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SUPPLY AND SUBSTITUTION OPTIONS FOR SELECTED CRITICAL RAW MATERIALS: COBALT, NIOBIUM, TUNGSTEN, YTTRIUM AND RARE EARTHS ELEMENTS

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ABSTRACT

European industry is dependent on the import of raw materials. The European Commission has recognized that some raw materials are crucial for the function of the European economy and show a high risk of supply shortage. This communication addresses supply and substitution options for selected critical raw materials: cobalt, niobium, tungsten, yttrium, and the rare earth elements. For each element, the most relevant data concerning mining, abundance, recycling rates and possible substitutes are summarized and discussed.

1. INTRODUCTION

The availability of certain raw materials is crucial to Europe's economy (EC 2014). The COST Action CA15102, Solutions for Critical Raw Materials (CRM) Under Extreme Conditions (www.crm-extreme.eu), focuses on the substitution of CRMs in high value alloys and metal-matrix composites used under extreme conditions of temperature, loading, friction, wear, corrosion, in energy, transportation and machinery manufacturing industries. Presently, the European Commission identifies 26 raw materials or groups of raw materials of strategic importance; these materials exhibit both a high supply risk and important economic impact (EU 2017). The present communication reviews the current situation for a subset of this list: cobalt, niobium, tungsten, yttrium, and the rare earth elements (REE). It is evident that a strategy should be developed for the identified materials to close the loop and minimize the demand for virgin resources.

2. STATE-OF-THE-ART

2.1 Cobalt

Cobalt (Co) belongs to group 9 of the periodic table.

The interest in Co is due to its industrially useful properties including ductility, malleability and magnetizability. These characteristics, combined with heat resistance (melting point 1495°C and boiling point 2870°C) and strength, make cobalt suitable for a wide variety of industrial and military applications (Minerals UK 2009).

Co has been known since ancient times. The first evidence dates to 2600 B.C., when blue glazed pottery was found in Egyptian tombs. Co-containing materials have been used as pigments for decades. The pure metal was isolated by Georg Brandt in 1735 (Donaldson and Beyersmann 2005).

The vast majority of Co is mined in Congo, which accounted for 54% of mine production in 2016. Furthermore, about half of the global reserves of Co are estimated to be in Congo. The importance of other countries is limited, with the individual share of other countries not exceeding 6%. Table 1 gives an overview of the geographical distribution of Co mining and reserves.

Typically, Co is used for metallurgical applications, as a component of superalloys, for the building of turbine engines for aircrafts, in the chemical sector (catalysts, adhesives, pigments, agriculture, and medicine), for the

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TABLE 1: World Mine Production and estimated reserves of Co (Shedd 2017a).

	Mine production 2016		Estimated reserves	
	[t]	Share	[1000 t]	Share
Congo	66,000	54%	3,400	49%
China	7,700	6%	80	1%
Canada	7,300	6%	270	4%
Russia	6,200	5%	250	4%
Australia	5,100	4%	1,000	14%
Zambia	4,600	4%	270	4%
Cuba	4,200	3%	500	7%
Philippines	3,500	3%	290	4%
Madagascar	3,300	3%	130	2%
New Caledonia	3,300	3%	64	1%
South Africa	3,000	2%	29	0%
United States	690	1%	21	0%
Other countries	8,300	7%	690	10%
World total (rounded)	123,000		7,000	

production of cemented carbides, and for the ceramics and enamels industry (CDI 2006). Nevertheless, the most common application is the manufacture of lithium-ion batteries, used for the power supply of electronic equipment. China is the leading consumer of cobalt, with nearly 80% of its consumption being used by the rechargeable battery industry (Shedd 2017a).

The recycling of Co is massively dependent on the application. Co-containing alloys are reprocessed into similar alloys and do not require a specific recycling technology. Hardmetal scrap is commonly recovered within the metal carbide sector. As lithium-ion batteries are the most common application, several recycling procedures have been developed for this area. The process commonly starts with reductive leaching (e.g. H_2SO_4 , H_2O_2) followed by extraction and cobalt precipitation (Chen et al 2011, Pagnanelli et al 2016, Jian et al 2012). Cobalt recycling from applications in pigments, glass, paints, etc. is not readily possible as these usages are dissipative (EU 2016).

Table 2 summarizes possible substitutes for Co. For some applications, however, Co is essential as substitution would lead to a loss of product performance. This is in particular the case for the application with the highest share, lithium-ion batteries (25 %). Even though intensive research is being conducted in this area, a short-term breakthrough cannot be expected (Nayak 2017).

Considering the many uses, the recent Co demand has grown and it is essential to counteract the increased production of waste with increased recovery efforts (Cheang and Mohamed, 2016). According to EC 1014b, the end-of-life recycling input rate in the European Union in 2014 was 16%. For the USA, a recycling rate of 32% was reported in 1998 (Shedd 2004). In a more recent document, however, the EU Commission estimates the end-of-life recycling input rate to be zero (EC 2017).

2.2 Niobium

Niobium is a transition element of group 5. Due to its properties, it belongs to the group of refractory metals

(Bauccio 1993). A Nb-containing oxide was first described by Charles Hatchett in 1801 who proposed the name Columbium (Hatchett 1802). Due to its similar properties, Nb could not be distinguished from Tantalum until 1865. Even if the official IUPAC name is Niobium (Nb), the name Columbium (Cb) is still widely used in North America.

Nb reserves are virtually inexhaustible (Schulz and Papp 2014), but are classified as critical due to the high production and deposit concentration in Brazil, as shown in Table 3.

Ferroniobium is by far the most important application for Nb and consumes almost 90% of the market (TIC 2016). Ferroniobium itself is used almost exclusively as an alloying element for steels containing Nb. In particular steel numbers starting with 1.45 or 1.46 may contain Nb, even if the concentration is below 1% (DIN 2014). Other end-uses are Nb chemicals, vacuum-grade Nb master alloys, pure Nb metal and Nb alloys such as NbTi (TIC 2016).

Commonly, Nb is not recycled as pure element but Nb-containing steels and superalloys are recycled for the same alloy. Thus, Nb recycling is not a question of technology, but of logistics. According to Papp (2017), the amount of recycled Nb is not available, but it may be as high as 20%. However, other sources report recycling rate of 56% (Birat and Sibley 2011). As Nb is used in relatively low concentrations (< 1%) in alloys (DIN 2014), separate handling of Nb is often not worthwhile. Therefore, the element is strongly diluted in iron scrap, where it no longer has any function. Only recently, the European Commission has claimed that the end-of-life recycling input rate is as low as 0.3% (EU 2017).

It is reported that Nb can be substituted by other materials, as summarized in Table 4. In any case, a loss of performance or higher cost accompany the substitutes (Papp 2017). It should also be noted that the possible substitutes themselves (e.g. W) are critical or mine production is much lower than for Nb (e.g. Ta). Therefore, it is essential to reintroduce Nb into the product cycle. Demand for new ore could be reduced through improved scrap management.

TABLE 2: Possible substitutes for Co (Shedd 2017a).

Application	Possible substitutes
Magnets	Barium or strontium ferrites, neodymium-iron-boron, nickel-iron alloys
Paints	Cerium, iron, lead, manganese, vanadium
For curing unsaturated polyester resins	Cobalt-iron-copper or iron-copper in diamond tools; copper-iron-manganese
Cutting and wear-resistant materials	Iron, iron-cobalt-nickel, nickel, cermets, ceramics
Lithium-ion batteries;	Iron-phosphorous, manganese, nickel-cobalt-aluminum, nickel-cobalt-manganese
Jet engines	Nickel-based alloys, ceramics
Petroleum catalysts	Nickel

TABLE 3: World Mine Production and estimated reserves of Nb (Papp 2017).

	Mine production 2016		Estimated reserves	
	[t]	Share	[1000 t]	Share
Brazil	58,000	90%	4,100	95%
Canada	5,750	9%	200	5%
Other countries	570	1%	n.a.	n.a.
World total (rounded)	64,300		4,300	

TABLE 4: Possible substitutes for Nb (Papp 2017).

Application	Possible substitutes
Alloying elements in high-strength low-alloy steels	Molybdenum and vanadium
Alloying elements in stainless - and high-strength steels	Tantalum and titanium
High-temperature applications	Ceramics, molybdenum, tantalum, and tungsten

Nb-containing steel grades should not be mixed with other steel grades, but rather should be remelted for similar alloys.

2.3 Tungsten

Tungsten (W) has the highest melting point of the pure metals and is irreplaceable in special industrial applications (BGS 2011). The name tungsten is derived from the Swedish words tung (heavy) and sten (stone) and goes back to Frederik Cronstedt, who described a high-density mineral in 1757 (ITIA 2011). Juan José de D'Elhuyar is considered to be the discoverer of tungsten. In 1783, he reduced tungsten oxide with charcoal (ITIA 2011).

Cemented carbides, also known as hardmetals, are the main use of tungsten and cover 56% of the market, followed by steel/alloys (20%), mill products (17%) and others (7%) (Somerley 2011). Other applications include catalysts, pigments, lubricants, electronics and electrical applications, solar power, medical and dental applications (Christian et al. 2011). Special attention is paid to W applications in materials under extreme conditions (Schubert et al. 2008).

As Table 5 shows, China is of paramount importance for tungsten production. In 2016, the country accounted for 82% of mine production. Vietnam, the second largest producer, is lagging behind and has a share of 7%. No data are available for the USA, but it has been reported that a new tungsten mine was opened in northwest Utah in 2016 (Shedd 2017b). In 2016, however, 76% of the tungsten imported into Europe came from Russia (EC 2014a).

According to Shedd (2011), the recycling rate for tung-

sten in the USA was 46% in 2000. A recent study (Zeiler et al 2018) shows that on a global scale the end-of-life recycling rate of tungsten (i.e. ratio of old scrap fed back) is 30% by 2016 and the recycling input rate (i.e. ratio of new and old scrap fed back) is 35%.

Possibilities for W-containing waste materials are described by Testa et al. (2014) and Shishkin et al. (2010), for example. Potential substitutes for W are summarized in Table 6. In some applications, however, substitution would lead to higher costs or loss of product performance (Shedd 2017b). Although depleted uranium or lead are not classified critical, their use is extremely problematic due to its toxicity. It should also be noted that tungsten carbide has unique properties which cannot be met by the suggested substitutes. For instance, Mohs hardness of WC is 9.5, while MoC lags far behind (5.5). It must be concluded that tungsten is indispensable for certain applications at the moment.

2.4 Yttrium

Yttrium (Y) is a transition metal but is also considered to be a rare earth element (REE) along with scandium and the lanthanoids (Connelly et al. 2005). Y is mainly consumed in the form of high-purity oxide compounds for phosphors, in ceramics, electronic devices, lasers, and metallurgical applications (Gambogi 2016).

World production of Y came almost exclusively from China, as Table 7 shows. Minor amounts of mine production are reported for Brazil, India and Malaysia. However, the estimated reserves are quite large (more than 0.5 Million t) and far exceed mine production, which was estimated at 8,000 to 10,000 t in 2015 (Gambogi 2016). In contrast to mine production, China's dominance of global reserves is less pronounced. As shown in Table 7, only 41% of reserves are estimated in China followed by the USA, Australia and India. The reserves of Y are linked to those of rare earths (Gambogi 2016).

In many cases, Y is irreplaceable, as substitutes are generally much less effective. Especially in electronics,

TABLE 5: World Mine Production and estimated reserves of W (Shedd 2017b).

	Mine production 2016		Estimated reserves	
	[t]	Share	[1000 t]	Share
China	71,000	82%	1,900	61%
Vietnam	6,000	7%	95	3%
Russia	2,600	3%	83	3%
Other countries	1,700	2%	680	22%
Canada	1,680 *	2%*	290	9%
Bolivia	1,400	2%	n.a.	n.a.
Austria	860	1%	10	0.3%
Spain	800	1%	32	1%
Rwanda	770	1%	n.a.	n.a.
United Kingdom	700	1%	51	2%
Portugal	570	1%	3	0.1%
United States	n.a.	n.a.	n.a.	n.a.
World total (rounded)	86,400		3,100	

* Data for 2015

TABLE 6: Possible substitutes for Co (Shedd 2017b).

Application	Possible substitutes
Cemented tungsten carbides	Carbides based on molybdenum carbide and titanium carbide, ceramics, ceramic-metallic composites (cermets), tool steel
Tungsten mill products	Molybdenum
Tungsten steels	Molybdenum steels
Lighting	Carbon nanotube filaments, induction technology, light-emitting diodes
Applications requiring high-density or the ability to shield radiation	Depleted uranium or lead
Armor-piercing projectiles	Depleted uranium alloys or hardened steel

TABLE 7: World Mine Production and estimated reserves of Y (Cordier 2012).

	Mine production 2011		Estimated reserves	
	[t]	Share	[1000 t]	Share
China	8,800	99%	220	41%
India	55	0.6%	72	13%
Brazil	15	0.2%	2.2	0.41%
Malaysia	4	0.04%	13	2.4%
USA	n.a.	n.a.	120	22%
Australia	n.a.	n.a.	100	19%
Sri Lanka	n.a.	n.a.	0.24	0.04%
Other countries	n.a.	n.a.	17	3%
World total (rounded)	8,900		540	

lasers, and phosphors, Y cannot be replaced by other elements. Yttrium oxide could be substituted by CaO or MgO as stabilizer in zirconia ceramics, but a lower toughness has to be accepted (Gambogi 2016).

Yttrium can be extracted from secondary resources preferably by hydrometallurgical processes, as they are also used for primary ores (Innocenzi 2014). Currently, no large scale Y recycling facility is documented (UNEP 2011), but progress is being made, including investigations into the recovery of Y from flat panel displays, spent optical

glass and ceramic dusts.

2.5 Rare Earth Elements

The rare earth elements (REE) comprise the group of 14 lanthanides, of which promethium exhibits the lowest natural abundance. In addition to the 14 lanthanides, scandium and yttrium also belong to the REE group (Connelly et al. 2005), since these elements have chemical and physical similarities with the lanthanides.

REE are considered to be of critical importance in sus-

tainable applications. REE and their compounds also find a multitude of applications in various branches of industry. Their demand is due to their use in various high-technology applications, for example, phosphors for fluorescent lamps, high strength permanent magnets, metallurgy, and applications in a number of green energy technologies. The main applications of REE are catalysts, metallurgy, magnets, electronics and in optical, medical, and nuclear technologies (Long et al. 2010).

China plays a dominate role in the production of REE. As shown in Table 8, China accounted 80% of mine production in 2016, followed by Australia with an 11% share. Other producers are of inferior importance. Global mine production in 2016 was around 132,000 t.

REE are relatively abundant in the earth's crust, and there are significant deposits outside China. Even if China hold 80% of mine production, only 37% of the estimated reserves are in China. Relevant deposits are located in Brazil, Thailand, Russia and India. As summarized in Table 8, minor REE deposits are estimated in several other countries.

Despite their highly fragmented applications, viable recycling technologies are already available today. In reality, however, less than 1% of REE are currently returned to the production cycle. (UNEP 2011, Tunsu et al. 2015). It is estimated that improvements in recycling can be achieved, particularly in the area of magnets, fluorescent lamps, batteries and catalysts (Jowitt 2018).

3. CONCLUSIONS

The present paper elucidates the availability, critical nature, and analysis of production value chains and downstream processes of for selected critical elements: cobalt, niobium, tungsten, yttrium, and the rare earth elements. The European share of reserves and mine production

of these crucial elements is very low or even zero. Mine production is often concentrated in a single or very few countries. For Yttrium, 99% of mine production is in China. As the selected elements are crucial for the European industry, actions to reduce the dependency are strongly encouraged. On the one hand, the COST Action CA15102 evaluates the possibilities of replacing these critical materials with common materials without significant loss of performance. On the other hand, the demand for critical materials can be reduced by substituting new ores by secondary raw materials. It is evident that recycling needs to be significantly increased, as current recycling rates fall to zero (e.g. for Co).

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TABLE 8: World Mine Production and estimated reserves of REE (Gambogi 2017).

	Mine production 2016		Estimated reserves	
	[t]	Share	[1000 t]	Share
China	105,000	80%	44,000	37%
Australia	14,000	11%	3,400	3%
United States	5,900*	4%	1,400	1%
Russia	3,000	2%	18,000	15%
India	1,700	1%	6,900	6%
Brazil	1,100	1%	22,000	18%
Thailand	800	1%	22,000	18%
Malaysia	300	0.2%	30	0.03%
Vietnam	300	0.2%	n.a.	n.a.
South Africa	n.a.	n.a.	860	1%
Canada	n.a.	n.a.	830	1%
Greenland	n.a.	n.a.	1,500	1%
Malawi	n.a.	n.a.	136	0.1%
World total (rounded)	132,000		120,000	

* Data for 2015

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