which can be seen in the figure below. 2009 was an exception, since imports were nearly halved due to the global economic crisis. As mentioned before, the demand for ferro-niobium depends on the demand for steel.

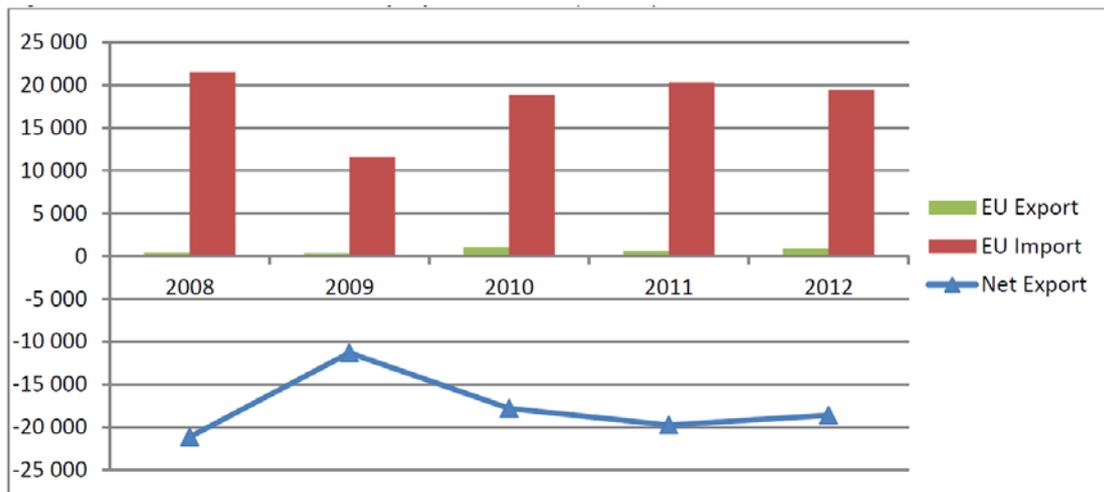


Figure 3 : Trends in extra-EU trade for ferro-niobium (tonnes). Reproduced from [1]

FeNb imports into the EU come from Brazil and Canada. Imports are negligible when compared to exports. However, material is exported to a number of countries, the major destinations being Iran and the USA.

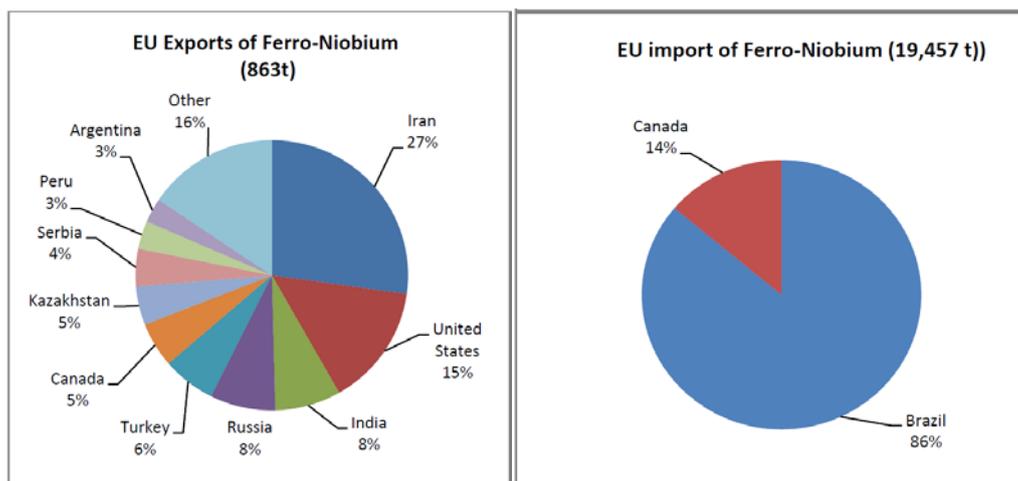


Figure 4: Import & Export statistics of FeNb. Reproduced from [1]. Original source : Eurostat-Comext Database, CN 7202 9300 [accessed August 2013]

The EU accounts for almost 24% of world consumption. Roskill Information Services comments that this is around 13,000 tonnes of contained niobium, which equates to a slightly lower estimate of 22% of the 60,300 tonnes of world niobium production. Other major niobium consuming regions include China (25%), Japan (10%), other Asian countries (11%), Americas (21%) and CIS (Commonwealth of Independent States) (7%).

#### References :

[1] Report on critical raw materials for the EU: Critical raw materials profiles. Ref. Ares(2015)3396873 - 14/08/2015

#### Substitutability in numbers

Substitutability of periodic table elements are described in Figure 4. Table 1 describes the applications, share and substitutability of niobium. Table 2. shows niobium economic importance and supply risk calculations.

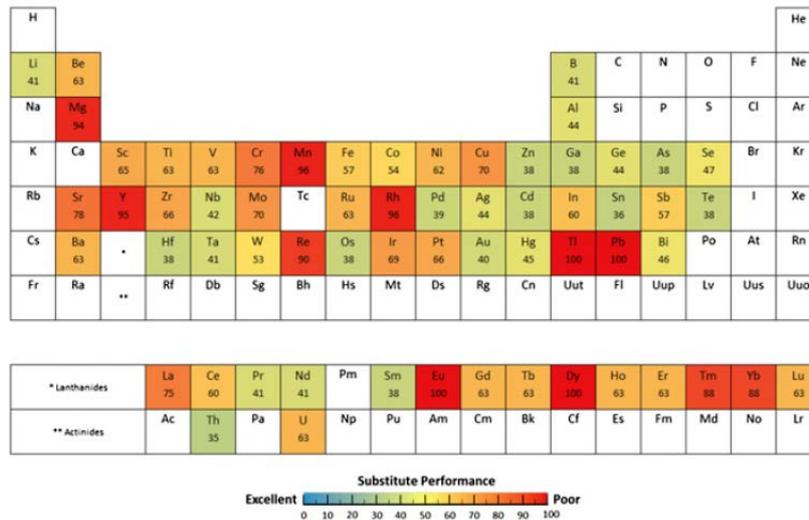


Figure 4: The periodic table of substitute performance. The results are scaled from 0 to 100, with 0 indicating that exemplary substitutes exist for all major uses and 100 indicating that no substitute with even adequate performance exists for any of the major uses. Niobium has a score of 42. Reproduced from [1]

Table 1 : End uses, megasector assignment and substitution values of Niobium. Reproduced from [2]

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 2 : Economic importance and supply risk calculations. Reproduced from [2] WGI – World Governance Indicator HHI - Herfindahl-Hirschman Index

Economic Importance (Raw)	Economic Importance (Scaled)	HHI	HHI – WGI (scaled)	Substitutability Index	Recycling Input rate (EOL %)	Supply Risk (WGI)
107	5.87	8504	4.008	0.69	11%	2.46

References:

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[1] Graedel, Thomas E., et al. "On the materials basis of modern society." *Proceedings of the National Academy of Sciences* 112.20 (2015): 6295-6300.

[2] Annexes to the report on critical raw materials for the EU: Report of the ad hoc working group on defining critical raw materials. Dated: 25/05/2014

### **Recycling of Niobium**

As we transition into the digital age, our consumption of materials is booming at a never-before-seen rate. The case of niobium is no different. Even though the applications are confined to a few fields, niobium usage has increased steadily over the years. Also, as stated above, the substitution potential of niobium is very limited due to a lot of factors.

As for any other metal, recycling offers a path for the sustainable use of niobium. Transforming the niobium production cycle based on the principles of circular economy will definitely decrease the load on niobium production. Niobium and Tantalum can be recovered from waste metals and scrap and up to 20% of the total supply can be accounted for by this. Niobium as mentioned before is recovered from niobium-steels and superalloys but the amount is not significant.

As mentioned in section 1, a major portion of niobium usage is confined to the steel industry. So, a change in this sphere will significantly impact the global niobium consumption. The recycling of steel is a developed process; it has been successfully incorporated into the production process by most of the global steel producers. Hitherto, niobium recycling has not received sufficient interest or attention from the steel producers. The best way to promote niobium recycling will be to integrate the same into the steel recycling process.

Another aspect worth considering is that, when niobium containing steels are recycled together with niobium free steels niobium might be lost in the Fe-C matrix. The overall niobium content will get reduced too. Hence, separation of niobium containing steel from other steel grades will offer a way to effectively recycle niobium. This however, has to start from the consumers. Since HSLA steel grades with niobium are mostly used in the automotive, construction and energy sector, it is evident that steel with niobium additives are used for specialist applications. This works in the favour of the proposal. Steels collected from such consumers may be recycled separately and hence niobium can be made to stay within the Fe-C matrix. This will also ensure that the niobium content does not get diluted to a large extent.

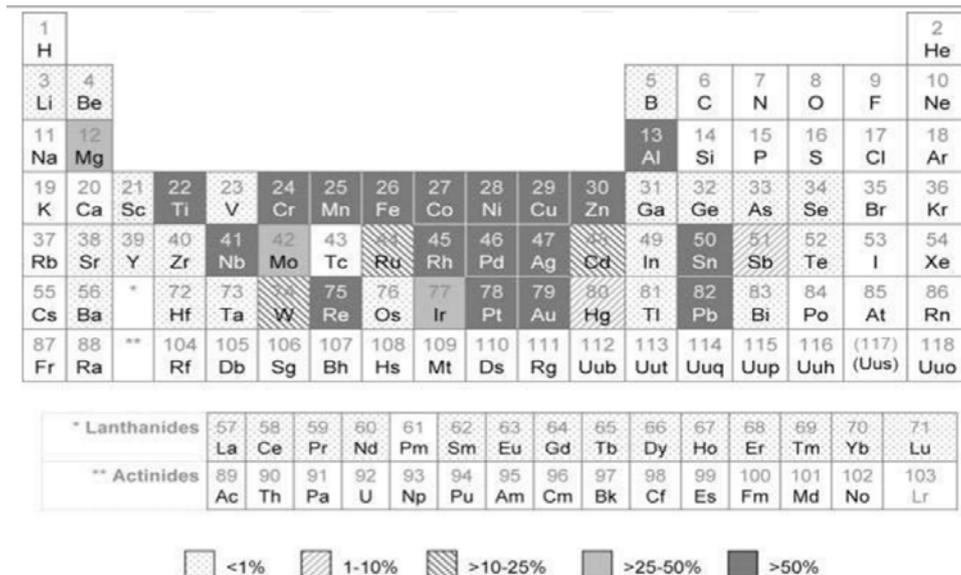
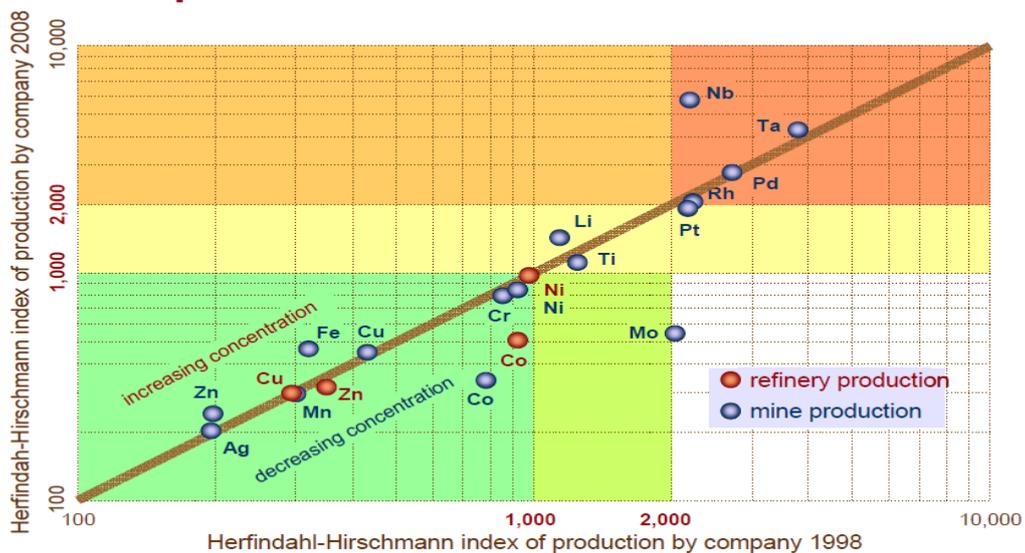


Figure 4: The periodic table of global average end-of-life functional recycling rates (EOL-RR) for 60 metals, with the individual metals categorized into one of five ranges. Unshaded entries indicate that no data or estimates are available.

Reference [1] gives an in-depth analysis about metal recycling. Niobium boasts of an EOL – RR (End of Life – Recycling Rate viz. the amount of metal in the collected waste that is actually recycled). It also has a recycled content(RC) of above 50% according to this paper. However, due to the extreme concentration of Nb resources to a few countries, the RC value might not give us the global picture, especially from a EU perspective. In the EU, the recycled share is 20% of the total consumption. [3] Figure 5 shows that niobium has an extremely high corporate concentration.

### Corporate Concentration 1998 / 2008



Source : RMG, BGR

Note: values above 2000 indicate a high level of corporate concentration.

Figure 5: Corporate concentration for selected metal ores and refined products in 1998 and 2008. Reproduced from [3]

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**References:**

- [1] Graedel, T. E., et al. "What do we know about metal recycling rates?" *Journal of Industrial Ecology* 15.3 (2011): 355-366.
- [2] British Geological survey document
- [3] EC-European Commission. "Critical raw materials for the EU." *Report of the ad-hoc working group on defining critical raw materials. Brussels* (2010).

## 2 EVALUATION OF SUBSTITUTION POTENTIAL

### 2.1 ALTERNATIVE MATERIAL. REPLACE ONE MATERIAL FOR ANOTHER WITHOUT LOSS OF FUNCTIONALITY

#### 2.1.1. TECHNICAL REVIEW

##### HSLA Steels

It is used as an alloying element in the production of HSLA and Stainless Steel to increase its overall strength and resistance towards corrosion and high temperatures. The effect of niobium on corrosion is that the presence of NbC will ensure that Cr will remain in the steel metal matrix by the preventing the formation of CrC. Basically, C has more affinity for Nb than Cr. This is relevant in the case of Stainless Steels rather than HSLA.

Two possible substitutes in this case are Vanadium(V) and Titanium(Ti). The available literature on the direct substitution potential of niobium by these elements is very less. A viable method to treat this issue would be to understand the effect of niobium (ferroniobium) on HSLA steels followed by studying the effects of the substitution elements on them. HSLA steels are known for its qualities of strength, fracture toughness, formability and weldability while being optimally priced. [1]

Thermomechanical rolling followed by accelerated cooling is the conventional production route employed for the manufacture of these steels. It is crucial to understand the effect of niobium here. Niobium microalloying helps in obtaining a finer grain size by austenite conditioning. The addition of niobium in a few hundredths of a weight percent leads to an increased strengthening of the steels, if the correct heat treatment is applied. The strength-enhancing effect is due to a reduction in the average grain size of the ferrite, which is due to the grain refining effect during the austenization treatment. The grain-refining effect is because the micro-alloying elements have a very strong affinity for the interstitial elements such as carbon and nitrogen, leading to the precipitation of extremely fine distributed precipitates. The existence of the precipitates leads to Zener pinning which prevents the growth of austenite. [2][3]

The alloy design of less than 0.05% carbon and up to 0.10% niobium content, the recrystallization stop temperature is shifted to higher temperature. Also, the retardation of the transformation promotes the bainite formation. The strength is also improved by the formation of niobium carbide. [2]

Considering the retardation of recrystallization by microalloying, the graph below shows the effect of various elements.

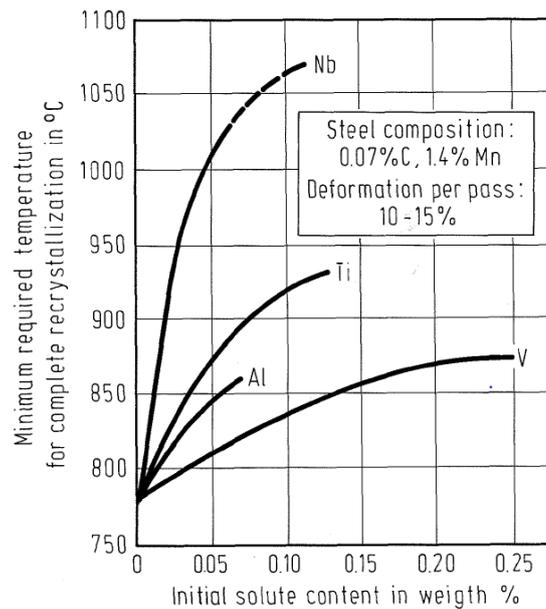


Figure 6 : Effect on retardation of recrystallization by various elements [2]

Even though the effect of niobium is more pronounced than the other elements, there is a potential for substitution. A case can be made for titanium with its higher affinity for nitrogen, which prevents the formation of niobium carbo-nitride. This allows a higher content of niobium to be dissolved during reheating for rolling. This can lead to increased precipitation of Niobium carbide which can contribute to the strength enhancement.

Niobium also has the effect of lowering the  $\gamma$  to  $\alpha$  (austenite to ferrite) transformation temperature. This lowering of transformation temperature has an effect on the thermo-mechanically rolled plus accelerated cooled plates by refining the grain size of polygonal ferrite and increasing the amount of bainite. The graph below serves as a comparison between Nb, Ti and V.

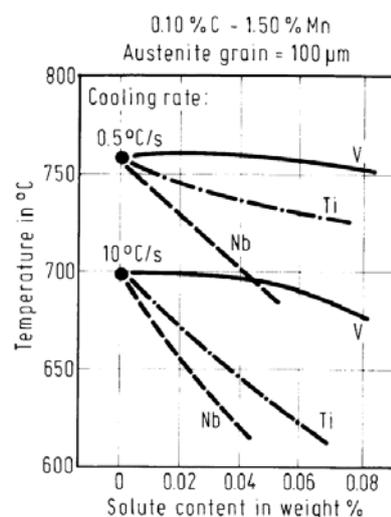


Figure 7: Transformation temperatures (Ar3) of micro-alloyed steels with equal austenite grain size [2]

This facet also offers an opportunity to study the substitution potential of niobium. The  $\gamma$  to  $\alpha$  (austenite to ferrite) transformation, which is a diffusion controlled process, is retarded more when the atomic size

difference between base element and the other element in the solid solution is high. Compared to iron, niobium has the biggest atomic size difference of 15.6%. The size difference of other potential substitutes is Ti 14.8%, V 6.2% and Mo 9.4%. Hence, it is obvious why niobium is the most effective in lowering the transformation temperature. [2]

To summarise, niobium has a 3-fold influence on the mechanical properties of steel. They are:

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

Grain refining is the only mechanism that provides strength and toughness simultaneously, thus making Nb the most effective microalloying element. [4]

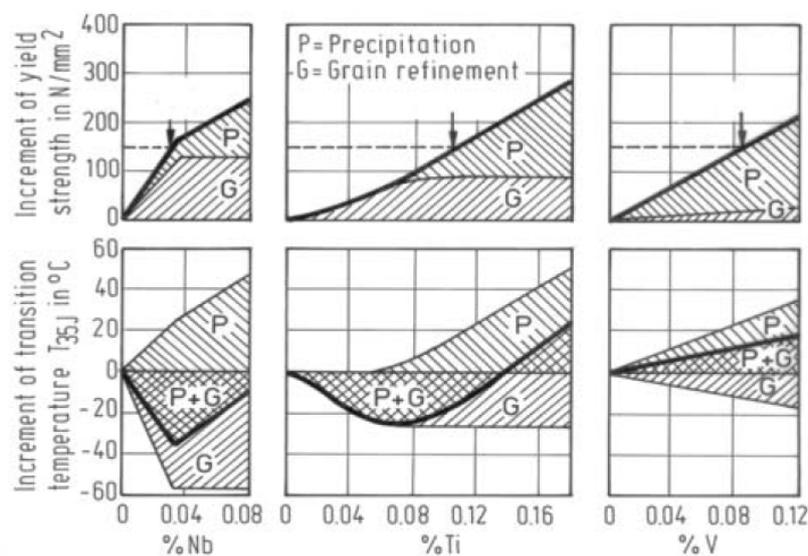


Figure 8: Effect of Nb, Ti and V on ductility and strength of 0.08%C and 0.90% steel. [4]

### Prospective Research

NANO-steels are new generation Advanced High-strength Steels which find extensive use in automotive industry. They are characterised by a single-phase ferrite matrix and nanometer sized precipitates. The precipitation hardening is achieved through the microalloying of a variety of elements like niobium, molybdenum, titanium, and/or vanadium. Hence, considering the ever-increasing production of steel, these elements are always in demand. To further understand the substitution potential of Nb, we must understand the effect of each alloying element on the steel grade. The research on NANO-steels currently undertaken by the group of Dr. ir. S.E.Offerman of TU Delft aims to study this aspect. The major focus of their research is disentanglement of properties of multiple alloying elements on the nano-precipitation kinetics & phase transformation (Austenite → Ferrite) kinetics. The indirect effect of alloying elements on nano-precipitation kinetics by their influence on phase transformation kinetics will also be studied.

Through these efforts, it is believed that a quantification of the effects of the alloying elements on the precipitation and phase transformation kinetics will be possible. This will also serve as a path for further research into this field since the lack of relevant literature is an issue.

### Availability

While considering the substitution potential of Nb with other elements, it is important to factor in the global availability of those elements. While the global market prices are subject to socio-economic factors and might fluctuate over the years, the global distribution of the mineral resources is important when looking from a geo-political perspective. In the case of niobium, Brazil is the world leader with 90% of the production. [5]

**Table 3 : Mine Production, Projected Reserves and countries with sizeable contribution statistics. Estimated from [5]**

Element	2015 Global Mine Production	Projected Reserves	No: of countries with sizeable contribution in production
Niobium	56,000	>4,300,000	2
Titanium	5,610 (Ilmenite) 6,090 (Rutile)	740,000(Ilmenite) 790,000(Rutile)	~ 15
Molybdenum	267,000	11,000 (thousand metric tons)	~12
Vanadium	79,400	15,000 (thousand metric tonnes)	~4

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[1] 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>

[2] Hulka, Klaus. "The role of niobium in low carbon bainitic HSLA steel." *1st International Conference "Super-High Strength Steels" Rome, Italy November. 2005.*

[3] Den Ouden, D., et al. "Modelling precipitate nucleation and growth with multiple precipitate species under isothermal conditions: Formulation and analysis." *Computational Materials Science* 79 (2013): 933-943.

[4] Klinkenberg, Christian. "Niobium in microalloyed structural and engineering steels." *Materials science forum*. Vol. 539. Trans Tech Publications, 2007.

[5] U.S. Department of the Interior & U.S. Geological Survey. "Mineral Commodity Summaries 2016" Access Online: Oct 2016. Link: <http://minerals.usgs.gov/minerals/pubs/mcs/2016/mcs2016.pdf>

### **Stainless steels**

Around 3% of the global demand per annum of niobium can be attributed to the production of various stainless steel grades. Niobium plays two important roles in cast and wrought austenitic stainless steels: as a stabilising agent to reduce the risk of intergranular corrosion and as a strengthening agent. Considering its effect on corrosion, niobium addition will ensure that the chromium will remain in the metal matrix dissolve by the precipitation of NbC. This is because carbon has a higher affinity to niobium than chromium. Hence, higher amounts of chromium can participate in corrosion protection.[1] In this scenario, the possible candidates for substitution are **Molybdenum, Titanium and Tantalum**. Like before, the problems of increased weight and cost persist. [2]

The strengthening mechanisms are based on the precipitation of fine dispersed niobium carbide (NbC). Also, it is well known that stabilising the steel grade by Nb addition prevents the risk of intergranular corrosion in heat affected zones. The niobium content added depends on the carbon and nitrogen (ferritic types) levels. The theoretical amount of niobium required for full stabilisation based on stoichiometric calculation is described by the equation:

$$\% \text{ Nb} \geq 0.2 + 5 (\% \text{ C} + \% \text{ N})$$

Hence, by controlling the amount of carbon and nitrogen in the steel grade, we can change the amount of niobium in the steel grade. [3]

Another alternative worth exploring are **High-nitrogen steels**. An austenitic stainless steel can be considered “high-nitrogen” if it contains more nitrogen than can be retained in the material by processing at atmospheric pressure; for most alloys, this limit is approximately 0.4 wt.%. These steel grades offer most of the good qualities offered by the niobium alloyed steel grades. Alloying with nitrogen has several advantages over alloying with carbon:

1. It is a more effective solid-solution strengthener than carbon and also enhances grain size (Hall-Petch) strengthening.
2. It is a strong austenite stabilizer thereby reducing the amount of other alloying elements required for stabilization.
3. It reduces the tendency to form ferrite and deformation-induced  $\alpha'$  and  $\epsilon$  martensites.
4. It has a greater solid-solubility than carbon, thus decreasing the tendency for precipitation at a given level of strengthening.
5. It is beneficial for pitting corrosion resistance.
6. It can increase yield and tensile strengths which can exceed those of conventional AISI 200 and 300 series stainless steels by 200-350% in the annealed condition, without sacrificing toughness. Cold deformation can produce further increases in strength resulting in materials with yield strengths above 2 GPa.

#### References:

[1] Ripoll, Manel Rodríguez, et al. "The role of niobium in improving toughness and corrosion resistance of high speed steel laser hardfacings." *Materials & Design* 99 (2016): 509-520.

[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>

[3] Cunat, Pierre-Jean. "Alloying elements in stainless steel and other chromium-containing alloys." *Euro Inox* 2004 (2004): 1-24.)

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#### Superalloys

Again, the properties required for superalloys can be obtained by alloying them with **Molybdenum, Titanium and (or) Tantalum**. [1]

Ceramics are another class of materials that can be used for the same purpose. [1] They offer reduced weight, strength and heat resistance but they are brittle and hence can shatter on impact. Composites of ceramic materials, especially **ceramic matrix composites** (CMCs) toughen the ceramics by incorporating fibres in them and thus exploit the good qualities of ceramics without risking a catastrophic failure.

CMCs are produced by embedding ceramic fibres in a ceramic matrix. Since, a variety of ceramic materials may be used for the fibres and matrix, it is possible to engineer their properties to endure harsh mechanical and thermal load. This renders them useful in the sphere of superalloys.

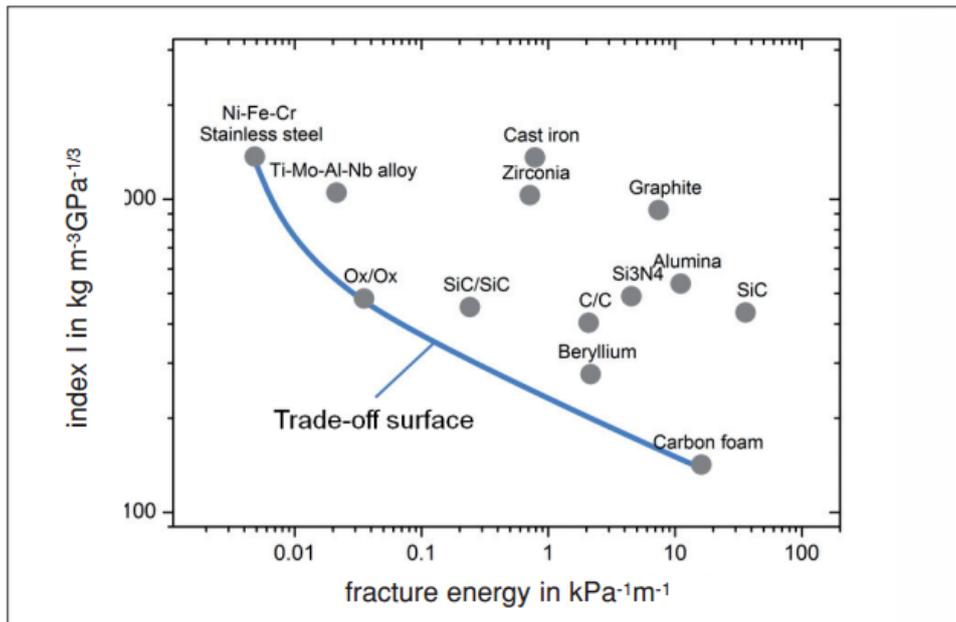


Figure 9 : Lightweight materials with maximum stiffness and maximum fracture energy selected from the Cambridge Engineering Selector. CMC dominate in a wide range of intermediate fracture energies and indices I [2]

CMCs are usually classified in terms of the fibre and matrix materials. For example, C/SiC is a CMC made of carbon fibres and a silicon carbide matrix. The materials commonly used are:

- Non-oxide fibres are mainly made of carbon or silicon carbide and oxide fibres of alumina, mullite or silica.
- Non-oxide matrices are mostly silicon carbide, carbon or mixtures of both. Oxide matrices consist of alumina, zirconia, mullite or other alumina-silicates.

In common practice, oxide fibres are combined with oxide matrices and non-oxide fibres with non-oxide matrices. Therefore, the main CMC types are C/C, C/SiC and Oxide/Oxide combinations. The CMC structure also contains about 1-30% pores. They are further classified according to their fibre structure, which impacts their material properties. The relevant properties are:

- Tensile strength – Ceramic fibres have a tensile strength between 1000-7000 MPa which is almost an order of magnitude higher than that of the matrix.
- Elastic modulus – It ranges between 200-900 GPa for the fibres and it is higher than that of the matrix.
- Temperature – The fibres usually degrade between 1000-2100 °C depending on the material and quality.

- Orientation – Fibres can be usually oriented in the unidirectional or planar. This leads to anisotropy in their properties.

**Table 4 :Material properties of CMC at ambient temperature. The range denotes the minimum and maximum of the respective property. (Ox/Ox includes CMC with alumina fibres and alumina or alumino-silicate matrix[2]**

Property	Unit	SiC/SiC	C/SiC	C/C	C/C
Fiber content	vol.-%	40–60	10–70	40–60	30–50
Porosity	vol.-%	10–15	1–20	8–23	10–40
Density	g/cm <sup>3</sup>	2.3–2.9	1.8–2.8	1.4–1.7	2.1–2.8
Tensile strength	MPa	150–360	80–540	14–1100	70–280
Bending strength	MPa	280–550	80–700	120– 1200	80–630
Strain-to-failure	%	0.1–0.7	0.5–1.1	0.1–0.8	0.12–0.4
Young’s modulus	GPa	70–270	30–150	10–480	50–210
Fracture toughness	MPa·m <sup>1/2</sup>	25–32	25–30	5.7–0.3	58–69
Thermal conductivity	W/m·K	6–20	10–130	10–70	1–4
Coefficient of thermal expansion	ppm/K	2.8–5.2	0–7	0.6–8.4	2–7.5
Maximum service temperature	°C	1100–1600	1350–2100	2000–2100	1000–1100

The costs of CMCs vary between some 100s to some 1000s euros/kg. Hence, they are expensive compared to other materials like metals and the initial high investment needs to pay off by longer service life or special performance features.

GE reported in September 2010 that they were successful in making CMC rotating parts and testing CMCs-based turbine blades. Similarly, in 2012, IHI, a leading aircraft engine manufacturer in Japan, announced that they would finalize mass-production technology of CMC parts for jet engines by 2015 and aim for commercialization of CMC parts in 2020. It is calculated that substitution of super alloys with CMCs in gas turbines, will lead to 15% more efficient systems due to the weight reduction. [1]

#### References :

[1] 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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## 2.2 ALTERNATIVE SYSTEM. REPLACE ONE/SEVERAL COMPONENT WITHIN THE SAME PRODUCT

## 2.2.1. TECHNICAL REVIEW

### Superconductors

A superconductor that can be put to practical use needs to possess superior high-critical-magnetic-field and high-critical-supercurrent-density properties coupled in addition to high critical temperature with affordability and good workability. Niobium – titanium alloys are employed for this purpose currently. They are used in MRI, particle accelerators and colliders. [1]

However, there are two possible alternatives for this purpose. They are:

- **Vanadium-Gallium alloys:** With a critical temperature of 14.2 K and the upper critical magnetic field over 19 Tesla, these alloys are viable alternatives. The structure of these alloys are similar to that of the niobium based superconductors. They are often used for the high field inset coils of superconducting electromagnets. Their properties can be improved by doping with high Z elements.[2][3]
- **High temperature superconductors (HTS):** They are ceramics which have higher critical temperature. Bismuth strontium calcium copper oxide (BSCCO)  $\text{Bi}_2\text{Sr}_{3-x}\text{Ca}_x\text{Cu}_2\text{O}_{8+y}$ , with x ranging from 0.4 to 0.9 (BSCCO) is a superconductor that has shown superconductivity onset behaviour near 120K. They have a pseudo-tetragonal structure based on an A-centred orthorhombic sub-cell with  $a = 5.399 \text{ \AA}$ ,  $b = 5.414 \text{ \AA}$  and  $c = 30.904 \text{ \AA}$ . It was the first HTS to not contain a rare earth element. They need to be hole-doped by an excess of oxygen atoms in order to show superconductivity. It was the first HTS to be used for making practical superconducting wires. [4]

### References :

[1] 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

### 1.1 MAIN APPLICATIONS OF RHENIUM

Rhenium is a refractory metal that has also a high chemical resistance. It is soluble only in oxidizing acids (nitric acid and hot, concentrated sulfuric acid), it is inert towards hydrochloric and hydrofluoric acids. As an alloying element it improves strength, ductility, weldability, improves recrystallization induced creep-rupture resistance. Such behaviour is called the rhenium effect [1-5]. Basic properties of rhenium are given in Table 1.

Table.1 Physical and mechanical properties of metallic rhenium.

Property	Ren
Density, g / cm <sup>3</sup>	21,09
Melting point, ° C	3186
Temperatura wrzenia, °C	5630
Boiling point, ° C	6.2
Thermal conductivity, W/(m·K)	48.0
Electrical resistivity, 20°C, nΩ·m	193
Young's modulus GPa	463
-Rm Tensile strength, MPa	1150-1200
-Re MPa yield strength	320
Elongation at. As 20oC-	24
Brinell hardness, MPa	1320–2500
Vickers hardness, MPa	1350–7850

Due to its properties rhenium is utilized in various applications such as nickel-base superalloys and catalysts, where its addition is about 3 and 0.3 % respectively. These applications account for over 90 % of total rhenium market demand with superalloys as a main use. In table 2. rhenium applications are given by form of Re.

The market of rhenium applications is divided into three categories:

- about 80% of the market is taken by nickel-base superalloys for single-crystal turbine blades and other components of gas turbine aero engines exposed to high pressure and temperature and land based industrial gas turbines (IGT). Within the applications the share is about 85/15 between aerospace and IGT;
- about 14 % is consumed by catalysts – 70 % of which is shared by catalysts for naphtha reforming and BTX production, other applications include 2.4tpy is used in catalysts for in gas-to-liquid (GTL) conversion and the production of ethylene oxide (EO).
- the last 6 % belongs to alloys such as molybdenum-rhenium (Mo-Re) and tungsten-rhenium (W-Re) used in filaments for thermocouples and lighting, medical equipment and W-Re for spray welding powders.

Such distribution highlights the importance of superalloys in terms of future rhenium market. During 2007-2009 period high rhenium price triggered investigation of new superalloys rhenium-free or with reduced Re content. It has been shown that at the moment it is not possible to totally remove rhenium from superalloys and keep the same high performance. However it is possible to reduce its content without significant loss of functionality. The development and replacement of air fleet expected in coming years by the largest manufacturers (GE, Pratt & Whitney, CFM, Snecma, Japanese Aero Engines Corporation, Rolls Royce, Aviadvigat, Aviation Engine Corporation plc) may influence the increase of demand for rhenium. However it seems that the current rhenium production from primary resources and strongly developed rhenium recycling will balance the increasing demand.

Table 2. Applications of rhenium by its form [1]

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 $\gamma'$ 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 <sub>2</sub> O <sub>3</sub> )
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

At first Ni-base superalloys were containing 3 % of rhenium which was increased in late 1990s up to 6 %. Further increase of rhenium content did not bring any positive effect and in the fourth generation of these superalloys Re content was decreased to 5 % due to ruthenium supplementation . In table 3. chemical composition of rhenium bearing superalloys is given [6].

Table.3 Chemical composition of rhenium bearing nickel-base superalloys[7]

Generacja	Stop	Cr	Co	Mo	Re	W	Al	Ti	Ta	Others	Ni	Density
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<b>Second generation</b>	CMSX-4	6.5	9.0	0.6	3.0	6.0	5.6	1.0	6.5	0.1Hf	Bal.	8.70
	PWA1484	5.0	10.0	2.0	3.0	6.0	5.6	-	8.7	0.1Hf	Bal.	8.95
	Rene' N5	7.0	8.0	2.0	3.0	5.0	6.2	-	7.0	0.2Hf	Bal.	8.70
	DD6	4.3	9.0	2.0	2.0	8.0	5.6	-	7.5	0.006C	Bal.	8.78
										0.1Hf		
										0.5Nb		
<b>Third generation</b>	CMSX-10	2.0	3.0	0.4	6.0	5.0	5.7	0.2	8.0	0.03Hf	Bal.	9.05
										0.1Nb		
	Rene' N6	4.2	12.5	1.4	5.4	6.0	5.75	-	7.2	0.05C	Bal.	8.97
										0.004B		
										0.01Y		
										0.15Hf		
<b>Fourth generation</b>	TMS-75	3.0	12.0	2.0	5.0	6.0	6.0	-	6.0	0.1Hf	Bal.	8.89
	TMS-138	2.8	5.8	2.9	5.1	6.1	5.8	-	5.6	0.05Hf	Bal.	8.95
										1.90Ru		
	TMS-162	2.9	5.8	3.9	4.9	5.8	5.8	-	5.6	0.09Hf	Bal.	9.04
										6.00Ru		

Currently an alternative to superalloys containing 3 % of rhenium are CMSX-8 alloy (1.5% Re) and Rene515. In comparison with CMSX-4 (3% Re), the CMSX-8 alloy (1.5% Re) has similar creep/stress-rupture properties up to 1010°C (1850°F) and exceed those of Rene' N5 (3% Re)/Rene' N515 (1.5% Re) alloys at all temperature/stress conditions [8,9].

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## 1.2 THE SUPPLY CHAIN IN EU

Rhenium is one of the rarest elements in the earth's crust and its abundance is 0.2-2.0ppm It is most often found in porphyry molybdenum and copper deposits. Geographically they are located mainly in South America (Chile, Peru), North America (Canada, USA, Mexico), West (Kazakhstan, Russia, Uzbekistan) and Central Asia. Rhenium concentration in molybdenum deposits is at the level of about 200 – 300 ppm. Global resources of rhenium in molybdenite deposits are estimated at about 13,000t, 34 % of which are localized in Chile, 22 % in USA and 14 % in Peru.

Rhenium is recovered mainly as a by-product in processing of porphyry copper and molybdenum deposits. It is found mainly in deposits of molybdenite from igneous rocks, with maximum fineness most often for molybdenite of younger generation [1].

Production of rhenium from primary deposits is based on a process of roasting of molybdenum concentrates. In the process of roasting of molybdenite ore, large amounts of dust, sulfur dioxide, and a vaporized rhenium in the form of rhenium heptoxide (Re<sub>2</sub>O<sub>7</sub>) are produced [2]. Rhenium heptoxide, soluble in water, is removed from the waste gas stream by a washing process. In the clean wash solution rhenium is recovered by precipitation of sparingly soluble sulfide or by using ion exchangers. Further treatment with strong mineral acids leads to the intermediate product in the form of ammonium perrhenate NH<sub>4</sub>ReO<sub>4</sub> (APR).

In Poland, KGHM Polish Copper produces rhenium by an innovative method involving the separation of rhenium from acidic waste produced in the process of obtaining copper [1]. During the smelting of copper in a slurry furnace rhenium, present in the copper concentrate, is distilled in the form of an oxide, and in a washing-flushing node it is passes from gases to the nascent weak sulfuric acid. In the first step the sewage is subjected to a filtration and then purification process, and further passed through special ion-exchange resin-filled column where the process of 'catch' of rhenium ions takes place. Rhenium is then washed out by the aqueous ammonia solution. Enriched solution is the starting material for obtaining ammonium perrhenate (NH<sub>4</sub>ReO<sub>4</sub>) which contains 69.4 % of rhenium.

Metallic rhenium is produced in the thermal reduction in a hydrogen atmosphere. Metallic rhenium is typically produced as a powder directly obtained during reduction of the APR or in the form of pellets formed during compacting and sintering of the metallic rhenium powder.

Recycled rhenium is recovered during the hydrometallurgical processes while treating used bi-metallic catalysts based on alumina and from waste nickel-base superalloys. Source of secondary raw materials of nickel superalloys are waste generated in production processes and spent parts of aero engines.

In 2015 production of rhenium in metallic form or in the form of ammonium perrhenate (APR) from primary sources was at a level of 46 T. Table 4 shows the production volumes for individual countries. In addition, production of rhenium from secondary sources is estimated to be: from scrap metal of about 10 T, from scrapped gas turbine parts ('engine revert') - 6 T. It is difficult to estimate the market for rhenium in the so-called "closed-loop" (producer-receiver) in case of producers of catalysts.

The largest producer of rhenium is Molymet - Chilean company that produces rhenium from molybdenite concentrate. The company produces concentrate in Peru, Mexico, the USA, Canada and Argentina. Most processed ores are from mines in Chile, Peru, the USA and Argentina, however material from

Canada and Mexico is sometimes also processed. Molybmet has additional molybdenite roasting plants in subsidiaries in Mexico and Belgium and these ores are processed with molybdenite from a variety of sources with lower rhenium content.

One of the world's leading manufacturers of rhenium is a Polish concern - KGHM Polish Copper, which manufactures about 17% world rhenium. The entire production of rhenium in Poland comes from domestic deposits.

**Table.4 World rhenium production from primary sources [3]**

Lp.	Kraj	Wielkość produkcji ze źródeł pierwotnych, kg		Rezerwy, kg [4]
		2014	2015	
1.	USA	8 500	8 500	390 000
2.	Armenia	351	350	95 000
3.	Kanada	-	-	32 000
4.	Chile*	25 000	26 000	1 300 000
5.	Chiny	NA	NA	NA
6.	Kazachstan	300	200	190 000
7.	Peru	-	-	45 000
8.	Polska	7 600	7 800	NA
9.	Rosja	NA	NA	310 000
10.	Uzbekistan	900	1 000	NA
11.	Inne	2 000	2 000	91 000
12.	Suma	44 700	46 000	2 500 000

\* Estimated rhenium recovered from roaster residues from Belgium, Chile, and Mexico.

The market of rhenium production from recycled materials is operated by European companies such as Heraeus Precious Metals, H.C. Starck, Buss & Buss Spezialmetalle GmbH (Sagard) and Toma Group. Heraeus Precious Metals GmbH & Co. KG which is a division of W. C. Heraeus GmbH was one of the leading recyclers of rhenium from catalysts. Its recycling facilities are based in Hanau and in Sante Fe Springs, California. H.C. Starck GmbH & Co. KG (Goslar) continued to recycle rhenium from catalysts and superalloy scrap (HC Starck GmbH & Co. KG). Rhenium-containing alloys, rhenium catalyst into scrap grade APR (99.9% rhenium), and rhenium pellets (99.9% rhenium) are recycled by Buss&Buss Spezialmetalle GmbH company (Sagard). Buss&Buss is a joint venture with Molycorp. Secondary rhenium production was estimated to be approximately 2.000 kg/yr (Buss & Buss Spezialmetalle GmbH) [4]. Another company, Estonian Toma Group deals with the recycling of metal alloys containing rhenium (Re) and manufacturing rhenium products. In the company rhenium is recovered from materials such as: WRe, MoRe, W/Mo/Re, Ni based super-alloys, metallic rhenium, ammonium perrhenate and other rhenium containing materials [5].

The greatest demand for rhenium occurs in the US, where most of the world production of rhenium alloys and catalysts is based. The leading U.S. Consumers Cannon-Muskegon Corp., General Electric Aviation (GE) and Pratt & Whitney in 2014 consumed an estimated 45.000 kg of rhenium (Minor Metals Trade Association, 2012) [4]. Europe is probably the second largest market of rhenium consumers, consuming about 6 tonnes per year.

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## 2 EVALUATION OF SUBSTITUTION POTENTIAL

### 2.1 ALTERNATIVE MATERIAL. REPLACE ONE MATERIAL FOR ANOTHER WITHOUT LOSS OF FUNCTIONALITY

#### Alternative materials with reduced content or without rhenium

The high price of rhenium during 2007-2009 period (10 000 \$USA /kg) forced rhenium users to search for methods to reduce rhenium content in superalloys used as monocrystalline turbine blades sited near the combustion chamber in aero engines and other gas turbines. As a result of research several alloys were designed such as CMSX-8 and Rene515 which contain 1.5% Re, and Re-free CMSX-7. However, still at the moment the addition of rhenium in superalloys seems inevitable as no element was found to provide equal high temperature (1600°C) creep resistance. Such temperatures/conditions are often found in large aero engines of twin-aisle civilian aircrafts but also in land based gas turbines used for continuous power generation.

The market of Gas-to-Liquid (GTL) catalysts is more likely to have rhenium substituted, for example by iron-based catalysts. Some works are ongoing in terms of Mo-based catalysts.

#### 2.1.1. TECHNICAL REVIEW

In order to substitute rhenium, Cannon-Muskegon company has developed new nickel-based superalloys [1,2,3]. The new alloy grades are CMSX<sup>®</sup>-8, CMSX-4<sup>®</sup> Plus and CMSX<sup>®</sup>-7. Their composition is presented in table 5.

The rhenium-free CMSX<sup>®</sup>-7 alloy was developed as a result of search for alloys with mechanical properties superior to SX grade superalloys. A balanced content of Ta, Mo, W in that alloy lead to improvement of creep-rupture properties. The alloy density is 8.8 g/cm<sup>3</sup>, with solidus and liquidus temperatures equal to 1325°C and 1381°C, respectively. The properties of CMSX<sup>®</sup>-7 are superior to those of CMSX<sup>®</sup>-2/3 for temperatures up to 1038°C.

The CMSX<sup>®</sup>-8 alloy has a density of 8.85 g/cm<sup>3</sup> and solidus and liquidus temperatures of 1338°C and 1389°C, respectively. Its creep-rupture resistance is similar to CMSX-4 up to temperature of 1010 °C, with a third of the rhenium content present in CMSX-4 alloy.

CMSX®-4 Plus alloy was developed in order to substitute third generation alloys that contain about 6 % of rhenium. The alloy density is 8.927 g/cm<sup>3</sup>, solidus and liquidus temperatures are 1351 °C and 1406 °C. The CMSX®-4 Plus alloy is, in terms of properties, on par with CMSX-10K alloy containing 10 % rhenium.

**Table 5. Chemical composition of novel nickel-based superalloys with reduced rhenium content.**

Lp.	Stop	Re	Cr	Co	Mo	W	Al	Ti	Ta	Hf	Ni
1.	CMSX-4 PLUS	4.80	3.5	10.0	0.60	6.00	5.70	0.85	8.00	0.10	bal.
3.	CMSX-7	-	6.00	10.0	0.60	9.00	5.70	0.80	9.00	0.20	bal.
4.	CMSX-8	1.50	5.40	10.0	0.60	8.00	5.70	0.70	8.00	0.20	bal.

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## 2.2 ALTERNATIVE SYSTEM. REPLACE ONE/SEVERAL COMPONENT WITHIN THE SAME PRODUCT

A possible alternative for superalloys are ceramic matrix composites (CMCs). For several years there has been ongoing works to develop CMCs applicable in aero engines, mainly in high-pressure turbines (HPT). Ceramic matrix composites are a group of materials built from ceramic fibers embedded in ceramic matrix. The reinforcing phase is often fibres or particles made of silicon carbide, aluminium oxide Al<sub>2</sub>O<sub>3</sub> and mullite (Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>) or carbon. The matrix is made of similar materials.

In contrast to standard ceramic materials, CMCs have a high fracture toughness, elongation at break up to 1 %, very high resistance to thermal shock and good mechanical load resistance.

### 2.2.1. TECHNICAL REVIEW

The GE company tested new engine GE<sub>9</sub>X, whose components in the high-pressure turbine (HPT) and combustion chamber were made of CMCs [1]. These activities are part of the technology maturation program for GE<sub>9</sub>X engine dedicated for the Boeing 777X. The first engine tests are scheduled for 2016, flight-testing on GE's flying testbed for 2017 and engine certification – for the following year.

CMC components tested for air applications are often built from SiC fibers built-in ceramic resin matrix. A definite advantage of CMC components is their low density (1/3 of metal density), which has a significant effect on reduction of weight and fuel usage. However utilizing CMCs for aero engines' components requires development of new methods for joining materials and new construction/shape of components. This is related to i.a. differences in heat dissipation as compared to metallic components [3].

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## 2.3 ALTERNATIVE PRODUCT. REPLACE EXIXTING TECHNOLOGY WITH DIFFERENT PRODUCTS AND/OR SERVICES

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### 2.3.1. TECHNICAL ANALYSIS

Technologies that can have an impact on consumption and usage of rhenium as alloying element in nickel-base superalloys are Additive Manufacturing (AM) technologies. The methods have been growing dynamically for several years. AM is currently described as being one of the fastest growing manufacturing technologies on the planet [1].

Already in 2007 the nickel alloys/superalloys were available for use in many laser based AM processes. Nowadays, AM techniques give rise to growth of nickel-base superalloys market, especially of the Inconel family that is characterized with a high demand. The growth of majority of nickel-base superalloys over the next decade is expected to be driven by the aerospace industry. As expected, this sector in 2022 will account for 460,000 kgs of nickel alloy consumption for AM processes [2]. The aerospace is already strongly benefiting from inconel and other nickel superalloys in combustion elements and fuel nozzles, hot air management and piping, and turbine components. The expected increase of use of AM techniques for manufacturing of nickel-base superalloys will require development of rhenium bearing superalloys in spherical powder form. Such powders should be characterized by certain properties, especially in terms of morphology and grain distribution suitable for AM processes [3].

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## 2.4 REFRACTORY METALS SUBSTITUTE OTHER ELEMENTS. IMPROVED FUNCTIONALITY

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### 2.4.1. TECHNICAL REVIEW

Some new applications for rhenium alloys with molybdenum or tungsten include components of high-temperature reactors or fuel cladding materials. The beneficial properties of these alloys include good thermal properties, high strength at elevated temperatures and good room temperature mechanical properties that

simplify components' manufacturing. Research indicate that both rhenium and rhenium dioxide are chemically inert up to 2500 K [1,2]. For the purpose of nuclear applications of rhenium alloys it is necessary to investigate structural changes occurring in the alloys when heated or irradiated, and significantly affecting mechanical properties [3].

The search for superhard materials, with diamond hardness but lower price, puts rhenium compounds as one of the possibilities. So far identified superhard materials group comprises of compounds of transition metals with light elements such as boron, carbon, nitrogen or oxygen. An example is rhenium diboride  $\text{ReB}_2$ . However its properties are not isotropic. Theoretical investigation of its mechanical properties indicate that  $\text{ReB}_2$  has extremely high shear modulus and  $c_{44}$  elastic constant as high as 70% of c-BN. These properties suggest it is ultraincompressible and therefore can be superhard [4]. The high hardness is thought to be related to covalent double bondings between of B-B type as well as six Re-B strongly directional covalent bondings [5,6]. All this indicates that the best possible properties should be obtained in highly textured  $\text{ReB}_2$  materials, preferably in thin film form. However overall material's hardness is a product of coatings and the used substrate [7].

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### 3 CONCLUSIONS

Refractory metals are widely used in various applications because of their remarkable properties and promising practical usefulness. This group of metals has extraordinary resistance to wear and heat, a high level of hardness at room temperature and a high melting point, especially when subjected to temperatures higher than 2000°C, making these metals perfect for drilling and cutting tools. These metals have also high density and are chemically inert. Also, these metals are highly resistant to factors like thermal shock, thus making them not to experience cracking, expansion or stress when cooled and heated repeatedly.

All in all, the five metals (i.e. W, Nb, Mo, Ta and Re) falling under this group have high density levels and good heat and electrical properties. Also, when they are exposed to very stressful environments or conditions, they undergo slow deformation given their resistant to creep, as refractory metals have the ability to create stable protective layers of oxide making them resistant to corrosion

Refractory metals had initially a limited use for lamp filaments, electron tube grids, heating elements and electrical contacts. Nonetheless, the high melting points of refractory metals make them highly stable materials and give them way to have widespread industrial applications nowadays in the aerospace, electronics, nuclear and high-energy physics and chemical processes.

Among these applications, the following table summarises those of more economical importance and its volume of the material used at EU level:

Refractory metal	Main industrial application	% of usage of current metal	Technical / economical viability for substitution
<b>W</b>	Cemented carbides - WC/Co	72% of usage in Europe	Mo, Ti
<b>Nb</b>	Steels - HSLA	90 % of usage for steels*	Ta/Ti+Mo, V+Mo
<b>Mo</b>	Steels	71%** usage for steels	B, Cr, Nb and V in alloy steels; W in tool steels
<b>Ta</b>	Capacitors	40% capacitors, 21% superalloys	Ceramic, Al, Nb-oxide (capacitors); V, Mo, Hf, Mo, Nb, Re, W
<b>Re</b>	Superalloys	83-90% superalloys***	CMCs

\* USGS Mineral Resources Program. *Niobium and Tantalum—Indispensable Twins*. s.l.: U.S. Geological Survey, 2014

\*\* <http://www.imoa.info/molybdenum/molybdenum-global-production-use.php>. International Molybdenum Association.

\*\*\* Adi Naor, Noam Eliaz, Eliezer Gileadi, Properties and applications of rhenium and its alloys, The AMMTIAC Quarterly, Volume 5, Number 1.

**Tungsten (W)** is the most abundant among the refractory metals. It has the highest melting point, a high density and it is highly resistant to corrosion. Due to its exceptional physical properties, tungsten is used for a wide range of applications such as wire filaments and in industrial arc lamps and lighting. When combined with carbon, it can be very hard, being thus tungsten the core of the technology in WCo carbides, which are used in the points for drilling machines in the manufacturing industry. Nearly 72% of the tungsten consumed in the EU is used in cemented carbide parts for cutting and wear-resistant materials, primarily in the construction, metalworking, mining, and oil and gas drilling industries. At global level, the largest share (60%)<sup>1</sup> of tungsten is

<sup>1</sup> Report on Critical Raw Materials for the EU Critical Raw Materials Profiles, European Commission, 2015

therefore used for the production of cemented carbides. The rest is used for fabricated products, alloy steels, super alloys and tungsten alloys.

Due to tungsten's unique properties, substitutes for most applications would result in increased cost or a loss in product performance. However, there are some potential substitutes for tungsten. For instance, potential substitutes for cemented tungsten carbides include cemented carbides based on molybdenum carbide and titanium carbide, ceramics, ceramic-metallic composites (cermets), and tool steels.

**Niobium (Nb)** and its alloys have properties that provide technological capabilities unique among refractory metals, although it is the least refractory of these. Niobium is a ductile and soft metal at elevated temperatures; hence, it can be easily worked to obtain high elasticity and strength. The world steel industry accounted for approximately 90% of world niobium consumption for High-strength low-alloy (HSLA) steels or microalloyed steels, which are designed to provide better mechanical properties and/or greater resistance to atmospheric corrosion. In Europe, the largest share (83%) of niobium is used for the production of HSLA steels, which are mainly used in the construction industry for structural purposes (31%), automotive industry (28%) and oil and gas pipelines (24%)<sup>2</sup>. Additionally, this refractory metal can be used in making electrolytic capacitors and superconductors and can be also found in nuclear reactors and vacuum tubes.

Substitution of niobium is possible, but it may involve higher costs and/or a loss in performance. The following materials can be substituted for niobium: tantalum and titanium, as alloying elements in stainless- and high-strength steels; molybdenum and vanadium, as alloying elements in HSLA steels; and ceramics, molybdenum, tantalum, and tungsten in hightemperature applications<sup>3</sup>.

**Molybdenum (Mo)** is one of the less expensive refractory metals, hence, it is consumed annually more than any other refractory metal. Mo has outstanding electrical and heat-conducting capabilities and relatively high tensile strength. Mo alloys can be very resistant to high temperatures and creep and as it does not create amalgams, it is resistant to corrosion. These alloys account for about 71% of the molybdenum consumed around the world. Therefore, the major use for molybdenum is as an alloying agent for alloy and tool steels, stainless steels, and nickel-base or cobalt-base superalloys to increase hot strength, toughness and corrosion resistance, particularly in structural piping and tubing. This metal also has excellent anti-friction qualities, making it an ideal component of oils and greases used in automobiles.

Potential substitutes for molybdenum in its major application as an alloying element in steels include boron, chromium, niobium and vanadium; tungsten in tool steels; graphite, tantalum, and tungsten for refractory materials in high-temperature electric furnaces; and cadmium-red, chrome-orange, and organic-orange pigments for molybdenum orange<sup>4</sup>.

**Tantalum (Ta)** is the most resistant against corrossions to a wide spectrum of reagents. Around 40% of the global share of tantalum is used in electrolytic capacitors and 21% in superalloys. Out of several commercial grade tantalum alloys (e.g. tungsten, niobium and molybdenum) generally retain the corrosion resistance of tantalum and provide higher mechanical properties. It is also used in the field of medicine and surgery as well as in environments where there is high acidity. Tantalum is also the major component of computer and phone circuits or capacitors.

Substitution of tantalum is possible, but it may involve higher costs and/or a loss in performance. For instance, molybdenum and vanadium, as alloying elements in HSLA steels; tantalum and titanium, as alloying elements in

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<sup>2</sup> Report on Critical Raw Materials for the EU Critical Raw Materials Profiles, European Commission, 2015

<sup>3</sup> Mineral Commodity Summaries: Niobium, U.S. Geological Survey, 2016

<sup>4</sup> Mineral Commodity Summaries: Molybdenum, U.S. Geological Survey, 2016

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stainless- and high-strength steels; and ceramics, molybdenum, tantalum, and tungsten in hightemperature applications<sup>5</sup>.

**Rhenium (Re)** is the most recently discovered refractory metal and due to its rarity, it can be really expensive. It is known for its high tensile strength and ductility. Rhenium has a high electrical resistivity over a wide temperature range. This characteristic, combined with a low vapor pressure, makes it ideally suited for filament applications. The major uses of rhenium (around 90% at global level) are in superalloys used in high-temperature turbine engine components and in petroleum-reforming catalysts, representing an estimated 70% and 20%, respectively, of end uses<sup>6</sup>. In addition, it is widely used in nuclear reactors, gyroscopes and other electric components.

Substitutes for rhenium in platinum-rhenium catalysts (e.g. iridium and tin) have achieved relatively commercial success. Other metals being evaluated for catalytic use include gallium, germanium, indium, selenium, silicon, tungsten and vanadium.

Despite the many applications and benefits of refractory metals, there are many that are not yet fully understood and studied. Thus, a wider research is required in the field of metallurgy and refractory metals in order to improve the variety of processes and applications that these materials can undergo.

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<sup>5</sup> Mineral Commodity Summaries: Tantalum, U.S. Geological Survey, 2016

<sup>6</sup> Mineral Commodity Summaries: Rhenium, U.S. Geological Survey, 2016