Lieferschein

ETH-Bibliothek Zuerich

- Dokumentlieferung –
Raemistr. 101

CH-8092 Zuerich

Tel.: 0041 44 632 21 52
Fax: 0041 44 632 10 87
Email: docdel@library.ethz.ch

Empfänger
Slovensk\341 pedagogick\341 kniznica -The Slovak Library of Education

MVS

SK-85101 Bratislava 5

H\341lova 6

Angaben zur Bestellung:

Bestelldatum:	2018-01-09 15:33:11
Bestellnummer:	SUBITO:2018010901184 E001330380
Name des Bestellers:	Slovensk\341 pedagogick\341 kniznica -The Slovak Library of Education
Benutzerkennung:	SLI08X00001E
Lieferdatum:	
Lieferpriorität:	NORMAL
Aktueller Lieferweg:	Email
E-Mail Adresse:	janette.gulcikova@spgk.sk

Bemerkungen zur Auslieferung:

Angaben zum Dokument:

Signatur:	P C 36 ETH-BIB E01
Autor:	
Titel:	Metall <Clausthal-Zellerfeld>
Jahr:	2017
Band / Jahrgang:	71/7-8
Seiten:	287-292
Aufsatzautor:	Laubertova,M.
Aufsatztitel:	Antimony as a critical raw material for the European Union
ISSN:	
ISBN:	0026-0746
CODEN:	

Ihre Bemerkung zur Bestellung: 3/2018

subito Urheberrechtshinweis

Die Bestellung und Nutzung der über subito gelieferten Aufsatzkopien unterliegen den urheberrechtlichen Bestimmungen. Mit der Registrierung bei subito verpflichten Sie sich, diese einzuhalten, d.h. insbesondere, dass die Kopien ausschließlich zum eigenen Gebrauch bestimmt sind und nicht an Dritte weitergegeben werden dürfen. Sie dürfen ohne Genehmigung des Verlags nicht zum Wiederverkauf, Wiederabdruck, zu systematischer Verteilung, Emailversand, Webhosting eingeschlossen institutionelle Repositorien/Archive oder jedweden anderen kommerziellen Zweck verwendet werden.

Sofern Sie eine Lieferung per Email oder FTP erhalten, dürfen Sie die Kopie nur einmal ausdrucken und müssen diese anschließend dauerhaft löschen.

Die Kopien sind mit einem Wasserzeichen versehen, welches ein Urheberrechtsvermerk enthält. Das von subito e.V. angebrachte Wasserzeichen darf nicht entfernt werden.

Antimony as a critical raw material for the European Union

Laubertová, M.; Trpčevská J.; Pirošková J.; Kostadinov. J. (1)

Antimony (Sb atomic number 51) is classified as a minor metal, growing in strategic importance. The European Union, the United States of America and Japanese economies are import dependent on this metal. It is used mainly in electrical engineering (micro capacitors, lead-acid batteries, flame retardants), and as an alloying element. Now antimony belongs to the critical raw materials in the European Union, and it is completely dependent on import. The main import sources to the EU are Bolivia and China, its main producers. World reserves of antimony are estimated at 1.8Mt of metal content, situated predominantly in China. Approximately 55 039 t (potentially economic resources) antimony are in Slovakia. Its stock is estimated for the period of 10 years. The antimony recycling rate is only 11 %, but due to its shortage, it is estimated to rise in the future. Substitutability of antimony is very low, although lead-acid batteries from old cars are replaced by other types. The aim of this work is to give a short review of antimony-containing waste streams and examine current and future possibilities of obtaining antimony from primary and secondary raw materials in European Union.

Critical raw materials for the EU are characterised by high supply risk and delivery shortage in the next 10 years, while they are extremely important for the value chain. Supply risk is associated with the concentration of production in countries with low political and economic stability, often worsened with a low rate of substitutability. The following critical raw materials were defined by the EU Commission report in 2010 for the EU: antimony (Sb), beryllium (Be), fluorspar, gallium (Ga), germanium (Ge), graphite, indium (In), magnesium (Mg), cobalt (Co), niobium (Nb), platinum group metals (Pt, Pd, Ir, Rh, Ru, Os), rare earth elements (lathanides, Sc), tantalum (Ta) and tungsten W. The list of critical raw materials was extended on May 26, 2014, six new materials entered the list: borates, chromium, coking coal, magnesite, phosphate rock, and silicon metal. The rare earth elements were divided into the light REE and the heavy REE. Only tantalum was selected from the old list. The EU authorities are aware of raw material shortages. The analysis of current requirements for the raw materials necessary for the further development of the European economy leads to setting new principles for the EU united policy on raw materials. It is expected that by 2030 the demand for a series of critical raw materials compared to 2006 will have more than tripled. There are two factors that cause the increase in demand: the growth of emerging economies and new technologies.

Relative supply risk index of economic value for antimony is 9.0 from 10. Antimony has low recycling rates and a limited number of substitutes. It is also almost exclusively mined as by-product metal.

Antimony

Antimony (Stibium) is a silver white, semi-glossy metal with the characteristic coarse-crystalline fracture. Its melting point is 631 °C, boiling point 1,587 °C

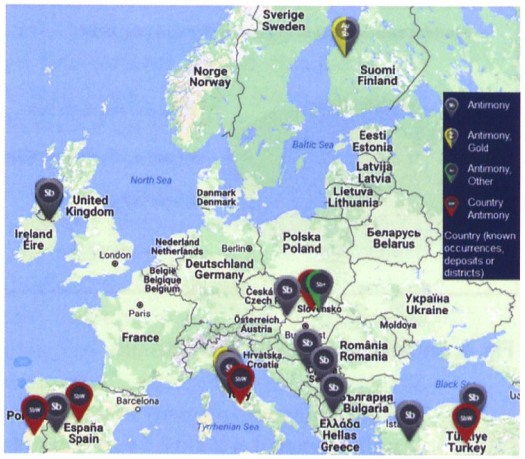

Fig. 1: Antimony in Europe Source The Antimony Mineral Database by Tri-Star Resources

with a specific gravity between 6.62 and 6.69 g·cm^{-3}. Typically antimony is not found alone in nature because of its high affinity for other metals (i.e. copper, lead, silver) and sulfur. It mostly occurs as an accompanying metal in lead, zinc, copper and silver ores. Sometimes it is also found as a pure metal in the form of solid or granular aggregates of the hydrothermal origin.

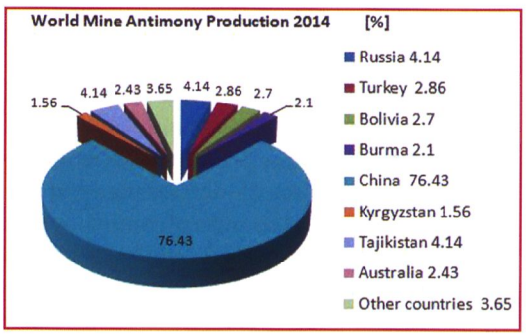

Fig. 2: World Mine Antimony Production in 2014

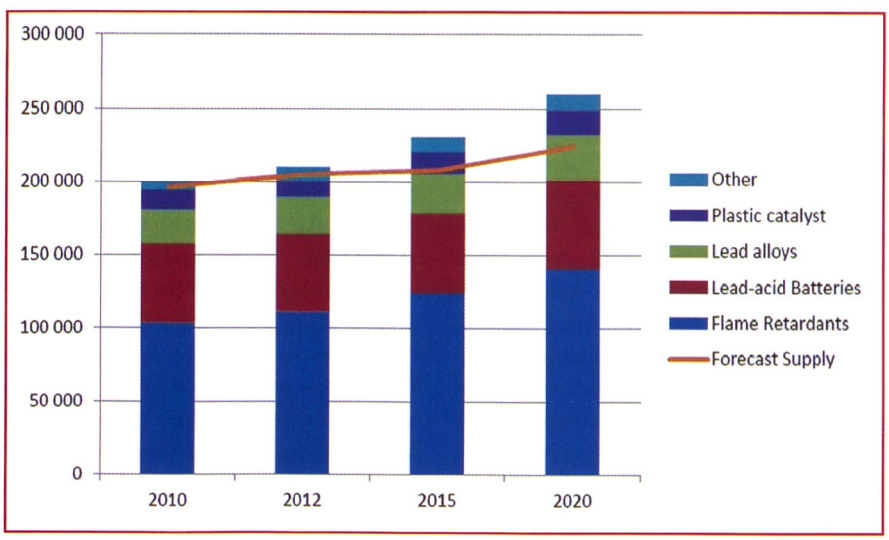

Fig. 3: World antimony supply and end-use forecasts to 2020 (tonnes)

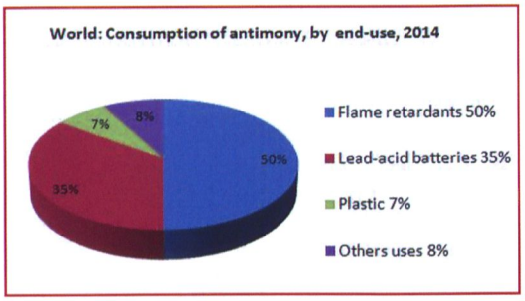

Fig. 4: Antimony consumption by Roskill

The abundance of antimony in the Earth's crust is estimated at 0.2 to 0.5 parts per million. Even though Sb is not abundant, it is found in over 100 mineral species. Antimony is sometimes found natively, but more frequently it is found in the sulfide stibnite (Sb_2S_3) which is the predominant ore mineral. Paradocrasite $Sb_2(Sb,As)_2$ (91.92% Sb), Senarmontite Sb_2O_3 (88.39% Sb) and Kieftite $CoSb_3$ (86.11% Sb) have the largest antimony content of all minerals. Stibnite, Tetrahedrite and Jamesonite are the most important raw materials in Slovakia. Totally, there are 24 deposits and 71 deposit and mineralogical occurrences in the Slovakian part of the Western Carpathians, if the Sb dominant role as the utility metal is considered. Antimony ores are not mined in Slovakia. The extraction of the most significant deposit Dubrava and the mining of Sb-Au ore at the Pezinok deposit ended in 1991. Totally, there are 55,039 tonnes of antimony non-balance reserves. Slovakia produced antimony in a former smelter Vajsková in Podbrezová. Antimony was obtained by the pyrometallurgical processing of domestic raw materials containing also relatively high concentrations of precious metals. Due to the gradual decrease in metal content in ores and the drop in the world prices, Sb production ended completely. Slovakia has the potential to restore the production and mining of antimony, as it has experience with its acquisition Fig 1.

China was the largest mine producer of antimony in 2014, with 76.43 % of world production (120,000 tonnes). The second largest were Tajikistan and Russia (with 4.14 % each), followed by Turkey (2.86 %) and Bolivia (2.7 %) Fig. 2. Global reserves of antimony are about 1.8 million tonnes of pure metal. The main source of raw materials for antimony production in Russia is concentrated in the Republic of Sakha (Yakutia), where its proven reserves comparable to those producing countries like Bolivia, South Africa, Thailand, Mexico, Malaysia, Italy and USA. It should be noted that if the average content of antimony in these countries reserves is of 2-5%, the Yakut ores reaches 20-25%. Larger antimony reserves are concentrated only in China, which is operated by about 100 years a unique field Siguanshan with antimony contents of up to 20%. The antimony market is very small. During the third quarter of 2016, the Rotterdam price per metric ton of antimony metal increased from $6,750.00 per ton to $7,750.00 ton.

Countries	Imports of antimony [t]				Exports of antimony [t]			
	2011	2012	2013	2014	2011	2012	2013	2014
Belgium								
Ores and concentrates	-	1	-	5864	274	1187	4	57
Metal	9 451	7195	7613	7216	732	259	271	138
Oxide	831	1822	786	794	10 417	7818	7751	8555
Estonia								
Metal	-	-	-	-	113	-	-	-
France								
Metal	7 413	6502	5372	6680	24	60	95	68
Oxide	2 854	1677	1572	1542	6 124	5482	5192	5470
Netherlands								
Metal	208	586	697	628	385	475	429	571
Oxide	26 729	18315	16031	1708	264	206	155	250
Germany								
Ores and concentrate	8	6	922	1202	-	-	-	-
Metal	456	376	462	280	239	103	86	20
Oxide	6 949	6013	5675	5997	1 132	688	669	662
Slovenia								
Metal	150	25	49	101	2	1	40	63
Spain								
Ores and concentrates	29	10	7	10	-	-	-	-
Metal	2 450	1553	2760	1609	50	247	2	11
Oxide	494	720	630	606	1 784	1204	2361	2457
Italy								
Ores and concentrates	1 169	1474	1964	2347	898	1311	1669	1970
Metal	298	132	332	188	80	2	7	61
Oxide	4 227	3538	3201	3284	261	215	399	450
Portugal								
Oxide	184	239	229	239	-	-	-	-
Metal	-	-	-	-	70	277	138	51
Turkey								
Ores and concentrates	121	0	11	13	2 977	2 450	3 150	2 935
Metal	245	256	273	249	6	113	554	367
United Kingdom								
Metal	120	257	280	375	57	237	425	525
Oxide	2466	1712	1688	1916	290	422	152	127

Tab. 1 List of countries trading with antimony

The market outlook forecast for world antimony supply and demand is shown in Fig. 3. For the largest market, flame retardants, growth is expected to be close to 3% per year to 2020. This is likely to be slightly above the growth of the overall market, due to the slower growth rates anticipated for antimony's use in lead acid batteries and plastics catalysts, where the intensity of antimony's use has decreased in these markets over the past years.

Company	Location	Capacity [t/year]	Products
Hsikwangshan Mining Administration	China	30 000	Sb, Sb_2O_3, Sb_2O_5, $NaSbO_3$
Kademjaisk Antimony Combine	Kyrgyzstan	20 000	Sb, Sb_2O_3
Amspec Chemical Corp.	USA	15 000	Sb_2O_3
Laurel Industries Inc.	USA	12 500	Sb_2O_3
Societe Industrielle et Chimique de L'Aisne	France/EU	12 000	Sb, Sb_2O_3
Dachang Mining Administration	China	10 000	Sb
Mines de la Lucette (PCDL)	France/EU	9 500	Sb
Enal	Bolivia	9 300	Sb_2O_3
Great Lakes Chemical (Anzon)	USA	6 000	Sb_2O_3
Union Miniere (Umicore)	Belgium/EU	6 000	NaSbO3
Guzhou Dushan Dongfeng	China	4 000	Sb, Sb2O3
Hubei Chongyang	China	4 000	Sb, Sb_2O_3
Sunshine Mining and Refining	USA	1 000	Sb, $NaSbO_3$
Total		139 300	

Tab. 2 Leading producers of refined antimony-performance

Antimony use

Antimony is one of the world's top critical elements for today's modern manufacturig and electronics sectors. Because of its excessive brittleness and the difficulty of shaping it, antimony has no direct applications, but is extensively used as an alloying element. Antimony is used as a flame retardant (50 % of use), lead acid batteries (35 %), and catalysts for the production of PET plastic (7%) and others metallurgical, ceramics and glass (8%) Fig 4. Antimony recycling rate refers to metal applications only, but about 70% of Sb mine production is used in oxide form, from which only a very small part is eventually recycled.

Antimony of high purity is used for making certain types of semiconductor devices (diodes and infrared detectors). The largest amount is consumed in a form of Sb_2S_3 and Na_3SbO_4 for the flame retardant production of some plastics. A significant amount of antimony is used in lead alloying in the manufacture of batteries, protective cable covers and ammunition. A minor use of antimony is in the production of alloys (metal printing, bearing compositions and solders). Hard lead contains 15 to 25% Sb. Also it presents in certain Pb–Sn–Sb anti-friction metals used to make bearings for large compressors and propeller shafts. The major outlet – approximately 65% of total antimony consumption - is in the form of the oxide Sb_2O_3, which is used to render fabrics and plastics fireproof. Its properties make it possible for plastics to be used in applications where, under normal circumstances they would melt, such as in computer casings and televisions. Sodium antimonate is used in certain special glasses - television screens, for example. The intermetallic compounds AsSb, GaSb and InSb have found some applications in electronics. The sulphide Sb_2S_3 is one of the components of brake linings.

Import and export of antimony in EU countries

Table 1 shows that Belgium and France import higher amounts of metal antimony, mostly from China, Russia, Kyrgyzstan and Tajikistan. In Belgium and France, there are companies which belong to the top producers of pure antimony. At the same time, antimony is exported in the form of oxides to other states which buy it in bulk (e.g. Italy, Germany, Netherlands). Table 1 contains data from European mineral statistics, 2011-2014.

Leading producers of refined antimony

Table 2 shows the summary of the largest plants involved in the production of refined antimony (2012). Most of them are in China. In recent years, China's import volume for antimony concentrate has been on the increase. In 2014, the China's volume came near to 60 million tons. From an international market standpoint, the United States, Europe, Japan and South Korea are the places where Chinese antimony products are mainly sold.

Umicore at Hoboken, Belgium produces antimony from secondary raw materials. The product is wet sodium antimonate ($NaSbO_3 \cdot 3H_2O$). Focusing on secondary raw materials makes this Belgian company less dependent on imports of antimony metal concentrates from China and more environmentally friendly in saving primary raw materials short in supply. The focus of the company has completely shifted from concentrates to the recyclable materials and industrial by-products by completion of major investments in the development, introduction and launch of new chemical and metallurgical plants. Over the last 10 years, the company has been completely redesigned. Umicore Precious Metals Refining has an annual production capacity of about 6,000 tonnes of sodium antimonate. It is produced as a dried or non-dried powder.

Technological steps are based on the comprehensive metallurgy (lead/copper/nickel), in the use of these essential elements as a gatherer of precious and other metals, called "impurities" such as antimony, bismuth, tin, selenium, tellurium and indium (Fig. 5). Its main advantage is the increased productivity combined with a higher efficiency resulting in the maximum degree of metal recovery and the creation of optimal yields in case of noble metals.

Campine N.V. is another company engaged in the manufacturing of Sb_2O_3 in the form of powder and granules, and Sb_2O_5 as colloidal suspensions (Fig.6). Campine is a high quality producer of antimony trioxide and antimony pentoxide for applications in fire retardant plastics, as a catalyst or as an additive in the glass or ceramics industries. As a second activity lead battery recycling operations expanded significantly. Campine is also the leading recycler of lead waste in Belgium. Lead bullion may contain varying amounts of copper, silver, bismuth, antimony, arsenic and tin. Lead recovered from secondary sources may contain similar impurities, but generally antimony dominates. There are two methods of refining crude lead: electrolytic refining and pyrometallurgical refining. Electrolytic refining uses anodes of decopperised lead bullion and starter cathodes of pure lead. This is an expensive process and is not currently

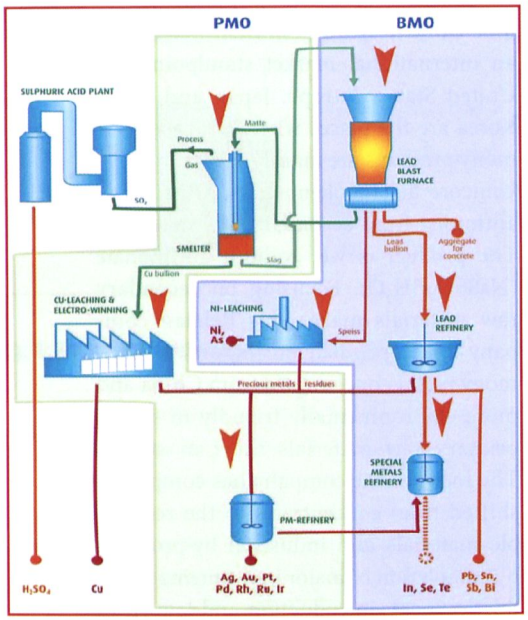

Fig. 5: Umicore Precious Metals Operations (PMO) Base Metals Operations (BMO)

used by plants in the EU-28, although it is used in a number of other countries worldwide.

Recycling of antimony

Antimony is also produced as a by product of lead refining in many countries. Antimony recycling can be divided into two categories: from end-of-life products, and from industrial process residues. Table 3 lists some examples of antimony-containing products and process residues that could be recycling targets. It should be noted that the average antimony ore (Stibnite) has a grade of approximately 2.7%. Antimony can be recovered in the residues from the lead refining process. The main end-of-life recycling option is from spent lead-acid batteries mainly recovered from old vehicles.

Conclusion

The question of obtaining antimony from primary and secondary raw materials and recycling is very relevant, especially due to its shortage in the next ten years. The analysis report of antimony import and export in the European Union shows that the EU is completely dependent on the import of raw materials. We buy and import ores and concentrates both from countries dominant in mining, and from countries with their largest reserves. These countries can greatly affect the price which has grown steadily in recent years, and this growth will probably continue. Supplies of secondary antimony from recycling of the very large amount of waste in lead-based batteries appear to be able to cover an increasing percentage of European needs in the near and medium term. In the long term, however, this will probably decrease because of the current use of lead-free batteries. Antimony can be partially replaced by another element, alloys with lead and flame-retardants. For example, a lead antimony battery is the main choice because of its recycling potential. In the past years, antimony was replaced by other technologies and raw materials, where the electrolyte is not in a liquid form but soaked in non-woven fabric of glass fibers. However, the old lead batteries are the main choice for recycling and recovery of antimony. As one of the EU countries, Slovakia has 55,000 tonnes of antimony non-balanced deposits.

	Antimony content (weight percentage grams per 100 grams)	Industry
End - of -life products		
Flame retardant plastics	5-15	Plastic/electronics
Lead-acid batteries	1-7	Automotive
Lamp phosphor waste	0.5-1	Electronic
Industrial residues		
Copper smelter flue dust	3	Copper processing
Copper electro – refining slime	3-20	Copper processing
Lead smelter flue dust	42	Lead processing
Lead electro-refining slime	64	Lead processing

Tab. 3 Antimony content of various end-of-life products and industrial residues

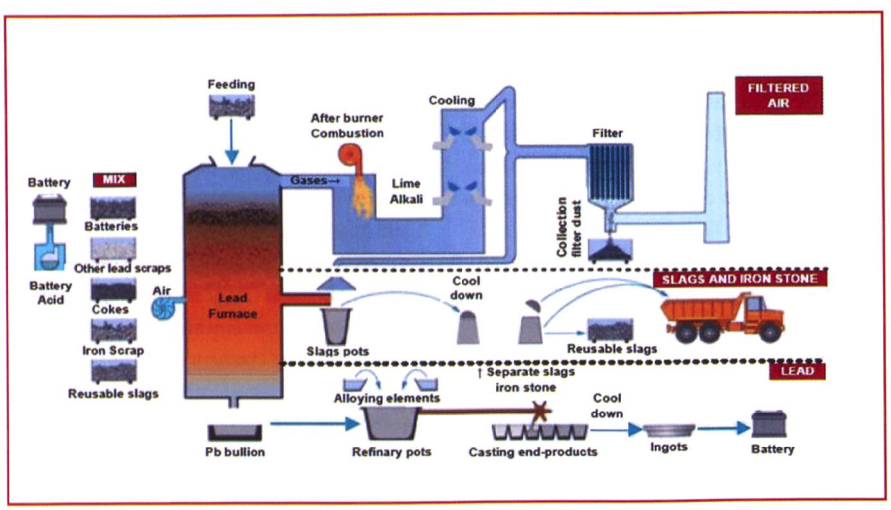

Fig. 6: Campine N.V. Lead Recycling process

Acknowledgement

This work was supported by the Ministry of Education of the Slovak Republic under grant VEGA 1/0442/17 and VEGA 1/0631/17. This work was supported by the Slovak Research and Development Agency under the contract No. APVV-14-0591.

References

[1] EUR-Lex: On the review of the list of critical raw materials for the EUand the implementation of the Raw Materials Initiative 2014 [cit. 2016-04-12]. Available at: http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52014DC0297&from=SK

[2] Bačo, P.: State Geological Institute of Dionýz Štúr: Critical Raw Materials of the EU. [cit. 2015-12-12]. Available at: http://www.fns.uniba.sk/uploads/media/P_Baco_KNS-PRiF_UK-2012A.pdf

[3] European commission: Report on critical raw materials for the EÚ. [cit. 2014-06-29]. Available at: http://ec.europa.eu/enterprise/policies/raw-materials/files/docs/crm-report-on-critical-raw-materials_en.pdf

[4] Havlík, T.: Material recycling of waste – past, present and future. [cit. 2014-03 -31]. Available at: http://www.censo.sk/clanky/Waste_Havlik.pdf

[5] Risk list 2015. British Geological Survey. [cit. 2016-10-12]. Available at: https://www.bgs.ac.uk/mineralsuk/statistics/riskList.html
[6] Antimony (Sb) - of ancient origin: [cit. 2016-10-24]. Available at: http://www.geodexminerals.com/s/antimony.asp
[7] Balaž, P., Kúšik, D.: Mineral resources of the Slovak Republic: Antimony. Bratislava: Dionýza Štúra, 2015. 155 s. ISBN 978-80-89343-61-4
[8] Minerals and ores of Slovakia: Dubrava. [cit. 2016-03-11]. Available at: http://www.mineraly.sk/files/zber/501-600/547_dub.htm
[9] Antimony World - Tristar resources. [cit. 2016-10-12].
Available at: http://www.antimonyworld.com/
[10] Roskill. Antimony: World market for Antimony to 2025, 12th Edition [cit. 2016-11-01]. Available at: https://roskill.com/product/antimony-world-market-forecast-2025/
[11] Brown,T.J. at all. World Mineral Statistics 2010-2014. British Geological Survey: [cit. 2016-10-17]. Available at https://www.bgs.ac.uk/mineralsuk/statistics/worldStatistics.html
[12] Midas gold: Antimony. [cit. 2016-10-07]. Available at: http://www.midasgoldcorp.com/i/pdf/ppt/midas-gold-antimony-infographic.pdf
[13] Beznoso G.F.: Trends in mining and production of antimony in the Republic of Sakha (Yakutia) [cit. 2016-10-07]. Available at: http://www.mining-media.ru/ru/article/company/1194-tendentsii-dobychi-i-proizvodstva-surmy-v-respublike-sakha-yakutiya
[14] Price of Antimony: [cit. 2016-10-17]. Available at http://ebusa.maceddns.com/Y-g4Antimony-Price-Per-Ton.html
[15] Price of Antimony: [cit. 2016-10-17]. Available at http://www.usantimony.com/pricing.htm
[16] European mineral statistics 2011-14. BRITISH GEOLOGICAL SURVEY 2016 [cit. 2016-09-22]. Available at: https://www.bgs.ac.uk/mineralsuk/statistics/europeanStatistics.html
[17] Anderson, Corby G.: The metallurgy of antimony. In: Chemie der Erde. Vol. 72, 2012, p. 3-8.
[18] Summary of antimony industry in 2014 and outlook for 2015 [cit. 2016-10-02]. Available at: http://www.asianmetal.com/Events_2015/2015SbF/Index_2015SbF_en.asp
[19] Umicore: [cit. 2016-09-05]. Available at: http://www.preciousmetals.umicore.com/metalsAndProducts/chemicalsAndDerivatedProducts/
[20] Campine: Antimony. [cit. 2016-09-05]. Available at: http://www.campine.com/?OpenForm&gui=&cat1=1&cat2=9&Language=English
[21] Dupond, D., Binneman,s K.: Preventing antimony from becoming the next rare earth. Recycling Technology 2017. By Recycling International p.18-20. 2016
[22] Report on Critical Raw Materials for the EU. Critical Raw Materials Profiles. [cit. 2016-10-24]. Available at: http://ec.europa.eu/DocsRoom/documents/11911/attachments/1/translations
[23] Laubertová, M., Pirošková, J., Kostadinov, J.: Environmetal aspects and impacts of Vajskova. ODPADY, 2016

(1) Technical University of Kosice, Faculty of Metallurgy, Institute of Recycling Technologies, Letna 9, 042 00, Kosice, Slovakia

Kombinierte Schmiede-/Ringwalzlinie für Titanlegierungen

VSMPO-AVISMA Corporation aus Jekaterinburg (Russland) hat der SMS group die Endabnahme für die gelieferte Ringwalzanlage zur Herstellung von Triebwerksringen aus Titanlegierungen erteilt.

Mit der neuen Ringwalzanlage, bestehend aus Ringrohlingpresse PL 8000-V3, Radial-Axial-Ringwalzmaschine RAW 400/200-3500/800DM sowie zwei Ringexpandern RKP 500 und RKP 1350 erweitert das russische Unternehmen seine Produktpalette für die Luftfahrtindustrie. VSMPO ist einer der weltweit größten Hersteller von Schmiedestücken aus Titanlegierungen und strategischer Partner namhafter Luftfahrtunternehmen wie Boeing und Airbus.

Eine Besonderheit der Ringwalzlinie bei VSMPO ist die Kombination des Schmiede- und Ringwalzprozesses. Mit dieser Technologie ist VSMPO in der Lage, Ringe mit extrem komplexem Innen- und Außenprofil herzustellen. Darüber hinaus ist der Materialeinsatz viel niedriger als beim konventionellen Schmiedeverfahren. VSMPO kann nun Titan-Ringe mit einem Durchmesser bis zu 3.500 mm und einer Höhe von bis zu 800 mm herstellen.

Radial-Axial-Ringwalzmaschine RAW 400/200 DM zum Ringwalzen von Superlegierungen, Titan- und Aluminiumlegierungen sowie rostfreiem Stahl

Ringrohlingpresse PL 8000-V3 mit einer Presskraft von 8.000 Tonnen

Fotos: SMS